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ISMEC 2017

International Symposium on Metal Complexes

Acta of the International Symposia on Metal Complexes

Université de Bourgogne – Franche-Comté (France)

ISMEC 2017

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Michel Meyer, Editor
Institut de Chimie Moléculaire de l'Université de Bourgogne, Dijon, France
Chairman of the Organizing Committee of ISMEC 2017

Antonio Bianchia, Editor
Università Degli Studi di Firenze, Italy
President of the International Scientific Committee

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Editors:

Michel Meyer *(Chairman of the Organizing Committee of ISMEC 2017)*
Université de Bourgogne – Franche-Comté
Institut de Chimie Moléculaire de l'Université de Bourgogne
UMR CNRS 6302
9, avenue A. Savary
BP 47870
21078 Dijon Cedex, FRANCE
michel.meyer@u-bourgogne.fr

Antonio Bianchi *(President of the International Scientific Committee of ISMEC)*
Università Degli Studi di Firenze
Department of Chemistry "Ugo Schiff"
Via della Lastruccia, 3
50019 Sesto Fiorentino, ITALY
antonio.bianchi@unifi.it

International Scientific Committee of ISMEC 2017

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Maria Amélia Santos	Instituto Superior Técnico de Lisboa, Portugal
Manuel Valiente	Universitat Autònoma de Barcelona, Spain

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Laurent Plasseraud	Université de Bourgogne – Franche-Comté, Dijon, France

Contacts

ISMEC 2017 Secretariat
Université de Bourgogne – Franche-Comté
Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302)
9, avenue A. Savary
BP 47870
21078 Dijon Cedex, FRANCE
Phone: (+33) 3 80 39 37 16
Fax: (+ 33) 3 80 39 61 17
Congress website: https://ismec2017.sciencesconf.org
Acta website: http://www.gtc2014.com/ and https://hal.archives-ouvertes.fr

Foreword

On behalf of the International Scientific Committee and of the Local Organization Committee, it is our great pleasure to cordially welcome you at the Université de Bourgogne – Franche-Comté in Dijon, France to attend the **International Symposium on Metal Complexes** (**ISMEC 2017**). This book gathers the abstracts of the 5 plenary lectures, 10 keynotes, 43 oral communications, and of the 86 posters that will be presented during the four-day symposium held at the Faculté des Sciences Mirande.

Initiated in 1974 as the annual congress of the Italian group of "Thermodynamics of complexes", ISMEC has become years after years a well-established series of international conferences focusing on the study and applications of metal complexes in the fields of analytical, biomedical, environmental, supramolecular, inorganic, physical, and industrial chemistry. Main topics to be discussed are:

- Speciation, solution equilibria and kinetics in relation to coordination chemistry
- Supramolecular chemistry
- Analytical methods and sensors based on metal complexes
- Solution equilibria and industrial processes (*e.g. hydrometallurgy, ion-exchange, catalysis…*)
- Nanostructured metal complexes
- Metal complexes of environmental and biological interests (*e.g. proteomics and metabolomics, interactions with metalloenzymes and biomolecules…*)
- Metals in health sciences (*e.g. transport, homeostasis, toxicity, therapy, diagnosis and imaging…*)
- Chemometrics and computational modelling for equilibrium analysis

Hosted for the first time in France, this 44th congress aims at providing an outstanding forum for sharing new ideas and discussing the most recent advances on the thermodynamics and kinetics of coordination processes. By gathering researchers from both academia and industry, ISMEC 2017 seeks to foster new collaborations among researchers from diverse backgrounds with complementary skills and goals. It is our privilege to host this year Dr **Jean-Pierre Sauvage**, 2016 Nobel Laureate in Chemistry, who kindly agreed to present the opening lecture on Monday 12th June 2017.

We are wishing to all of you the best profit from your participation at ISMEC 2017 and a pleasant stay in the historical city of Dijon and in the Burgundy region.

Michel Meyer
and
Antonio Bianchi
June 2017

CONFERENCE PROGRAM

Sunday, June 11th

15:00-20:00	**Registration and Welcome Reception (International House, Campus)**

Monday, June 12th

08:30-09:00	**Opening Ceremony (Amphithéâtre Recoura - Faculté des Sciences Mirande)**
	Chairperson: Jean-Claude CHAMBRON
09:00-09:45	**Nobel Lecture:** From chemical topology to molecular machines: The transition metal approach *Jean-Pierre SAUVAGE*
09:45-10:00	**Pulidori communication:** Polyhalide complexes of Bi(III) and Sb(III) *Sergey ADONIN, Igor D. GOROKH, Maxim N. SOKOLOV*
10:00-10:15	**OC 1:** Redox responsive coordination polymers based on the viologen units *Wathiq Sattar ABDUL-HASSAN, Denis ROUX, Saioa COBO, Eric SAINT-AMAN, Christophe BUCHER, Florian MOLTON, Guy ROYAL*
10:15-10:45	**Coffee break**
	Chairperson: Charles DEVILLERS
10:45-11:15	**KN 1:** Metal complexes grafted on nanoparticles and surfaces: Stability and controlled release *Piersandro PALLAVICINI, Giacomo Dacarro, Franck Denat, Nicolas Sok*
11:15-11:30	**OC 2:** Mapping the frontier orbitals of magnetic POMs on Au and in solution *Xiaofeng YI, Natalya V. IZAROVA, Maria STUCKART, David GUERIN, Stéphane LENFANT, Dominique VUILLAUME, Paul KÖGERLER*
11:30-11:45	**OC 3:** Study of solvation and complexation of a ionic resorcin[4]arene in aqueous solution *Nicolás MORENO, Paula GUERRERO, Edgar F. VARGAS, Richard BUCHNER*
11:45-12:15	**KN 2:** Lanthanide and actinide complexation with bio-inspired ligand platforms: Exploring trends in f-orbital bonding *Gauthier J.-P. DEBLONDE, Julian A. REES, Peter B. RUPERT, Wibe A. De JONG, Roland K. STRONG, Rebecca J. ABERGEL*
12:30-13:45	**Lunch break**

	Chairperson: Claude GROS
14:00-14:45	**PL 1:** Chromo-fluorogenic probes and sensing materials *Ramon MARTINEZ MAÑEZ*
14:45-15:00	**OC 4:** Biomedical activity of metallodendrimers modified with 1,8-naphthalimide *Ivo GRABCHEV, Desislava STANEVA, Evgenia VASILEVA-TONKOVA*
15:00-15:15	**OC 5:** The design of perfluorinated extractants for the removal of perfluorooctanoic acid from water and metals from e-waste *Harrison OMORODION, Robert BAKER*
15:15-16:00	**Poster Session 1**
16:00-16:30	**Coffee break**
	Chairperson: Michel MEYER
16:30-17:00	**KN 3:** Importance of thermochemistry in the development of actinides extraction processes *Marie-Christine CHARBONNEL, Florian RODRIGUES, Nathalie BOUBALS*
17:00-17:15	**OC 6:** Accumulation and *in vivo* speciation of uranium in *P. lividus* sea urchin *Maria Rosa BECCIA, Benjamin REEVES, Minja MATARA-AHO, Hervé MICHEL, Pier Lorenzo SOLARI, Luisa MANGIALAJO, Marguerite MONFORT, Christophe MOULIN, Christophe DEN AUWER*
17:15-17:30	**OC 7:** Complexation of protactinium(V) with nitrilotriacetic acid *Coralie LUCHINI, Sébastien LEGUAY, Claire LE NAOUR, Jean AUPIAIS, Jérome ROQUES, Christophe DEN AUWER, Xavier DOLIGEZ, Céline CANNES*
17:30-17:45	**OC 8:** Transition metals binding and stability of phosphine-oxide resins in silver nitrate electrolyte *Ancuta MUSINA, Charly FARADJI, Vasile LAVRIC, Steven VAN ZUTPHEN*
17:45-18:00	**OC 9:** Investigating the ruthenium speciation in TBP/TPH organic phases with coupled spectroscopic techniques. *Claire LEFEBVRE, Thomas DUMAS, Christelle TAMAIN, Marie-Christine CHARBONNEL, Pier Lorenzo SOLARI*
18:00-18:30	**Transfer to the City Hall by bus**
18:30-20:00	**Mayor's Reception (Palais des Ducs)**

Tuesday, June 13th

	Chairperson: Maria Amélia SANTOS
08:30-09:15	**PL 2:** Ln-based MRI diagnostic probes at work: From small chelates to nanosized conjugates *Mauro BOTTA*
09:15-09:30	**OC 10:** Porous nanostructures as versatile stable chelates for complexation of lanthanides for pH responsive MR imaging *Kristina DJANASHVILI, Joop A. PETERS, Célia S. BONNET, Éva TÓTH*
09:30-09:45	**OC 11:** Unexpectedly high kinetic inertness of a bis-hydrated Gd-complex formed with the cyclohexyl ring fused AAZTA-like ligand *Massimo VISIGALLI, Zsolt BARANYAI, Adrienn VÁGNER, Lorenzo TEI, Alessandro MAIOCCHI*
09:45-10:00	**OC 12:** Mn^{2+}-based magnetic resonance imaging contrast agent candidates: How far can we go with open-chain ligands in terms of inertness ? *Gyula TIRCSÓ, Zoltán GARDA, Ferenc K. KÁLMÁN, Kristóf PÓTA, Enikő MOLNÁR, Balázs VÁRADI, Richard BOTÁR, Éva TÓTH, Imre TÓTH*
10:00-10:15	**Sponsors:** Agilent / Glindemann
10:15-10:45	**Coffee break**
	Chairperson: Enrique GARCÍA-ESPAÑA
10:45-11:15	**KN 4:** Self-assembled lanthanide complexes: Thermodynamic and kinetic aspects *Josef HAMACEK*
11:15-11:30	**OC 13:** Novel class of Pt_2L_4 metallacages: Design, self-assembly and host-guest chemistry *Emmanuel PUIG, Christophe DESMARETS, Lise-Marie CHAMOREAU, Hani AMOURI*
11:30-11:45	**OC 14:** Extended metal compounds. From 1D metallophilic polymers to metallogels and coordination polymers *Matti HAUKKA*
11:45-12:15	**KN 5:** Cyclopeptide-derived molecular containers for inorganic anions - Thermodynamic and kinetic aspects of complex formation *Stefan KUBIK*
12:30-13:45	**Lunch break**

13:45-14:45	**GTC Meeting**
	Chairperson: Tarita BIVER
14:45-15:15	**KN 6:** From selective to differential receptors. Real case studies *Raffaela BIESUZ, Maria Pesavento, Giancarla ALBERTI*
15:15-15:30	**OC 15:** Kojic acid derivatives as sensors for phosphate anions. Complex stability, DNA binding and cellular study *Joanna I. LACHOWICZ, Valeria M. NURCHI, Guido CRISPONI, Claudia CALTAGIRONE, Sergio MURGIA, Giuseppina PICHIRI, Pierpaolo CONI*
15:30-15:45	**OC 16:** New bis-cyclometalated iridium and rhodium complexes coordinated to heteroaromatic ancillary ligands: Photoreactivity and selective binding to G-quadruplexes *Matteo LARI, Natalia BUSTO, Gustavo ESPINO, Francesco MANOLI, Hector J. LOZANO, Marta MARTINEZ-ALONSO, José M. LEAL, Ilse MANET, Begoña GARCÍA*
15:45-16:00	**OC 17:** DNA interaction studies of new bis-anthracene polyaza macrocyclic derivatives *Lluis GUIJARRO, Mario INCLÁN, Begoña VERDEJO, Àlvar MARTINEZ, Enrique GARCÍA-ESPAÑA*
16:00-16:30	**Coffee break**
	Chairperson: Antonio BIANCHI
16:30-17:00	**KN 7:** Quantification of Ni-L'-Ni bonding interactions in macrocyclic dinickel complexes of the type $[Ni_2L(\mu\text{-}L')]^+$ ($L' = F^-, Cl^-, Br^-, I^-, OH^-, N_3^-$) by ITC and DFT *Alexander JEREMIES, Michel MEYER, Berthold KERSTING, Vitaly MATULIS, Oleg A. IVASHKEVICH*
17:00-17:15	**OC 18:** Selective and sensitive detection of cyanide and sulfide in water by metal-macrocycle-based capped silica mesoporous nanoparticles *Sameh EL SAYED, Maurizio LICCHELLI, Ramón MARTÍNEZ MÁÑEZ, Felix SANCENON*
17:15-17:30	**OC 19:** Luminescent lanthanide(III) complexes for anions sensing: Spectroscopy, speciation and modelling studies *Andrea MELCHIOR, Fabio PICCINELLI, Lorenzo DI BARI, Georgina FAURA, Marco LEONZIO, Francesco ZINNA, Marilena TOLAZZI, Marco BETTINELLI*
17:30-17:45	**OC 20:** Multifaceted coordination ability of phytate: Unprecedented structural data *Nicolás VEIGA, Delfina QUIÑONE, Julia TORRES, Carla BAZZICALUPI, Antonio BIANCHI, Carlos KREMER*

17:45-18:00 **OC 21:** Solution synthesis, structure and properties of bioctahedral rhenium clusters with mixed inner ligands
Yakov M. GAYFULIN, Anton I. SMOLENTSEV, Yuri V. MIRONOV

18:00-18:15 **Sponsors:** Triskem / Dostal

18:15-18:30 **Announcement of ISMEC 2018**
Antonio BIANCHI

18:30-20:00 **Poster Session 2**

Wednesday, June 14th

	Chairperson: Dominique LUCAS
08:30-09:15	**PL 3:** Cu(II)/Cu(I) electron transfer coupled to dioxygen activation in biomimetic complexes: from calix-zymes in solution to calix-zymes grafted on an electrode *Yves LE MEST*
09:15-09:30	**OC 22:** Designing an aromatic oligoamide foldamer based artificial second coordination sphere for a biologically inspired [2Fe–2S] hydrogenase cluster *Antoine MEUNIER, Michael SINGLETON, Thierry GRANIER, Ivan HUC, Yann FERRAND*
09:30-09:45	**OC 23:** Electronic interactions in transition metal linked oligoporphyrins *Hervé DEKKICHE, Mary-Ambre CARVALHO, Romain RUPPERT, Laurent RUHLMANN, Sébastien RICHETER, Adam LANGLOIS, Paul-Ludovic KARSENTI, Pierre HARVEY*
09:45-10:00	**OC 24:** Phosphorescent metal complexes and their bioconjugates in imaging using one- and two-photon excitation and PLIM technology *Sergey TUNIK, Pavel CHELUSHKIN, Anastasiya SOLOMATINA*
10:00-10:15	**Sponsors:** Magpie / Micromeritics
10:15-10:45	**Coffee break**
	Chairperson: Michael KNORR
10:45-11:15	**KN 8:** Polyazamacrocycles with phosphorus acid pendant arms as ligands for divalent copper *Přemysl LUBAL, Vojtěch KUBÍČEK, Jan KOTEK, Petr HERMANN*
11:15-11:30	**OC 25:** Tailoring the local environment around metal ions by multidentate tripodal ligands *Ferenc MATYUSKA, Attila SZORCSIK, Nóra V. MAY, Éva KOVÁTS, Attila BÉNYEI, Tamás GAJDA*
11:30-11:45	**OC 26:** Versatility of coordination modes in complexes of monohydroxamic acids with some half-sandwich type cations *Etelka FARKAS, Péter László PARAJDI-LOSONCZI, Linda BÍRÓ, Norbert LIHI, Péter BUGLYÓ*
11:45-12:00	**OC 27:** Copper complexation with tacn based bifunctional picolinate ligands for potential PET application *Amaury GUILLOU, Luís M. P. LIMA, Mélissa ROGER, David ESTEBAN-GÓMEZ, Rita DELGADO, Calos PLATAS-IGLESIAS, Véronique PATINEC, Raphaël TRIPIER*

12:00-12:15	**OC 28:** Tacrine-hydroxypyridinone hybrids as anti-acetylcholinesterase agents with metal ion binding capacity *M. Amélia SANTOS, Rajeshwari RAJESHWARI, Karam CHAND, Sílvia CHAVES*
12:30-13:45	**Lunch break**
14:00-19:00	**Excursion to Beaune**
19:00-23:30	**Banquet at the Bastion de Beaune**

Thursday, June 15th

Chairperson: Laurent PLASSERAUD

09:00-09:45 **PL 4:** Ruthenium, iridium and iron complexes in hydrogen/energy storage
Gábor LAURENCZY

09:45-10:00 **OC 29:** Structural investigation of bioactive metal complexes with coumarin derviatives using X-ray absorption spectroscopy
Marcin KLEPKA, Aleksandra DRZEWIECKA-ANTONIK, Anna WOLSKA, Paweł REJMAK, Marta STRUGA

10:00-10:15 **OC 30:** HypCal, a versatile program for the determination of standard reaction enthalpy and equilibrium constant values from calorimetric data
Giuseppe ARENA, Peter GANS, Carmelo SGARLATA

10:15-10:45 **Coffee break**

Chairperson: Raffaela BIESUZ

10:45-11:00 **OC 31:** Monoamide vs TBP: A comparative study of uranium and plutonium mass transfer in solvent extraction
Romain BERLEMONT, Anne LELIAS-VANDERPERRE, Christian SOREL, Jean-Pierre SIMONIN

11:00-11:15 **OC 32:** Organic and inorganic-organic hybrid systems for chemical sensing in liquid and gas media
Olga FEDOROVA, Elena GULAKOVA, Nikolai SCHEPE, Pavel PANCHENKO, Yuri FEDOROV

11:15-11:30 **OC 33:** Metal coordination with ESIPT-enabled 2,6-di(1H-imidazol-2-yl)phenols in turn-on fluorescent chemosensing for Cr(III), Zn(II) and Cd(II): Studies on molecular tuning for sensor selectivity
Abiodun O. ESEOLA, Helmar GÖRLS, Winfried PLASS

11:30-11:45 **OC 34:** Solvent extraction: Structure of the liquid/liquid interface containing a diamide ligand
Ernesto SCOPPOLA, Thanh PHAM, Luc GIRARD, Jean-François DUFRÊCHE, Giovanna FRAGNETO, Olivier DIAT

11:45-12:15 **KN 9:** On the equilibrium dynamics of metal complexes: NMR for coordination chemistry
István BÁNYAI

12:30-13:45 **Lunch break**

	Chairperson: Maurizio REMELLI
14:00-14:30	**KN 10:** How UV-visible and Mössbauer spectroscopies evidenced the electron reservoir capability of a pentanuclear iron complex *Geneviève BLONDIN, Eric GOURÉ, Martin CLÉMANCEY, Jacques PÉCAUT, Marie-Noëlle COLLOMB, Jean-Marc LATOUR*
14:30-14:45	**OC 35:** In vitro studies of dermally absorbed Cu(II) tripeptide complexes as potential anti-inflammatory drugs *Graham JACKSON, Ahmed HAMMOUDA, Fatin ELMAGBARI*
14:45-15:00	**OC 36:** Structural analysis and quantitation of low-valent iron species in Fe-catalyzed Kumada cross-coupling: insights from Mössbauer and EPR spectroscopies *Martin CLEMANCEY, Thibault CANTAT, Geneviève BLONDIN, Jean-Marc LATOUR, Pierre DORLET, Guillaume LEFEVRE*
15:00-15:15	**OC 37:** Modelling the dependence on medium, ionic strength and temperature of N-acetyl-L-cysteine acid-base properties, and its interactions with Na^+, Mg^{2+}, Ca^{2+} and Zn^{2+} *Clemente BRETTI, Concetta DE STEFANO, Gabriele LANDO, Demetrio MILEA, Alberto PETTIGNANO, Silvio SAMMARTANO*
15:15-15:30	**OC 38:** Mapping chemical species of selenium in wheat plants under various nutrient conditions *M. Angels SUBIRANA, Mercè LLUGANY, Gordon E. BROWN, Samuel M. WEBB, Laura SIMONELLI, Carlo MARINI, Manuel VALIENTE*
15:30-16:00	**Coffee break**
	Chairperson: Ewen BODIO
16:00-16:15	**OC 39:** Complexation of two divalent cations with a multisite flavonoid ligand *Aurélien MONCOMBLE, Diksha Jani THAVILIGADU, Jean-Paul CORNARD*
16:15-16:30	**OC 40:** Thermodynamic and kinetic study of lead(II) complexes with tetraazamacrocyclic ligands *Viktorie REICHOVÁ, Přemysl LUBAL, Petr HERMANN*
16:30-16:45	**OC 41:** Heavy metal complexes in recycling and waste disposal: Application of the PSI chemical thermodynamic database *Wolfgang HUMMEL, Gisela WEIBEL*
16:45-17:00	**OC 42:** The ambivalent properties of lead(II) and related metal ions in complexes of nucleoside phosphorothioates *Astrid SIGEL, Bert P. OPERSCHALL, Helmut SIGEL*
17:00-17:30	**Award and closing ceremony**

Plenary lectures

From chemical topology to molecular machines: The transition metal approach

Jean-Pierre SAUVAGE

Institut de Science et d'ingénierie Supramoléculaire de l'Université de Strasbourg (ISIS, UMR 7006), 8 allée Gaspard Monge, BP70028, 67083 STRASBOURG Cedex, France
isis-nobel2016@unistra.fr

The area named "Chemical Topology" is mostly concerned with molecules whose molecular graph is non planar, i.e. which can not be represented in a plane without crossing points. The most important family of such compounds is that of catenanes. The simplest catenane, a [2]catenane, consists of two interlocking rings. Rotaxanes consist of rings threaded by acyclic fragments (axes). The simplest rotaxane, a [2]rotaxane, contains two non-covalently connected components: a ring and an axis, the axis being end-functionalised by bulky groups preventing unthreading of the non cyclic fragment from the cycle. Interlocking ring compounds have attracted much interest in the molecular sciences, first as pure synthetic challenges and, more recently, as components of functional materials. In recent years, spectacular progress has been made. Highly functional and complex systems have been reported by several research teams, demonstrating the power of modern synthetic tools based on "template effects".

Separately, the field of artificial molecular machines has experienced a spectacular development, in relation to molecular devices at the nanometric level or mimics of biological motors. In biology, motor proteins are of the utmost importance in a large variety of processes essential to life (ATPase, a rotary motor, or the myosin-actin complex of striated muscles behaving as a linear motor responsible for contraction or elongation). A few recent examples are based on simple or more complex rotaxanes or catenanes molecular machines. Particularly significant examples include "molecular shuttles" as well as multi-rotaxanes reminiscent of muscles or able to act as switchable receptors. The molecules are set in motion using electrochemical, photonic or chemical signals. Examples will be given which cover the various approaches used for triggering the molecular motions implied in various synthetic molecular machine prototypes. Finally, potential applications of molecular machines will be discussed.

Chromo-fluorogenic probes and sensing materials

Ramón MARTÍNEZ-MÁÑEZ [a,b,c)]

[a] *Instituto Interuniversitario de Investigación de Reconocimiento Molecular y Desarrollo Tecnológico (IDM), Universitat Politècnica de València, VALENCIA, Spain*
[b] *Departamento de Química, Universitat Politècnica de València, Camino de Vera s/n, 46022, VALENCIA, Spain*
[c] *CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN)*
rmaez@qim.upv.es

The development of new chromo-fluorogenic probes for the detection of anions, cations, or neutral molecules has gained interest in the last years due to the importance of detecting target species in environmental and biological samples. In this filed designed receptors are able to transform, upon coordination, host-guest interactions into a measurable signal which allows analyte recognition and sensing [1]. Moreover, apart from the traditional design and synthesis of sometimes complex hosts, enhanced selectivity can be achieved by using selected probes coupled to inorganic supports. Examples in the use of metal complexes for the design of chromo-fluorogenic probes for sensing applications are also included [2].

From another point of view, there is an interest in the development of stimuli-responsive nanoscopic hybrid gated materials involving (bio)molecules as caps and showing the ability to release entrapped guests upon application of predefined external stimuli. These devices contain a support, that constitutes a reservoir in which certain compounds can be stored, and molecules or molecularly appended objects attached on these containers that act as “gates”, allowing the controlled release of entrapped payloads at-will [3]. Capped materials have been mainly used in drug delivery [4]. Examples of gated nanoparticles in advanced applications related with the communication between nanoparticles [5] and sensing [6] are also reported.

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Ln-based MRI diagnostic probes at work: From small chelates to nanosized conjugates

Mauro BOTTA

Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale
"Amedeo Avogadro", Viale Teresa Michel 11, 15121 ALESSANDRIA, Italy
mauro.botta@uniupo.it

In the 44 years since Paul C. Lauterbur obtained the first image, the field of magnetic resonance imaging (MRI) has evolved into an immensely valuable tool for biological molecular imaging and clinical diagnosis. As in other imaging modalities, also MRI has been combined with the use of dedicated contrast media, to further enhance the visualization of morphology and physiology. In particular, the established results and the recent advances have been favoured by extraordinary success in the development of new lanthanide-based probes that are both biocompatible and highly efficient [1]. While the advances in the chemistry of *f*-elements has contributed to develop the technique, in turn the need to improve the performance of contrast media has stimulated the study of the chemical properties of the compounds of these elements.

Gd^{III} complexes are in current clinical use as MRI contrast agents. Their ability to enhance the MR image is termed relaxivity and it depends upon many molecular factors, including speciation, protein binding affinity, chemical structure, and dynamic processes, such as water exchange kinetics and rotational tumbling rates. A significant portion of research in the field of contrast agent development is devoted to controlling the relaxivity (efficiency) of Gd^{III} complexes [2]. The structure of the chelate determines the interaction between the ion and the surrounding water molecules, and consequently the relaxivity of the complex. However, clinically used Gd-based contrast agents possess only fraction of the efficacy predicted by the theoretical models [3].

The enhancement of the efficiency of the probe is based on the structural modification of the clinical complexes, guided by a detailed understanding of the relationship between the relaxation parameters and the chemical structure. The purpose of this lecture is to discuss recent results in the search for relaxivity enhancement, probably the most widely studied area of MR contrast agent research.

Along with the optimization of the molecular parameters that govern the efficiency of the Gd-chelates, the use of macromolecular constructs, including dendrimers, micelles, liposomes, dendrimersomes and silica nanoparticles represents a well-established technology for the development of high relaxivity MRI contrast agents [4]. These nanoprobes make it possible to deliver to the site of interest a large number of Gd^{III} ions, thus increasing the sensitivity of the technique. The optimisation of several physico-chemical parameters of the active Gd^{III} centres (hydration number q, water exchange rate and local rotational flexibility of the chelate) allows obtaining dramatic relaxivity enhancement (> 200%) of the individual paramagnetic building blocks without compromising their stability [5-6]. Selected examples will be discussed with a special focus on the characterization of the systems using fast field-cycling NMR relaxometric techniques.

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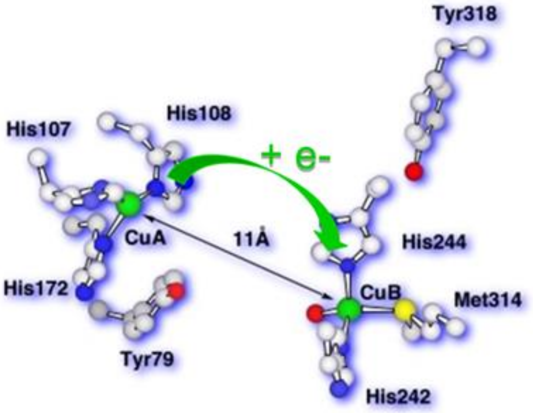
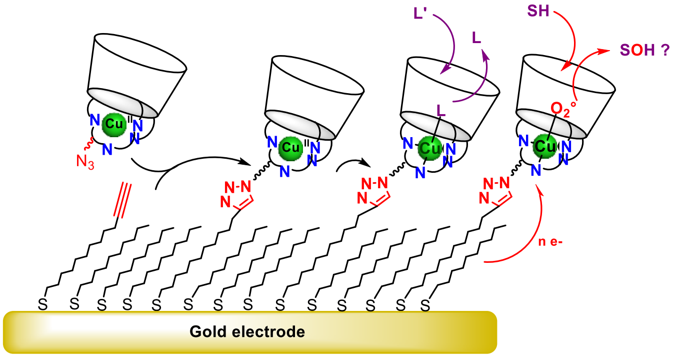
Cu(II)/Cu(I) electron transfer coupled to dioxygen activation in biomimetic complexes: From calix-zymes in solution to calix-zymes grafted on an electrode

Yves LE MEST

"Chimie, Electrochimie Moléculaires et Chimie Analytique" (CEMCA)
UMR 6521 CNRS - Université de Bretagne Occidentale,
6 Avenue Le Gorgeu, CS 93837, 29238 BREST Cedex 3, France
Yves.lemest@univ-brest.fr

Controlled immobilization onto electrode surfaces of functionnal systems is of specific importance for the development of sensing, catalytic… devices as well as for energy conversion. On one hand, it raises the fundamental question of coupling electron transfer to a metal active site. On the other hand, it appeals to the question of substrate selectivity and reactivity of the immobilized active site. In Nature, copper enzymes play a prominent role for dioxygen activation either at mononuclear copper sites (Cu_1O_2) [e.g. peptidyl glycine α-hydroxylating monooxygenase (PHM)] or at dinuclear sites (Cu_2O_2) [e.g. tyrosinase]. The functionality of the processes is based on the Cu^{II}/Cu^{I} electron exchange intimately associated to O_2 activation. Interestingly, in the case of PHM, a cavitary CuB site for the catalytic process is associated with a second Cu_A site devoted to electron transfer during the activation process. Hence this biological system is a prototypical example of a device associating a host-guest catalytic site to an electrode surface.





During the last two decades, we have been developing synthesis and electrochemistry of Cu-calix[6]azacryptand model complexes which preclude any bimetallic interaction and enforce exogenous ligation exclusively through the funnel, modeling a protecting protein cavity [1]. Supramolecular control of the Cu(II)/Cu(I) redox process has been emphasized through electrochemical studies in solution [2]. As well the structure allows the formation of mononuclear Cu_1O_2 adduct which are able to activate the oxidation of alkylamine substrates as encountered in mononuclear Cu enzymes [3]. As a counterpart we have developed a strategy for surface immobilization of these bio-inspired systems in self-assembled monolayers (SAM) onto a gold electrode, based on the "click" Cu-catalyzed Huisgen's cycloaddition reaction [4]. The grafted Cu complex displays a well-defined quasi-reversible system in cyclic voltammetry associated with the Cu(II)/Cu(I) redox process. Remarkably, this redox process triggers a powerful selective detection of primary alkylamines, based on a cavitary recognition process [5].

Hence we are now at the point of the activation of guest substrates by O_2, final process of the PHM modeling.

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Ruthenium, iridium and iron complexes in hydrogen/energy storage

Gábor LAURENCZY

École Polytechnique Fédérale de Lausanne, EPFL, ISIC – LCOM, Group of Catalysis for Energy and Environment, Avenue de Forel 2, 1015 LAUSANNE, Switzerland
gabor.laurenczy@epfl.ch

Converting CO_2 into useful feedstock chemicals and fuels represents an important strategy that not only removes CO_2 from the atmosphere, but also reduces dependence on petrochemicals. Among the potential reduction products, formic acid and methanol may be utilized as easy to handle H_2 storage media. These hydrogenation/dehydrogenation reactions ideally take place in water, and the catalysts are predominantly soluble transition metal complexes.

Formic acid can be selectively decomposed into CO free carbon dioxide and hydrogen in a homogeneous catalytic reaction [1]. It has been shown, that beside the ruthenium(II)-*m*tppts complex, (*m*tppts= triphenylphosphine *meta*trisulfonate) [2], the iron(II)–hydrido tris[(2-diphenyl-phosphino)ethyl]-phosphine complex also catalyses formic acid cleavage with an exceptionally high rate and efficiency (turnover frequency, TOF= 9'425 $h^{-1}mol^{-1}$; turnover number, TON= 92'400) [3]. This opens the way for inexpensive, non-noble metal based catalysts for this reaction.

Bicarbonates and carbonates have been proven to be viable H_2 vectors, as these widely available natural C_1 sources can be easily hydrogenated to formates or to formic acid derivatives [4]. Although ruthenium(II) and other platinum group metal complexes are the predominant catalysts in these reactions, Fe(II) complexes can be also active, giving a new perspective for the use of abundant and cheap Fe-based catalysts in HCO_3^- reduction [5].

Aqueous solutions of cesium formate and bicarbonate represent an effective hydrogen storage-delivery couple that undergoes either release or take up of hydrogen in the presence of $\{RuCl_2(m\text{tppts})_2\}_2$ and excess *m*tppts ligand: $H_2O + HCOO^- \Leftrightarrow HCO_3^- + H_2$; with no other additives required. Cesium salt solutions offer the advantage of improved volumetric and gravimetric H_2 density compared to their sodium and potassium analogs, owing to their high water solubility. A catalytic cycle is proposed for the formate dehydrogenation step, the pentacoordinated $[RuH(H_2O)(m\text{tppts})_3]$ hydride complex was identified being indispensable for promoting the formate dehydrogenation reaction [6].

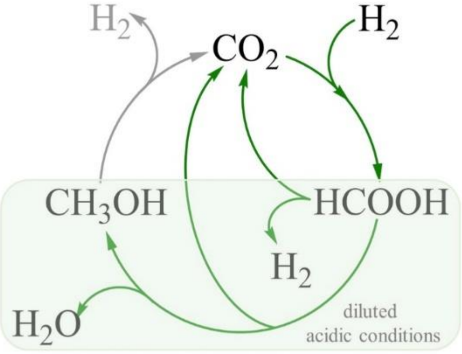

Figure 1. H_2 storage–delivery in $CO_2/HCOOH/CH_3OH$ systems catalyzed by Ru, Ir, Fe complexes.

Entirely rechargeable hydrogen storage devices have been developed based on the hydrogenation of bicarbonates, or CO_2 – amine systems and decomposition of formates in aqueous solution or organic solvents with the same catalysts, [{$RuCl_2$(*m*tppms)$_2$}$_2$] [7] (*m*tppms= triphenylphosphine *meta*monosulfonate) or [RuH_2(dppm)$_2$] [8] (dppm= diphenylphosphinomethane), in both directions without needing to isolate either the formates or bicarbonate salts to start new cycles.

For the first time, we realised the direct hydrogenation of CO_2 into formic acid using the [Ru(pta)$_4$$Cl_2$] complex (pta= 1,3,5-triaza-7-phosphaadamantane) in homogeneous catalytic reactions, in aqueous solution and in dimethyl sulfoxide, without any additives [9]. In water, at 40°C, 0.2 M formic acid can be obtained under 200 bar, however, in DMSO the same catalyst affords 1.9 M formic acid [10].

The hydrogenation of carbon dioxide to formic acid and the disproportionation of formic acid into methanol can be realized in a homogeneous catalytic reaction at ambient temperatures and in aqueous, acidic solution, with an iridium complex [(Cp*)Ir(dhbp)(OH_2)][SO_4], (dhbp = 4,4′-dihydroxy-2,2′-bipyridine, Cp* = pentamethylcyclo-pentadienyl). The formic acid yield is maximized in water without additives, while acidification results in complete (98%) and selective (96%) formic acid disproportionation into methanol [11-12].

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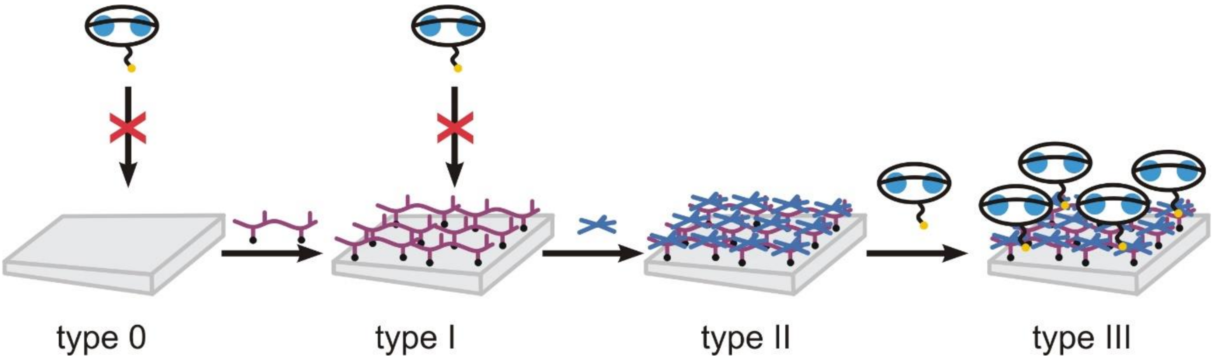
Keynote lectures

Metal complexes grafted on nanoparticles and surfaces: Stability and controlled release

Piersandro PALLAVICINI, [a] **Giacomo DACARRO**, [a] **Franck DENAT**, [b] **Nicolas SOK** [c]

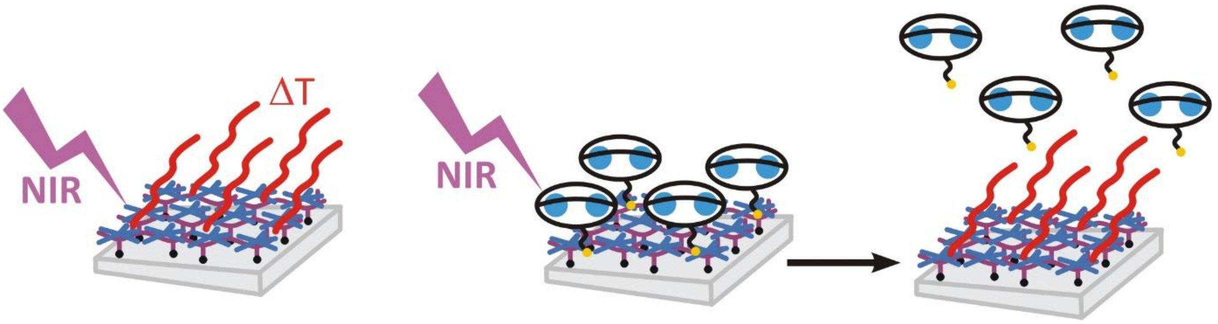
[a] *Dipartimento di Chimica, Università di Pavia, viale Taramelli 12, 27100 PAVIA, Italy*
[b] *Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR CNRS 6302, Université de Bourgogne Franche-Comté, 21078 DIJON Cedex, France*
[c] *UMR PAM A 02.102 Procédés Alimentaires et Microbiologiques, Université de Bourgogne Franche-Comté/AgroSup Dijon, 1 esplanade Erasme, 21000 DIJON, France*
piersandro.pallavicini@unipv.it

Metal complexes can be obtained as monolayers on bulk surfaces and on the surface of nanoparticles, provided that they feature a pendant function with a remote group capable of stable interactions with the chosen surface. Three approaches are possible [1]: a) grafting of the ligand with a second step for metal complexation; b) grafting of the preformed metal complex; c) grafting of a precursor reactive molecule, capable of coupling with a functional ligand or with a functional complex. In this talk, examples will be given regarding complexes grafted to bulk silica surfaces [2,3] and about complexes grafted on non-spherical gold nanoparticles (nanostars) as a colloidal dispersion in water [4]. In addition, and towards the attainment of multifunctional materials, a further category of surfaces will be illustrated, obtained by the layer by layer technique: first, a molecular monolayer is formed on a bulk surface (type 0, Scheme 1), bearing a terminal 'adhesive' function for a given nanoparticles type (as in type I, Scheme 1); then, a monolayer of grafted nanoparticles if formed on it (type II, Scheme 1); finally, a monolayer of metal complexes (or ligands) can be grafted on the free surface portion of the already grafted nanoparticles (type III, Scheme 1), with a process in which a grafting function/surface selectivity is required [5].



Scheme 1

Due to our research addressed to antibacterial applications of such surfaces for indwelling devices, particular attention is dedicated to the surface concentration of the metal complexes (and – if antibacterially active – of the metal nanoparticles) and to the release of active cations such as Ag^+ and Cu^{2+}. When working with type III surfaces or with complexes bound to gold nanoparticles, the further functionalities brought by the nanoparticles are to be considered. In particular, we use the photothermal effect, i.e. the conversion into heat of the radiation absorbed by Au nanoparticles plasmon resonances, due to non-radiative relaxation processes. The local temperature increase may either accelerate the M^{n+} decomplexation kinetics or induce the release of the whole complex, due to the weaposterpostersing of the gold-grafting function (typically S) bond [6], as it is pictorially illustrated in Scheme 2.



Scheme 2

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Lanthanide and actinide complexation with bio-inspired ligand platforms: Exploring trends in f-orbital bonding

**Gauthier J.-P. DEBLONDE, [a)] Julian A. REES, [a)] Peter B. RUPERT, [b)]
Wibe A. DE JONG, [a)] Roland K. STRONG, [b)] Rebecca J. ABERGEL [a)]**

[a)] *Lawrence Berkeley National Laboratory, 1 Cyclotron Road, BERKELEY, CA 94720, USA*
[b)] *Fred Hutchinson Cancer Research Center, 1100 Fairview Ave N, SEATTLE, WA 98109, USA*
rjabergel@lbl.gov

From potential contamination of individuals with radioactive fission products after a nuclear accident to the therapeutic use of radio-isotopes for cancer diagnostics and treatment, the biological chemistry of lanthanides and actinides has become increasingly relevant to a number of applied problems. Understanding the fundamental bonding interactions of selective metal assemblies presents a rich set of scientific challenges and is critical to the characterization of *f*-element coordination chemistry in environmentally and biologically relevant species, and to the development of highly efficient separation reagents or new therapeutic agents. Our approach to these challenges uses a combination of biochemical and spectroscopic studies on both *in vitro* and *in vivo* systems to characterize the selective binding of *f*-block metal ions by natural and biomimetic hard oxygen-donor architectures and the subsequent macromolecular recognition of the resulting assemblies.

The photophysics and solution thermodynamics behaviors of trivalent and tetravalent lanthanide and actinide complexes formed with selected siderophores and synthetic analogs such as multidentate hydroxypyridinonate and catecholate ligands were characterized [1-4]. Intramolecular sensitization of metal luminescence using these chromophore-bearing ligands was observed with a series of commonly luminescent ions such as Eu(III), Tb(III), Am(III) and Cm(III) [1-3], but also with the less accessible Bk(IV) [5]. Moreover, while most investigated ligands were shown to sensitize the luminescence of one or several metal ions, subsequent specific binding of the metal complexes to secondary entities such as proteins that participate in endogenous metal homeostasis mechanisms resulted in significant enhancement of the intramolecular energy transfer processes [2]. Particular metal-uptake pathways may therefore be used to create “double-antennas” for the sensitization of *f*-element luminescence, which in turn may lead to gains in sensitivity and enhanced detection of these ions in complex environmental samples.

Among those probed, one outstanding metal complex transporter is the mammalian siderophore-binding protein siderocalin (Scn), which appears as a potential player in the physiological transport of actinides. X-ray diffraction studies using Scn as a crystallization matrix revealed remarkable aspects of the protein’s interactions with chelated metals, establishing series of isostructural systems that can be used to derive trends along the 4*f*- and 5*f*-element sequences.

These results will be discussed with a perspective on how such studies have important implications for the use of spectroscopic and thermodynamic methods to exploit the fundamental knowledge of the role of *f*-electrons in actinide bonding for the development of new transport, separation, luminescence, and therapeutic applications [6].

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Importance of thermochemistry in the development of actinides extraction processes

Marie-Christine CHARBONNEL, Florian RODRIGUES, Nathalie BOUBALS

CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes, Service of Dissolution and Separation Processes, BP 17171,
30207 BAGNOLS-SUR-CÈZE, France
marie-christine.charbonnel@cea.fr

The research for efficient and robust ligands for the selective complexation and extraction of actinide (An) is a topic of high priority not only for a sustainable development and public acceptance of nuclear energy but also for the management of the existing radioactive wastes. The main current solvent-extraction process is Plutonium Uranium Refining by Extraction (PUREX) in which tri-n-butyl phosphate (TBP) extractant is used to separate uranium(VI) and plutonium(IV) from fission products dissolved in nitric acid solution. Due to increasing amount of plutonium in the future fuels, the replacement of TBP by new extractants has been considered.

In addition, different partitioning processes have been studied during the last decades to propose a closed cycle and/or reduce the toxicity and heat power of nuclear wastes. The aim of such processes is the recycling of minor actinides (as americium and curium), a challenging task if we consider the high amount of lanthanides (fission products) and the similar properties of Ln(III) and An(III).

The design of new molecules in the nuclear field requires the strict follow-up of process specifications but also high efficiency in terms of chemical affinity and selectivity towards the actinide target. A deep understanding of the related driving force could help the researcher in this first step of process development.

To study such biphasic systems, a methodology has been applied with combined approaches: the speciation in each phase could be obtained from different spectroscopic methods, molecular dynamics simulations and DFT calculations, and thermodynamic properties related to the main equilibria (stability constants, variation of free energy $\Delta G°$, enthalpy $\Delta H°$ and entropy $\Delta S°$) are deduced from calorimetry and/or Van't Hoff method. If the studies are performed inside a family, relationships between extraction performances and the structure of the molecule could be established.

Two examples will be presented to illustrate the interest of such a methodology:

- A first example with different hydrophilic ligands like diglycolamides $[R_2NCOCH_2]_2O$ which help to the selective separation of actinides(III) [1-2],

- A second example with several N,N-dialkylamides RR'NCOR", ligands of interest to separate major actinides U(VI) and Pu(IV). The influence of the alkyl groups R, R' and R" on the extraction and physico-chemical properties will be discussed. The difficulty lies in the high uranium concentrations [3-4].

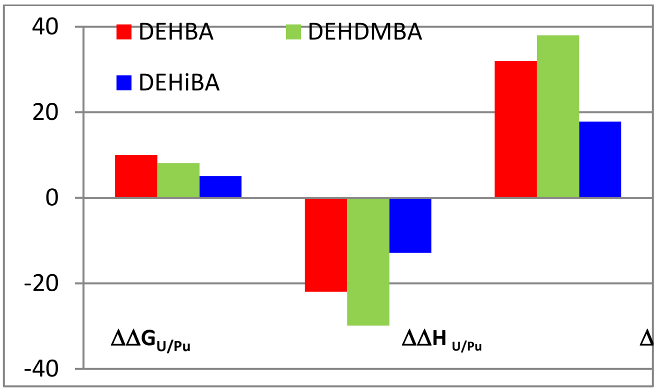

Figure 1. Thermodynamic properties related to the extraction of U(VI) and Pu(IV) by N,N-dialkylamides R_2NCOR' (R = 2-ethyl-hexyl, R' = nC_3H_7 (DEHBA), iC_3H_7 (DEHiBA) and $CH_2C(CH_3)_3$ (DEHDMBA)) diluted in TPH (mixture of alkanes).

This study helps to support the modelisation of the related liquid-liquid process but also to design new efficient molecules.

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Self-assembled lanthanide complexes: Thermodynamic and kinetic aspects

Josef HAMACEK

Center for Molecular Biophysics (CBM, UPR 4301), CNRS Orléans, rue Charles Sadron,
45071 ORLEANS, France
josef.hamacek@cnrs.fr

Lanthanide-containing compounds have found numerous applications as catalysts, in material sciences and in bioanalysis due to their exciting photophysical and magnetic properties. The preparation of such molecular devices, including very often several metal ions, requires a good control of metal complexation, especially in solution, since lanthanide cations are kinetically labile and have high coordination numbers. This is particularly true for multicomponent discrete compounds self-assembled from simple organic ligands and metal ions. The organization of such mixtures into thermodynamically stable products becomes a complicated process with a number of self-repairing steps. This mechanism was revealed for the first time by us for the case of dinuclear triple-stranded helicate with Eu(III) [1]. Nowadays, the formation of large well-organized edifices with lanthanides is well managed in acetonitrile, but the self-assemblies occurring in water are rare [2] and remain challenging.

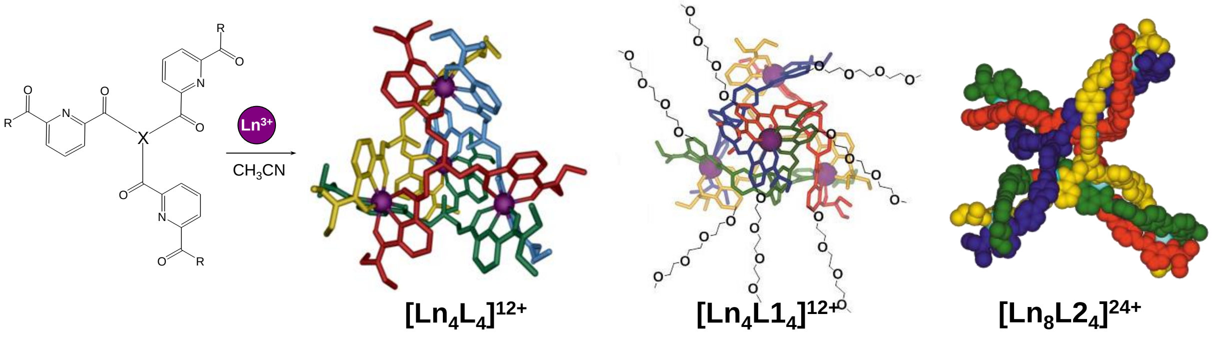

Figure 1. Self-assembly of tetranuclear and octanuclear lanthanide complexes.

In this contribution we will present thermodynamic and kinetic aspects of self-assembly processes in polynuclear lanthanide helicates formed with different polytopic ligands [3 - 5]. When the system complexity increases, the kinetic evolution slows down due to re-equilibrating steps. The formation of large assemblies often becomes more sensitive to subtle differences in ionic radii along the lanthanide series and this behaviour will be illustrated for tetranuclear assemblies with tripodal ligands. In addition, the structural match between ligands and lanthanide cations strongly influences the speciation of complex systems.

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Cyclopeptide-derived molecular containers for inorganic anions - Thermodynamic and kinetic aspects of complex formation

Stefan KUBIK

Fachbereich Chemie - Organische Chemie, Technische Universität Kaiserslautern,
Erwin-Schrödinger-Straße, 67663 KAISERSLAUTERN, Germany
kubik@chemie.uni-kl.de

Anion recognition in aqueous solution was for a long time believed to be restricted to receptors containing multiple positive charges and/or metal ions while interactions of neutral receptors with anions were considered to be too weak to be efficient in water. Independent work in several groups has shown, however, that even neutral receptors, which interact with anions only by hydrogen bond (or halogen bond) formation, can possess considerable anion affinity in aqueous media [1]. One example is the cyclic hexapeptide **1** developed by us (Figure 1), which binds to inorganic anions (halides, sulfate) in 80% water/methanol [2].

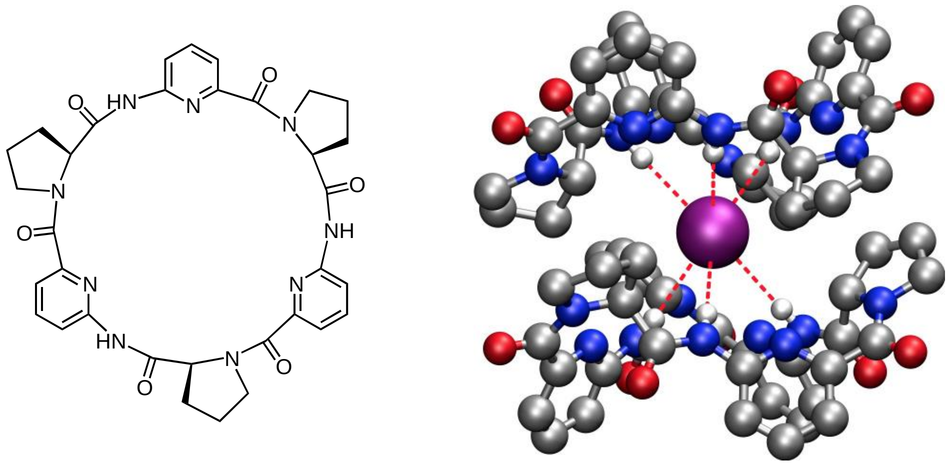

Figure 1. Structure of cyclopeptide **1** (left) and 2:1 sandwich-type solid state structure of its iodide complex (right).

The initially serendipitous discovery of this anion receptor prompted us to elucidate in more detail the reasons for its unique binding properties. Clues came from the characteristic structure of the anion complexes of **1**, characterized by two interdigitating cyclopeptide rings that bind the anion in a cavity between them (Figure 1) [2]. Complex stability thus derives not only from direct receptor-substrate interactions but also from interactions between areas of the two cyclopeptide rings, specifically the hydrophobic surfaces of the proline subunits, not directly involved in anion-binding [3]. This finding turned out to be an ideal starting point for further investigations.

In this context, we showed that the sandwich-type 2:1 complexes of **1** can be converted into 1:1 complexes by covalently connecting the two cyclic peptide rings *via* suitable linkers.

As expected, the corresponding bis(cyclopeptides) more efficiently interact with anions thanks to the chelate effect [4]. While the overall anion affinity of singly-linked bis(cyclopeptides) turned out to be relatively independent of the structure of the linkers investigated by us, the individual thermodynamic parameters associated with anion complexation depend on linker structure in a characteristic fashion [5].

Varying the number of connection points between the cyclopeptide rings was used as another means to influence binding properties. We indeed found that increasing the number of linkers not only affects the thermodynamics but also the kinetics of complex formation because of the associated progressive closing of the receptor portals. Particularly interesting properties were observed for a bis(cyclopeptide) with three linkers.

A disadvantage of most bis(cyclopeptides) is their generally lower water solubility in comparison to **1**. We therefore also pursued strategies to improve the solubility of our anion receptors to allow binding studies in water. In this context, the introduction of hydrophilic substituents into the aromatic cyclopeptide subunits and into the linkers turned out to be the method of choice [6]. This structural modification gave rise to a bis(cyclopeptide) whose anion affinity could be studied in a wide range of solvent mixtures from 100% water to 100% methanol, DMSO, or acetonitrile. Detailed characterization of the thermodynamics of anion binding in these solvents and in corresponding mixtures showed that solvent effects mediate anion affinity of the respective bis(cyclopeptide) in a relatively complex fashion.

In this keynote lecture, the evolution of our cyclopeptide-based anion receptors and the lessons learned from our binding studies will be summarized and discussed.

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From selective to differential receptors. Real case studies

Raffaela BIESUZ, Maria PESAVENTO, Giancarla ALBERTI

Dipartimento di Chimica, Università degli Studi di Pavia,
via Taramelli 12 27100 PAVIA, Italy
rbiesuz@unipv.it

Generally speaking, when we think to a sensor we have in mind the idea of finding an active site, specifically designed to vary its properties after interaction with a single target analyte; at least under some specific conditions, the interaction between them is desirably "highly selective". As well described by Ansyln and Lavigne [1], we are primarily driven by a desire to mimic nature's exquisitely specific binding interactions simplified by the "lock and key" analogy. Most of the huge amount of works done on sensors in the last decades are indeed exactly on this line. From this point of view unfortunately, molecular recognition in natural systems is very often not reducible simply to that, but is much more sophisticated. More often a "differential" binding is found, meaning that receptors exhibit different binding characteristic, none of which are necessarily "specific" or even "selective". This evidence, that receptors could be generalized more than specialized indeed has open a new branch of application developing array of sensors, responsible of a sort soft interaction and that produces a composite signal. The analogy of this interaction is still found in nature in the mammalian sense of taste and smell. Of course specific multivariate approaches must be used to analyse these signals, (most of time optic signals) and based on this new idea many examples of differential receptors produced by synthetic chemistry have been presented [1].

Our research has been, and still is, based on the study of different solid phases that exhibit chelating properties towards metal ions. Many efforts have been devoted to the characterisation of the sorption mechanism of many metal ions, manly conducted on commercial products, such as Chelex 100, defining a method to assess the exchange reactions and their intrinsic complexation constants [2]. In this way, the behaviour of a sorbent material is predictable exactly as that of a soluble chelating reagent, since the equilibrium is defined through, not operational, but independent properties. In this early stage, in any case, the resins were used not as a sensor, but to pre- concentrate metal ions from a water solution. The metal ions simultaneously sorbed by the resin were desorbed in an acid solution, and determined independently. From the data analysis, the total metal ion, but also its degree of complexation, were established and the method was applied to a large series of environmental samples where metals are generally present at sub-trace levels [3].

In the following years, we started to develop new solid phases specifically designed, and the core example still is the immobilisation of DFO on silica gel and the application to urine samples for quantification of Fe(III) and the evaluation of its speciation [4-5]. The same ligand was successfully immobilized also on filtering paper [6]. I consider this as our first attempt to develop a sensor, based on the strong "selective" complex of iron(III) with DFO. The same strategy is present is other reasearches of the following years: an azacryptand containing two tripodal tetra-amine receptor was fixed on silica MCM41 and Amberlite CG-50 supports for separation and extraction of perrhenate and pertechnetate from water solution [7], or a methacrylate membrane which includes kojic acid, giving a film-like membrane was used in small sensory discs for iron(III) sensing and quantification [8].

Our idea is now to switch to a "sensor on demand" depending of the strategy, or on a specific need. Consequently, we can decided to move toward a lock and key inspired receptor, focused on one specific analyte, as all the cases shown above, or to a differential receptor(s) for multi-analyte sensing. Here we present, in the poster section, a sensor for Pd(II) determination at extreme pH values based on the first strategy, due to the extraordinary selectivity of this metal ion for an azosulphonated ligand, and consequent to the fact that Pd(II) must be often detected in solutions coming from a dissolution under strong acidic conditions. Conversely, we also present a contribution which is inspired to the multiple interaction that can be included in the second strategy of differential receptor. A sensor for the simultaneous determination of Fe(III), Al(III) and Cu(II) is proposed where Alizarin Red S is fixed by anion exchange on a material more similar to a fabric, or a soft paper, insoluble in water. It is sold in the laundry detergents section of any supermarket and called "*Colour Catcher®"*. Results seems really encouraging, and for sure it has a topic characteristic a sensor must have, being extremely cheap. We are not still in the way of a multi-detector array, but at the beginning. Presently we based our investigation on a single receptor, that simultaneously interacts with more than one metal ion, each of them able to modify the signal, in this case the colour, depending on the type of cation and on its concentration. The signal becomes the entire vis spectra. The gold point is that selectivity is not a problem, since we have the tool to discriminate the contributions of the single metal ion to the signal. The tool is PLS (Partial Least Square Regression) a traditional chemometric analysis. In a way nothing really new, simply we are teaching an old indicator, Alizarin Red S, a new trick.

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Quantification of Ni-L'-Ni bonding interactions in macrocyclic dinickel complexes of the type $[Ni_2L(\mu\text{-}L')]^+$ (L' = F^-, Cl^-, Br^-, I^-, OH^-, N_3^-) by ITC and DFT

Alexander JEREMIES, [a] **Michel MEYER,** [b] **Berthold KERSTING,** [a]
Vitaly MATULIS, [c] **Oleg A. IVASHKEVICH** [d]

[a] *Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29,*
04103 LEIPZIG, Germany
[b] *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),*
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[c] *Research Institute for Physical Chemical Problems of Belarusian State University,*
Leningradskaya 14, 220030 MINSK, Belarus
[d] *Belarusian State University, 4 Nezavisimisti avenue, 220050 MINSK, Belarus*
b.kersting@uni-leipzig.de

The coordination of small spherical halide (F^-, Cl^-, Br^-) [1] and linear di- and triatomic anions (hydroxide [2], azide [3]) by the dinuclear cavitand $[Ni_2(L^{N6S2})]^{2+}$, where $(L^{N6S2})^{2-}$ is a macrobinucleating hexaaza-dithiophenolate ligand, has been investigated.

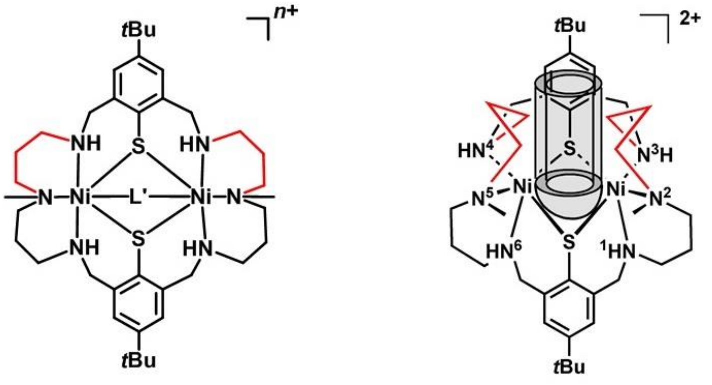

Figure 1. Left: Structure of the $[Ni_2L^{N6S2}(\mu\text{-}L')]^+$ complexes (L' = F^-, Cl^-, Br^-, OH^-, N_3^-). Right: Anion binding pocket of $[Ni_2L]^{2+}$. The selectivity is essentially governed by the two opposing propylene linkers acting as a pair of jaws (highlighted in red).

The cavitand exhibits a chelating $N_3Ni(\mu\text{-}S)_2NiN_3$ moiety with two square-pyramidal $Ni^{II}N_3S_2$ units situated in an anion binding pocket of ~ 4 Å diameter formed by the organic backbone of the $(L^{N6S2})^{2-}$ macrocycle. The receptor reacts readily with fluoride, chloride, bromide, hydroxide and azide ions to afford an isostructural series of $[Ni_2(L^{N6S2})(\mu\text{-}L')]^+$ complexes featuring a $N_3Ni(\mu\text{-}S)_2(\mu\text{-}L')NiN_3$ core structure. No reaction occurs with iodide or other polyatomic anions (ClO_4^-, NO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_4^-, SO_4^{2-}). The binding events are accompanied by discrete UV–vis spectral changes, due to a switch of the coordination geometry from square-pyramidal (N_3S_2 donor set in the precursor) to octahedral in the products. This allows the determination of the respective 1:1 equilibrium constants for the 1:1 complexes by absorption spectrophotometry. In MeCN/MeOH (1/1 v/v) the log K_{11} values for the 1:1 complexes determined by absorption spectrometry are 7.77(9) (F^-), 5.98(1) (OH^-), 5.20(4) (N_3^-), 4.06(7) (Cl^-), and 2.0(1) (Br^-). These values were found to compare favorably well with those determined by isothermal titration calorimetry and to correlate with the hardness of these ions. X-ray crystallographic analyses and computational studies reveal a significant increase of the intramolecular distance between two propylene groups at the cavity entrance upon going from F^- to I^- (for the DFT computed structure), indicative of a high degree of pre-organization of the $[Ni_2(L^{Me2H4})]^{2+}$ receptor and a size-fit mismatch of the receptors binding cavity for anions larger than F^-. Results from IR, ESI-MS, UV-vis, cyclic voltammetry, SQUID magnetometry, and X-ray crystallography will be discussed.

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Polyazamacrocycles with phosphorus acid pendant arms as ligands for divalent copper

Přemysl LUBAL, [a)] Vojtěch KUBÍČEK, [b)] Jan KOTEK, [b)] Petr HERMANN [b)]

[a)] Department of Chemistry & Central European Institute of Technology (CEITEC), Masaryk University, Kotlářská 2, 61137 BRNO, Czech Republic
[b)] Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 12840 PRAGUE, Czech Republic
petrh@natur.cuni.cz

Copper has several radioisotopes suitable for molecular imaging with PET. To use the radioisotopes *in-vivo*, they must be bound by ligands with suitable properties. Among ligands suggested till now, macrocycles with coordinating pendant arms have been the most common ones. To modify their coordination chemistry, acetic acid pendants can be replaced with methylphosphonic/phosphinic acid ones. Both phosphorus acids are very acidic and, thus, they are able to bind metal ions even in very acidic solutions. The fully deprotonated double-charged phosphonate group increases basicity of the neighbouring amine group, and, on the other hand, phosphinate is an electron-withdrawing group decreasing the amine group basicity. Both groups are considered to be harder than the carboxylate group and they are able to form strong hydrogen bonds suggesting alternation of properties of protons in their vicinity.

The parent carboxylic acid macrocycles, **NOTA**, **DOTA** and **TETA** (Figure 1) have been all labelled with copper radioisotopes. Upon modification with phosphorus acid pendant arms, their coordination properties toward copper(II) are altered in various ways. Thermodynamic stability of the complexes is changed according to basicity of the ligand ring amines: if compared with the parent carboxylate ligands, it is increased for the more basic phosphonate derivatives and decreased for the less basic phosphinate ones. Selectivity for divalent copper over other metal ions is the highest for cyclam derivatives. Complex formation is generally faster for the phosphorus acid derivatives. The acceleration can be attributed to high acidity of phosphorus acid-containing ligands and/or their better ability to form *out-of-cage* complexes as shown e.g. for **te1ppi** (Figure 1). However, these properties should be carefully tuned as too stable *out-of-cage* complexes decrease the complexation rate (as shown e.g. for ligands in the **Me_3te1p^R** series; Figure 1). Kinetic inertness of the complexes is less predictable. For complexes of the **DOTA** analogues, kinetic inertness is gradually decreased with more phosphorus acid pendant arms. Generally, copper(II) complexes of cyclam derivatives are highly inert. The inertness depends on a degree of substitution of the ring amine groups and complexes of fully substituted cyclam derivatives are the least inert. The inertness of the complexes also depends on a kind of substituents on the phosphorus atom(s).

For selected ligands, radiolabelling with non-carrier-added (NCA) 64-Cu was tested and it was shown that these ligands (e.g. **te1pp**, **1,8-te2p** or **cb-te2ppi**; Figure 1) are labelled with much better efficiency than the parent ligands (Figure 2). As only low molar excess of the ligands over copper radioisotope is necessary for efficient labelling, a high specific activity of the labelled compounds is obtained.

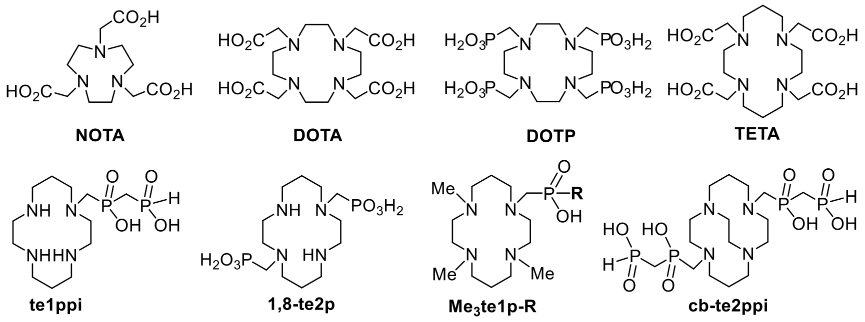

Figure 1. Structures of selected ligands.

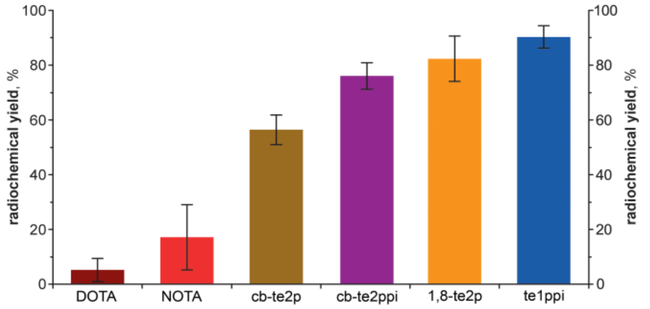

Figure 2. Radiolabelling with 64-Cu (25 °C, pH 6.5, 100-times molar excess of ligands).

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On the equilibrium dynamics of metal complexes: NMR for coordination chemistry

István BÁNYAI

Department of Physical Chemistry, University of Debrecen, Egyetem tér 1,
4032 DEBRECEN, Hungary
banyai.istvan@science.unideb.hu

Chemical kinetics is the science studying the time course of chemical reactions. It means that during reactions the change of free energy is smaller than zero, $\Delta_r G < 0$. There are two extreme states of chemical reactions. First, the reaction is very far from the equilibrium, $\Delta_r G << 0$ but for some reason no macroscopic, only periodical changes may occur in the system (stationary state) during the observation time. These systems are the subject of non-linear dynamics. When the systems are in thermodynamic equilibrium, $\Delta_r G = 0$, there are neither macroscopic nor periodic changes, however we know that equilibrium is dynamic. Equilibrium dynamics deals with the microscopic (molecular level) motions at $\Delta_r G = 0$ situation.

In coordination chemistry there are three important actors in solution: the metal ion, the ligand and the solvent from which complexes form in equilibrium. We are interested in three basic features: speciation, structure and the dynamics of the complexes. Multinuclear NMR (Nuclear Magnetic Resonance) may help to clarify the composition of complexes formed and is useful to determine the structure in solution, but for the dynamics of equilibrium it is irreplaceable. For most spectroscopy the equilibrium is slow, that is, we have as many resonances as are complexes in the system, therefore there is no information about the dynamics.

NMR has many important features. The life time of excited states are very long compared to other spectroscopies, it is in the range from ms to min. These are the typical timescales of fast chemical reactions. NMR has two relaxation timescales, the longitudinal and the transverse, which determine very different characteristics of the NMR spectra. In practice the FT-NMR signal can be described with a set of differential equations (McConnel-Bloch equations) and since the excitation is in microsecond range we are free to plan and change the initial conditions and analyze the response functions by appropriate models. Another important point is that solvent, ligands and metal ions may have NMR active nucleus(i) with different timescales, therefore if one timescale is too short or too long the other can be suitable. Dynamic NMR is unique for studying the dynamics in cases when not only $\Delta_r G = 0$ but $\Delta_r G^\theta = 0$ as well, like fluxionality of metal complexes.

The complex equilibria are ideal for dynamic NMR analysis as well as the dynamic NMR is ideal for studying complex equilibria. In this lecture I will show the basic techniques and the wide variety of information that can be extracted from dynamic NMR data. I will compare the one and two dimensional techniques and show the kinetic analysis of NMR data.

How UV-visible and Mössbauer spectroscopies evidenced the electron reservoir capability of a pentanuclear iron complex

Geneviève BLONDIN, [a] **Eric GOURÉ**, [b] **Martin CLÉMANCEY**, [a] **Jacques PÉCAUT**, [c] **Marie-Noëlle COLLOMB**, [b] **Jean-Marc LATOUR** [a]

[a] BIG/LCBM/pmb, UMR 5249 CEA-CNRS-Univ. Grenoble Alpes,
38000 GRENOBLE, France
[b] DCM, UMR 5250 CNRS-Univ. Grenoble Alpes, 38000 GRENOBLE, France
[c] INAC/SyMMES/ricc, CEA-Univ. Grenoble Alpes, 38000 GRENOBLE, France
genevieve.blondin@cea.fr

Spontaneous self-assembly is a very efficient way to synthesize high-nuclearity metal complexes. The ditopic 3,5-bis(pyridin-2-yl)pyrazole (Hbpp) with an iron salt gives under inert atmosphere and in the presence of base the bis(triple-stranded) helical pentanuclear iron complex $[\{Fe^{II}(bpp)_3\}_2Fe^{II}_3(\mu\text{–}O)]^{2+}$ [1]. When the synthesis is performed under air, the same complex is obtained but it presents a $4Fe^{II}1Fe^{III}$ composition [2, 3]. In both complexes, X-ray diffraction shows that the iron ions are located at the vertices of a trigonal bipyramid.

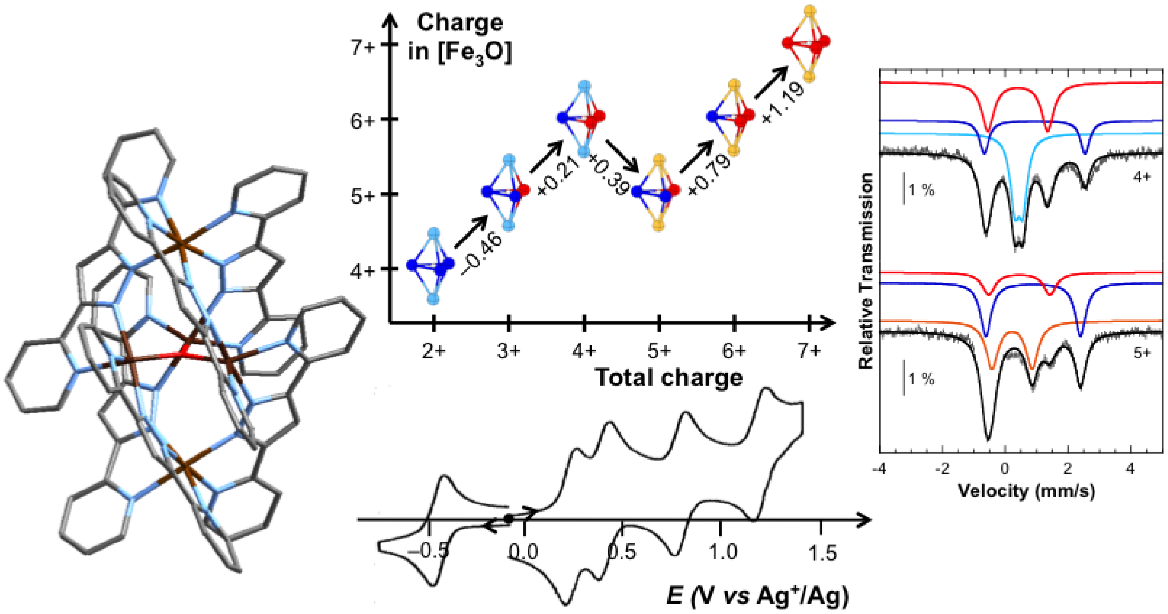

Figure 1. X-ray structure of $[\{Fe^{II}(bpp)_3\}_2Fe^{II}_2Fe^{III}(\mu\text{–}O)]^{3+}$ (left), 80 K Mössbauer spectra of the 4+ and 5+ complexes (right), cyclovoltammogram recorded in CH_3CN and location of the Fe^{II} and Fe^{III} ions for the six different redox states (centre).

This complex presents a very rich redox behavior as evidenced by the five reversible waves detected in cyclic voltammetry. A powerful tool to investigate iron complexes is Mössbauer spectroscopy that indeed allows here the location of all the Fe^{II} and Fe^{III} ions in the different redox states, in full agreement with the UV-visible studies. Remarkably, whereas a single electron is exchanged between de 4+ and 5+ species, the two iron ions in axial positions are simultaneously oxidized (or reduced), the $Fe_3(\mu\text{–}O)$ equatorial unit displaying a compensating one-electron reduction (or oxidation). This presentation will fully explain this electronic redistribution and evidence a redox bistability thwarted by an intramolecular electron transfer. This outstanding electron reservoir capability is a strong asset for multielectron catalysis, as proposed for this complex regarding water oxidation [3].

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Oral communications

Polyhalide complexes of Bi(III) and Sb(III)

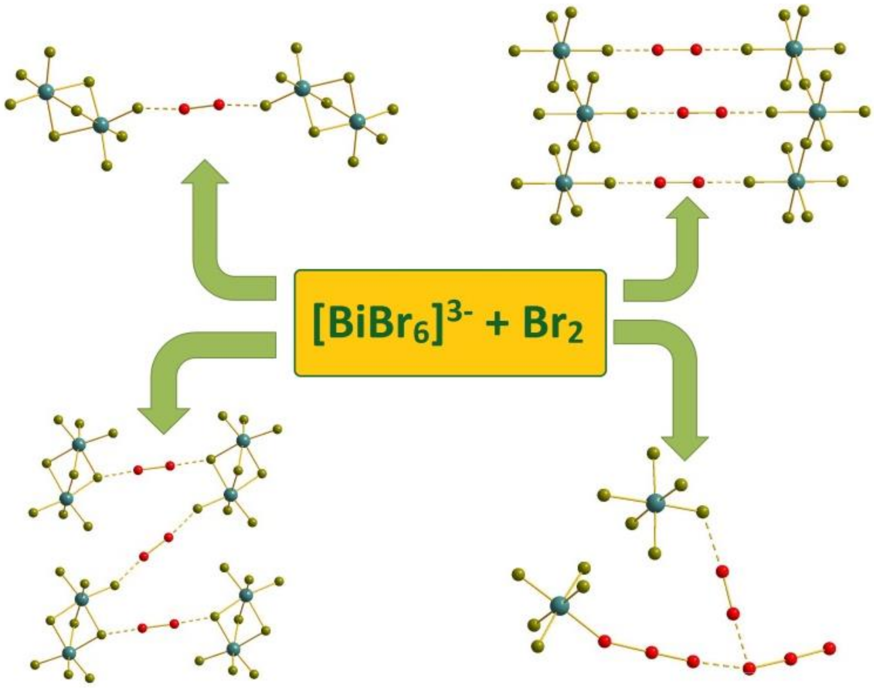
Sergey A. ADONIN, [a,b] Igor D. GOROKH, [b] Maxim N. SOKOLOV [a,b]

[a] Nikolaev Institute of Inorganic Chemistry SB RAS, Lavrentieva St. 3,
630090 NOVOSIBIRSK, Russia
[b] Novosibirsk State University, Pirogova St. 2, 630090 NOVOSIBIRSK, Russia
adonin@niic.nsc.ru

Halide complexes of post-transition metals attract an interest due to their optical properties and possible applications in phorovoltaics. During our studies of bromobismuthates (III), we have found that reactions

$$[BiBr_6]^{3-} + Br_2 + (cation)Br_x$$

in HBr solutions may result in anionic polybromide Bi(III) complexes where $\{Br_2\}$ units are connected with bromide lidands of Bi(III) coordination sphere by specific supramolecular contacts, yielding in $\{Br_x\}^{y-}$ type polymeric ligands. In some cases, there also form tribromide $\{Br_3\}^-$ ligands coordinated to bismuth atoms. The structure of anionic part strongly depends on the nature of cation used in reaction.



The complexes demonstrate remarkable thermal stability (typically decomposition does not occur up to 120-150°C). At the same time, the “captured” $\{Br_2\}$ units preserve their ability to react with unsaturated hydrocarbons; selectivity of these reactions towards various alkenes was studied [1-3]. Mixed-halide complexes – polybromide-chlorobismuthates [4] and polyodide-bromobismuthates – may be obtained by similar strategy. Besides, it was found that polyiodo-bromoantimonates (III) may be obtained in similar way, revealing several additional structural types, including those where Sb atom is 5-coordinated (pyramidal environment) [4].

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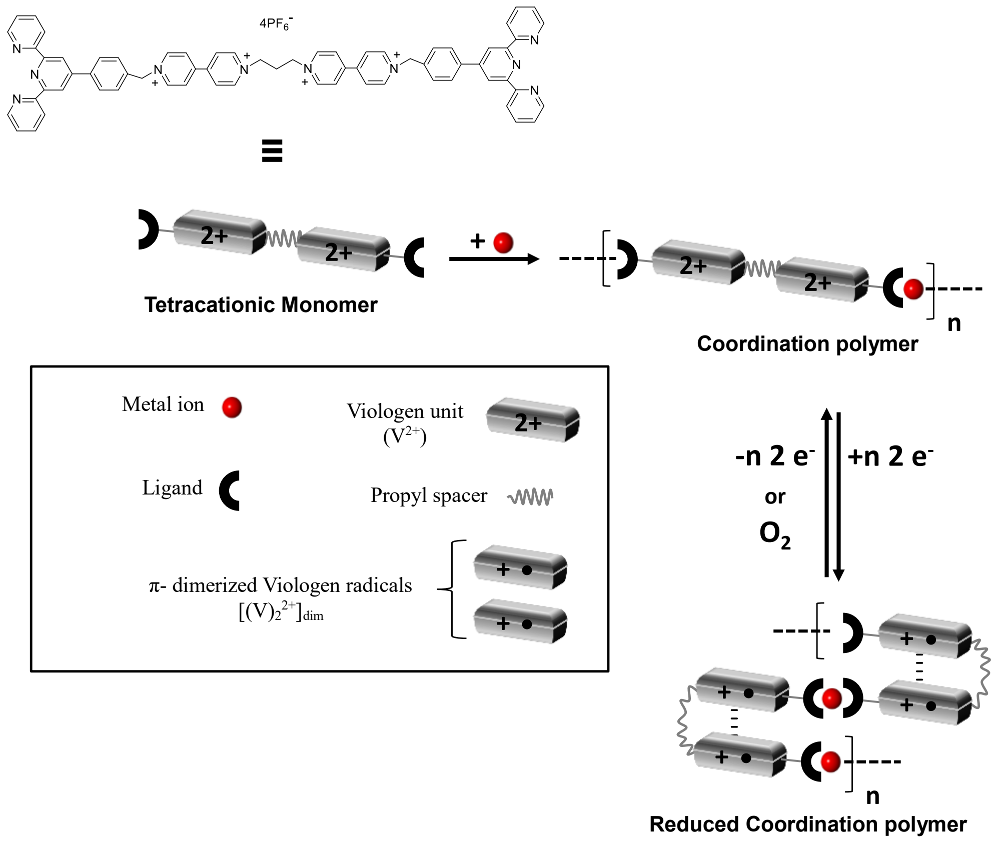
Redox responsive coordination polymers based on the viologen units

Wathiq Sattar ABDUL-HASSAN, [a,b] Denis ROUX, [c] Saioa COBO, [a]
Eric SAINT-AMAN, [a] Christophe BUCHER, [d] Florian MOLTON, [a] Guy ROYAL [a]

[a] Laboratoire de chimie Inorganique Redox, Département de Chimie Moléculaire UMR 5250, Université Grenoble Alpes/CNRS, 38000 GRENOBLE, France
[b] Department of Chemistry, College of Science, Thi-Qar University, 64001 NASIRIYA, Iraq
[c] Laboratoire Rhéologie et Procédés, Université Grenoble Alpes/CNRS, 38000 GRENOBLE, France
[d] Laboratoire de Chimie (UMR5182), Ecole Normale Supérieure de Lyon/CNRS Université de Lyon 1, LYON, France
wathiq-sattar.abdul-hassan@univ-grenoble-alpes.fr and wathiq1977@yahoo.com

Responsive polymers are of particular interest for the development of smart materials. We developed switchable π-dimers that are constructed by the association between two viologen cation radicals. These dimerized structures are employed to control an organization within metal-ligand bonded assemblies. First we designed the π-dimerizable monomer functionalized with two metal bonding units (see scheme below). These monomers are based on the propylene spacered bis-viologens featuring two terminal terpyridine units. Secondly, the reversible movements between the tetracation monomer and the intramolecular π-dimerized monomer form are induced by redox stimuli. In the presence of transition metal ions, the tetracation monomer forms self-assembled metal-ligand coordination bonds between repeated terpyridine units leading to extended 1D coordination polymers. Then after electron transfer to the viologen units, a zig-zag intramolecularlly dimerized coordination polymers could be adopted. The nature of these electrogenerated switchable coordination polymers depends mandatorily on the repeated coordination complexes, the bulkiness of the coordination polymers, and finally the dimerization between viologen radicals whether intra- or intermolecularly process. The essential comprehension of the nature (and the variables which drive it) of the targeted switchable coordination polymers will be necessary to modify the properties of these polymers according to the required needs.



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Mapping the frontier orbitals of magnetic POMs on Au and in solution

Xiaofeng YI, [a,b] **Natalya V. IZAROVA**, [b] **Maria STUCKART**, [a,b] **David GUERIN**, [c]
Stéphane LENFANT, [c] **Dominique VUILLAUME**, [c] **Paul KÖGERLER** [a,b]

[a] *Institute of Inorganic Chemistry, RWTH Aachen University, 52074 AACHEN, Germany*
[b] *Peter Grünberg Institute, Electronic Properties (PGI-6), Forschungszentrum Jülich,*
52425 JÜLICH, Germany
[c] *Institute of Electronics, Microelectronics and Nanotechnology, CNRS,*
59652 VILLENEUVE D'ASCQ Cedex, France
x.yi@fz-juelich.de

Controlled molecular surface deposition/chemisorption represents a key challenge in the fabrication of molecule-based devices [1]. One approach utilizes suitable linker groups that covalently bind to metallic surfaces, as well as to the molecules of interest, in our case transition metal complexes of polyoxometalates (POMs, discrete anionic metal-oxides most commonly composed of early transition metal ions in their higher oxidation states such as $Mo^{V/VI}$, W^{VI}, $V^{IV/V}$, Nb^{V} etc.), motivated by their features attractive for molecular electronics and spintronics (e.g. structural versatility, redox and thermal stability, tuneability of molecular magnetic and charge transport properties) [2].

Focusing on a nanoscaled amino-organoarsonate-functionalized cobalt-polyoxotungstate (**NH_2-POM**, Figure 1), which was synthesized through self-assembly reaction and characterized in solid state by XRD / IR / TGA / XPS / SQUID, as well as in solution by cyclic-voltammetry (CV) and UV-Vis spectroscopy [3], we explore the electronic consequences of its covalent attachment on gold (Figure 2).

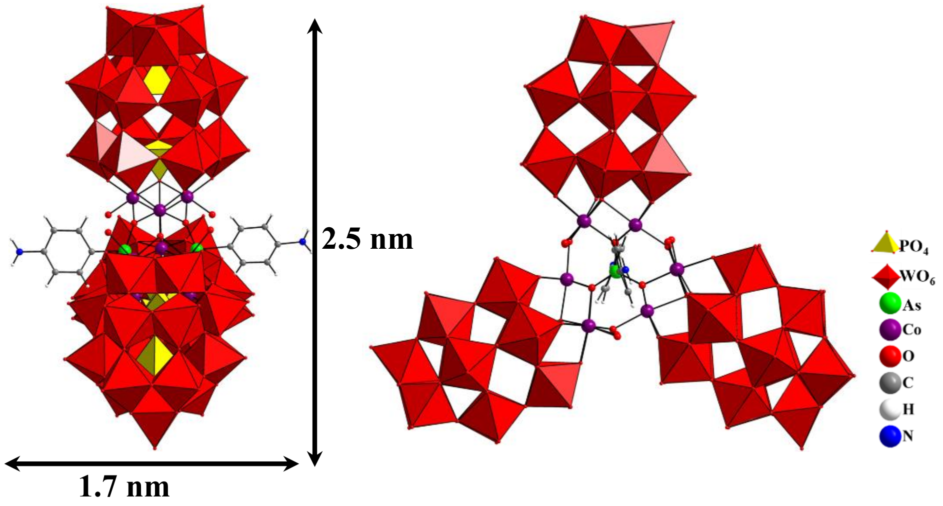

Figure1. Structure of $[Co_9(H_2O)_6(OH)_3(P_2W_{15}O_{56})_3(H_2N\text{-}C_6H_5AsO_3)_2]^{25-}$ (NH_2-POM).

The NH_2-POM-coated gold sample was characterized by ellipsometry, X-ray photoemission spectroscopy (XPS), CV, C-AFM and eutectic GaIn drop contact measurements

[3]. We will discuss the relation between the frontier orbitals as derived from the chemisorbed POM and for the POM in solution.

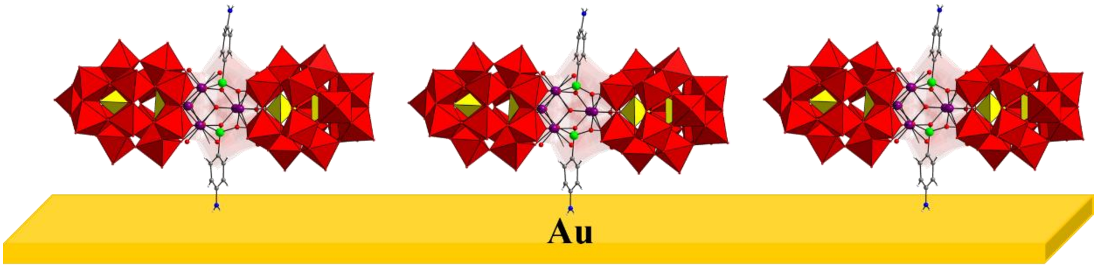

Figure 2. Coating of a gold surface with NH_2-POM.

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Study of solvation and complexation of a ionic resorcin[4]arene in aqueous solution

Nicolás MORENO, [a,b] **Paula GUERRERO**, [a] **Edgar F. VARGAS**, [a]
Richard BUCHNER [b]

[a] Laboratorio de Termodinámica de Soluciones de la Universidad de los Andes,
Cra 1ª No. 18 A 12, 111711 BOGOTÁ, Colombia
[b] Institut für Physikalische und Theoretische Chemie, Universität Regensburg,
Universitätstrasse 31, 93051 REGENSBURG, Germany
nic-more@uniandes.edu.co

Supramolecular chemistry accounts the design of host molecules to maximize affinity and selectivity towards a specific guest. This process however, finds some limitations in the use of the designed molecules due to low solubility, weaker affinity or no selectivity. These problems are associated to the solvation phenomena and they are not usually taken it into account during the design process; although is well known that solvation is a limiting process in assembly, molecular recognition and complexation. In this work aqueous solutions of a ionic resorcin[4]arene are studied using dielectric relaxation spectroscopy (DRS) at 298.15 K. Moreover, speciation of the ionic resorcin[4]arene is studied using potentiometric titration and tested against different metallic cations in water using isothermal titration calorimetry (ITC). The obtained results were evaluated to elucidate the relationship between solute-solvent interactions and host-guest complexation.

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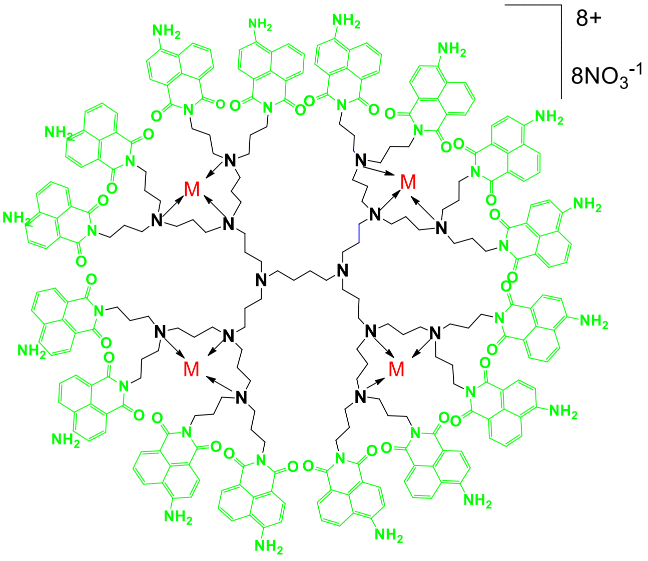
Biomedical activity of metallodendrimers modified with 1,8-naphthalimide

Ivo GRABCHEV, [a] **Desislava STANEVA**, [b] **Evgenia VASILEVA-TONKOVA** [c]

[a] *Sofia University "St. Kliment Ohridski", Faculty of Medicine, 1407 SOFIA, Bulgaria*
[b] *University of Chemical Technology and Metallurgy, 1756 SOFIA, Bulgaria*
[c] *Institute of Microbiology, Bulgarian Academy of Sciences, 1113 SOFIA, Bulgaria*

In the recent three decades dendrimers have been a part of a very important research area due to their diverse biological and biomedical activities. They are a special class of synthetic polymers with highly branched well defined three-dimensional and monodisperse structure, which allows them to play an important role in the fields of nanomedicine, pharmaceutical and medical chemistry. A new area of the intensive investigations on dendrimers has been their application as antibacterial and antifungal agents due to the high concentration of surface functional groups. In the case when the peripheral functional groups are modified with different microbiological monomer agents the obtained new dendrimer is of high bioactivity. Incorporation of metal ions into the dendrimer structure opens the opportunity of having a new interesting and prospective role in dendrimer chemistry.



1,8-naphthalimides and their derivatives are important class of compounds with diverse sensor, pharmacological and biomedical applications. Special attention has been paid to investigating them as antibacterial, antifungal, antiviral, or anticancer therapeutics. The possibility of combining the activity of 1,8-naphthalimides with that of the dendrimers has emerged as a very interesting and prospective research trend.

In this study the synthesis of metallodendrimers based on PPA or PAMAM dendrimers from different generations modified with 1,8-naphthalimide is presented. Their microbiological and anticancer activity against diverse pathogens and human cancer cells are discussed. Metallodendrimers also have been deposited onto the surface of cotton fabric and their activity has been investigated as potential antibacterial wound dressings.

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The design of perfluorinated extractants for the removal of perfluorooctanoic acid from water and metals from e-waste

Harrison OMORODION, Robert BAKER

School of Chemistry, University of Dublin, Trinity College, DUBLIN 2, Ireland
bakerrj@tcd.ie

The proliferation of new technology has resulted in a large increase in electronic waste (e-waste) that in some cases are richer in precious metals than virgin ores. However, extracting pure metals from this heterogeneous mixture is challenging. Some of these metals have been defined as energy critical [1] e.g. Nd is important for many applications including magnets for hard-disc drives or wind turbines. Solvent extraction methods have been used to some extent, but there is room for improvement. One method is to design extractant ligands that will coordinate the metal ions in acidic aqueous solutions and enhance solubility in an organic solvent. Here we use long chain fluorinated groups to enhance solubility in the benign solvent $scCO_2$ - firstly using fluorinated solvents as a convenient model system; some of the extractants we have synthesised are shown in Figure 1a [2]. We have used these to extract a series of precious metals (Ag, Au, Pd, Pt) and lanthanide ions and excellent extractions have been observed (Fig 1b). The nature of the extractable species has been elucidated via small angle X-ray scattering, NMR spectroscopy both in solution and the solid state and binding constants determined. The extractable species are outer sphere and principally hydrogen bonding in nature.

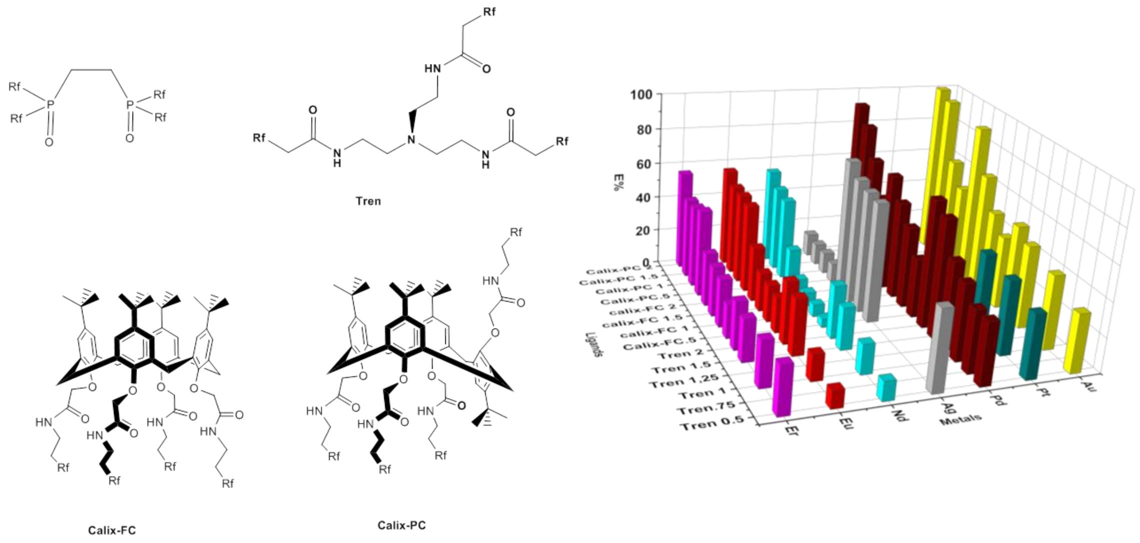

Figure 1. New fluorous ligands (Rf = $(CF_2)_5CF_3$) for extraction of metals (left) and summary of extraction results (right).

Moreover, we have also found that the same extractants can quantitatively remove the persistent organic pollutant perfluorooctanoic acid [3] from water, utilizing the fluorinated cavity of the ligands and hydrogen bonding. We have also sorbed these onto Teflon tape and used these as solid extractants with good efficiencies. These results offer a new technology to recover precious or energy critical metals from waste streams.

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Accumulation and *in vivo* speciation of uranium in *P. lividus* sea urchin

Maria Rosa BECCIA, [a] **Benjamin REEVES,** [a] **Minja MATARA-AHO,** [a,b]
Hervé MICHEL, [a] **Pier Lorenzo SOLARI,** [c] **Luisa MANGIALAJO,** [d]
Marguerite MONFORT, [e] **Christophe MOULIN,** [e] **Christophe DEN AUWER** [a]

[a] Université Côte D'Azur, CNRS, Institut de Chimie de Nice, UMR7272, Parc Valrose, 06108 NICE, France
[b] Laboratory of Radiochemistry, Department of Chemistry, University of Helsinki, 00014 HELSINKI, Finland
[c] Synchrotron SOLEIL, MARS beam line, 91192 GIF SUR YVETTE, France
[d] Observatoire Océanologique de Villefranche-sur-Mer, Laboratoire d'Océanographie de Villefranche, 181 Chemin du Lazaret, 06230 VILLEFRANCHE SUR MER, France
[e] Commissariat à l'Energie Atomique, DAM/DIF, 91297 ARPAJON, France
maria-rosa.beccia@unice.fr

The fate of radionuclides in the marine environment is an issue in terms of risk assessment and management because seawater covers most of the earth's surface [1]. The Fukushima accident in 2011 exemplified that non-negligible amounts of radionuclides may be released in seawater.

Among the radionuclides of concern, actinides are heavy elements that are directly related to the nuclear activity. Uranium is one of the two actinides that are naturally occurring on earth. Besides its radioactivity (low), uranium (under its ubiquitous uranyl form $\{UO_2^{2+}\}$) presents a chemical toxicity, as it is able to interact with various biological molecules [2]. Uranyl, when bioavailable, may bind to these molecules and affect their biological role [3]. However, the bioavailability and toxicity of uranyl strongly depends on its physico-chemical speciation [4]. Note also that uranyl is a convenient and easily handled model for other actinyls. Therefore, it is essential to understand its speciation in order to evaluate the factors and mechanisms of accumulation in living organisms, especially in the case of marine species. Very little is known about uranium speciation in seawater, mostly because it is present at the ultra-trace scale in "normal conditions" but also in accidental conditions due to enormous dilution factors.

In the past we have investigated the chemical speciation of uranium(VI) in seawater, showing that in these conditions, it is mainly present as a uranyl carbonato calcic complex, $Ca_2UO_2(CO_3)_3$ [5].

We present here a study on the accumulation mechanism of uranyl in a model marine organism, the sea urchin *P. lividus*. We estimated the uranium uptake curve for *P. lividus* (exposed for 10 days to uranyl-doped seawater, $[UO_2^{2+}]$ from $2 \cdot 10^{-5}$ to $2 \cdot 10^{-4}$ M) and evaluated the total amount of accumulated uranium in the separated sea urchin tissues by ICP-OES and alpha radiometry. The accumulation of uranium is ranked in the order: digestive tube > gonads >> test. We also determined the speciation of uranyl *in vivo*, by Extended X-ray Absorption Fine Structure (EXAFS) at the uranium L_{III} edge in the gonads, the digestive tube and the test compartments. Our results suggest that a specific family of proteins is involved in the uranium uptake in the first two compartments.

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Complexation of protactinium(V) with nitrilotriacetic acid

Coralie LUCHINI, [a,b] **Sébastien LEGUAY,** [a] **Claire LE NAOUR,** [a] **Jean AUPIAIS,** [b]
Jérôme ROQUES, [a] **Chistophe DEN AUWER,** [c] **Xavier DOLIGEZ,** [a]
Céline CANNES [a]

[a] Institut de physique Nucléaire (UMR 8608), 15 rue Georges Clemenceau,
91406 ORSAY Cedex, France
[b] CEA, DAM, DIF, 91297 ARPAJON, France
[c] Université de Nice Sofia Antipolis, Institut de Chimie de Nice, 28 avenue Valrose,
06108 NICE Cedex 2, France
luchini@ipno.in2p3.fr

The behavior of actinides in the environment (in the surroundings of uranium mining sites, waste storage sites, contaminated sites) depends on the interaction of these elements with the organic ligands present in these different systems. The interactions of actinides with polyfunctional organic ligands could trap the element or inversely, favor their migration.
The work presented in this context, concerns a study on the chemical properties of a particular element: protactinium. Protactinium is a radioelement of atomic number 91, present in the environment essentially as ^{231}Pa isotope (alpha emitter with a half-life of 32,400 years, ^{235}U decay-chain). Over the years, this isotope is accumulated in uranium tailings and in stocks of yellow cake. Furthermore, potential use of thorium in future nuclear fuels will result in the formation of ^{233}Pa and ^{231}Pa isotopes and therefore in the presence of this radioelement during the spent fuel reprocessing and packaging of waste. Due to its position in the periodic table, protactinium presents a fundamental interest. It is the first actinide element with 5f orbitals involved in bonding. Unlike other actinides at oxidation states +5 and +6 that form a linear transdioxo moiety, protactinium is most commonly characterized by one mono oxo bond. The presence or absence of this mono oxo bond depends on the media [1].

The chelating agent of interest for this study is nitrilotriacetic acid (NTA) (Figure 1). This ligand has been considered as a simple model of polyaminocarboxylic acids because of its three identical carboxylic functions and one tertiary amine, all of which can act as coordinating groups.

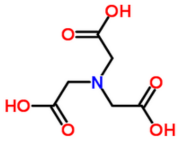

Figure 1. Nitrilotriacetic acid (NTA).

To define the speciation and related migration behavior of protactinium in the environment, a dual approach is presented in this work. A thermodynamic one, where protactinium is at trace scale ($C_{^{233}\mathrm{Pa}} < 10^{-10}$ M), because of the strong tendency of Pa(V) towards polymerization, has been implemented in order to determine the stoichiometry and the mean charge of the complexes, and the associated formation constants. This method has been used recently to study various protactinium complexes (sulphate, oxalate, DTPA (diethylenetriamine pentaacetic acid) [2,3]. In addition, a structural approach with protactinium in weighable quantity ($C_{^{231}\mathrm{Pa}} \approx 10^{-3}$M) was also conducted in order to determine the coordination geometry of complexes and interatomic distances. Both isotopes have been purified by ion exchange chromatography. Thermodynamic study was carried out by liquid-liquid extraction in the system TTA/Toluene/$HClO_4$/$NaClO_4$/Pa(V)/NTA. The variations of the distribution coefficient of Pa(V) as a function of the total ligand concentration are determined at different values of temperatures (10, 25, 40, 50 and 60°C) (Figure 2) and at constant ionic strength (1 M (Na,H)ClO_4). Thus, a maximum stoichiometry of two has been observed for the Pa-NTA system and the complexation reaction was found to be exothermic. The results presented will be compared with thermodynamic data of other actinides.

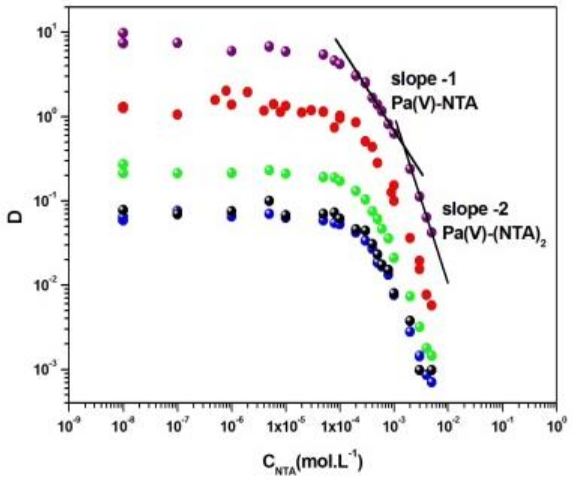

Figure 2. Distribution coefficient of Pa(V) as function of total nitrilotriacetic acid concentration at μ=1 M (Na,H)ClO_4, $[H^+]$=0,1 M for different values of temperature.

To our knowledge, there are no detailed structural studies of protactinium(V)-NTA complexes in solution or in the solid state available in the literature. To ascertain the presence or absence of mono oxo bond in Pa(V)-$(NTA)_2$ complex, XAS measurement were performed. So as to interpret EXAFS spectra, DFT calculations have been performed in order to determine the most probable formula of the Pa(V)-$(NTA)_2$ complex, which could be either $PaO(NTA)_2^{3-}$ or $Pa(NTA)_2^{-}$, including possibly one or more molecules of water in the coordination sphere and protonation.

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Transition metals binding and stability of phosphine-oxide resins in silver nitrate electrolyte

Ancuta MUSINA, [a,b] **Charly FARADJI**, [a] **Vasile LAVRIC**, [b] **Steven VAN ZUTPHEN** [a]

[a] Magpie Polymers, 108 Avenue Carnot, 77140 ST. PIERRE LES NEMOURS, France
[b] Chemical and Biochemical Engineering Department, University Politechnica of Bucharest,
Polizu 1-7, 011061 BUCHAREST, Romania
ancuta@magpie-polymers.com

Silver is one of the eight precious metals, along with gold and the six platinum-group metals (PGM). In 2015 the world mine production was close to 30 000 tons. Only 30% of the mine production comes from silver ores, 14% from recycling or secondary mining, while most of the silver is being obtained as by-product of other metals mining and refining [1]. With its unique features of high thermal and electrical conductivity, silver is used in many industrial applications (electronics, solar panels, etc.). For most of the applications, high purity silver (3 N or 4 N) is needed.

Fine silver is produced via an electrolytic processes, using either silver anodes (electrolytic refining) or inert anodes (electrowinning) and acidified silver nitrate electrolyte. Because of the high standards for refined silver, it is very important to control the level of the main impurities, such as copper and palladium in the silver electrolyte [2]. Depending on the refining process parameters, it is not uncommon to find traces of other precious metals, such as platinum, rhodium or even gold, dissolved in the electrolyte. In particular, palladium is a challenge because of its standard oxidation-reduction potential similar to the one of silver ($E^0_{Pd/Pd2+} = 0.987$ V, $E^0_{Ag/Ag+} = 0.799$ V) [3]. Nitric acid has an important role in the refining process, by keeping a high conductivity in the electrolyte [4] helping to produce large, non-adherent crystals of silver [5] and also preventing silver precipitation [6]. However, its concentration also influences the solubility of palladium.

Industry is looking to develop methods to recover palladium and platinum from the silver refining processes for two reasons: (1) to produce high quality silver and (2) to minimize the loss of valuable precious metals. In nitric acid solution, palladium is stable in divalent state, while rhodium is stable only in trivalent state [7]. The state of palladium in aqueous nitric acid media is not completely understood, but it is known that Pd can form a series of complexes with the nitrate ions, such as $[Pd(NO_3)]^+$, $[Pd(NO_3)_2]$, $[Pd(NO_3)_3]^-$, $[Pd(NO_3)_4]^{2-}$, and also aqua-nitrate species, such as $[Pd(H_2O)_3(NO_3)]^+$, $[Pd(H_2O)_2(NO_3)_2]$, $[Pd(H_2O)(NO_3)_3]^-$ [8], much less stable than those with chloride [9].

Using filtration resins for PGM recovery from silver refining process presents a risk of hazard as it involves the contact of an organic resin in an oxidant media, in presence of a high content of heavy metals (especially Ag and Cu). The reactivity of a resin depends on many parameters such as the polymeric backbone, the type and the concentration of functionalities or the cross-linking extent.

In this presentation, we will highlight the use of MPX-310, produced by Magpie Polymers for the purification of silver electrolyte. It is a resin based on a polyacrylic support cross-linked with divinylbenzene that contains amino phosphine oxide functionalities and presents very good stability in aggressive media, as nitric acid was studied for this application.

Laboratory scale studies, in batch and dynamic modes, have shown the ability of MPX-310 to capture palladium from a matrix of highly concentrated silver (up to 110 g/L) and Cu (up to 70 g/L) from different industrial electrolytes. The presentation will cover the solution chemistry as well as the calorimetric studies that were carried out to be able to find the optimal conditions with which this resin can be safely used in an industrial process. We will show how these studies were used in the scaling up of the application from laboratory to pilot, and to full industrial scale.

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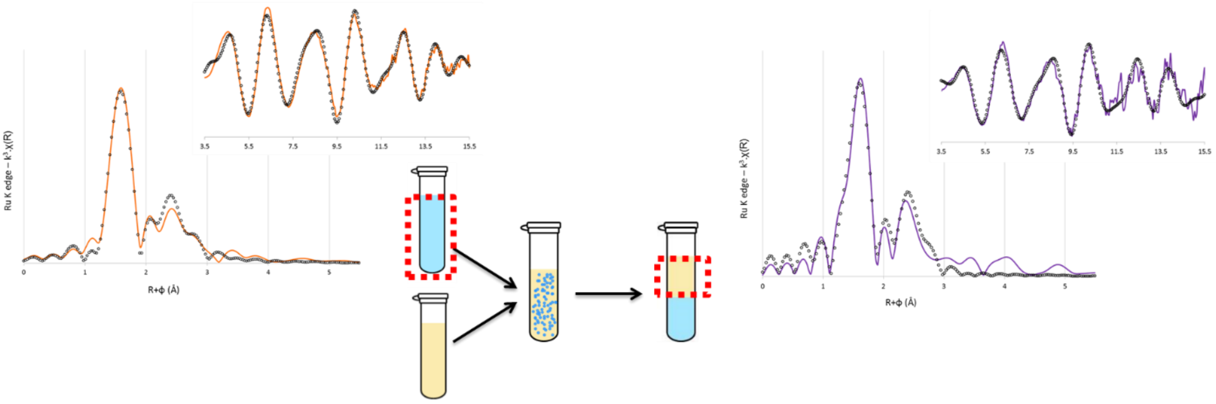
Investigating the ruthenium speciation in TBP/TPH organic phases with coupled spectroscopic techniques

Claire LEFEBVRE, [a] **Thomas DUMAS**, [a] **Christelle TAMAIN**, [a]
Marie-Christine CHARBONNEL, [a] **Pier Lorenzo SOLARI** [b]

[a] *French Atomic Energy and Alternative Energies(CEA), Nuclear Energy Division (DEN), Marcoule site, Research Department on Mining and Fuel Recycling ProCesses (DMRC), SPDS/LILA, BP 17171, 30207 BAGNOLS-SUR-CÈZE, France*
[b] *Synchrotron SOLEIL, L'Orme les Merisiers, BP 48, 91192 GIF-SUR-YVETTE, France*
Claire.lefebvre@cea.fr



The liquid-liquid extraction process PUREX enables the recovery of uranium and plutonium from spent nuclear fuels. The fission product ruthenium remains one troublesome element due to its complexed chemistry, its high contribution to the β–γ radioactivity in the process and difficulty to remove ruthenium when quantities are extracted in the organic phase. Different teams have performed studies to better describe the numerous complexes with Ru [1] but this issue remains important to simulate the behavior in the PUREX process.

During the first step of PUREX (dissolution of the spent nuclear fuel in nitric acid), ruthenium forms trivalent nitrosyl complexes with nitrate, nitrite, hydroxo and aquo ligands. The general formula for these complexes is $[RuNO(NO_3)_x(NO_2)_y(OH)_z(H_2O)_{5-x-y-z}]^{3-(x+y+z)}$ where x, y, z depend on the chemical conditions. During extraction steps, ruthenium is slightly extracted with uranium and plutonium by the solvent (TBP 30% in TPH) [1].It is assumed that only the tri- and tetra- nitrate complexes are extracted to the organic phase with a quantitative yield [2,3].

The study of Ru complexes is made difficult because of the co-existence of several species with low ligand exchange kinetics in nitric acid solutions [4]. There must therefore be several extracted species and polydispersity in the organic phase, like in the aqueous phase.

In this study, different complementary spectroscopic techniques were used to have a better understanding of the ruthenium local environment in surrogate reprocessing solutions. It includes especially infrared spectroscopy (IR) and X-ray absorption spectroscopy (EXAFS). EXAFS spectra were recorded on the MARS beamline on the Synchrotron SOLEIL (France).

This study was supported by synthesis of reference compounds under monocrystalline form and then structurally characterized by XRD. Their EXAFS and IR spectra were recorded and used as references to interpret the spectra of experimental solutions.

The Ru nitrosyl form was firstly confirmed in both phases, and then the coordination sphere of this core was probed. The ruthenium extraction mode by TBP (direct complexation with Ru and/or second sphere coordination) was investigated. Hydrolysis of ruthenium complexes was highlighted at low acidity. The speciation of ruthenium was studied as a function of the initial chemical conditions in the aqueous phase and it was shown that the resultant speciation in organic phase was different. It was also demonstrated that the equilibrium was not reached after extraction and the speciation could evolve with time in organic phases.

The major challenge was to propose a method to fit EXAFS data because of the polydispersity of the ruthenium species, and the lack of available models. The reference solid compounds and theoretical calculations provided useful information in order to build the missing structures.

This innovating method enables an accurate determination of the average stoichiometry of the complexes in both the aqueous and the organic phases. The effects of the initial concentration of nitrates, of the initial acidity and the ageing of the solutions could be consequently qualitatively characterized.

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Porous nanostructures as versatile stable chelates for complexation of lanthanides for pH responsive magnetic resonance imaging

Kristina DJANASHVILI, [a,b,c] Joop A. PETERS, [a] Célia S. BONNET, [b] Éva TÓTH [b]

[a] Delft University of Technology, Julianalaan 136, 2628BL, DELFT, The Netherlands
[b] Centre de Biophysique Moléculaire, CNRS, Rue Charles Sadron, 45071 ORLEANS, France
[c] Le Studium, Loire Valley Institute for Advanced Studies, 1 Rue Dupanloup,
45000 ORLÉANS, France
k.djanashvili@tudelft.nl

The immense structural diversity of more than 200 known zeolites is the basis for the big variety of applications of these porous materials, ranging from catalysts and molecular filtration to agricultural uses. Despite this versatility, the potential of zeolites in medical imaging has not been much explored. In our work, we investigate a novel application for these fascinating materials based on their ability to complex metal ions within the inner cavities resulting in a nanosystem with promising imaging properties.

The crystalline aliminosilicate framework of nanozeolite LTL, formed by AlO_4-tetrahedra arranged in well-defined cavities, possess negative charges that are originally counterbalanced by loosely bound cations. These are accessible for the surrounding solution due to the porosity, and as a result can be ion-exchanged by any metal-ion of choice that fits into the pores. The fact that rare earth elements and especially the elements of the lanthanide series are widely applied in medical imaging, drew our attention towards utilization of LTL as a carrier for paramagnetic Gd^{III} ions for contrast enhancement in magnetic resonance imaging (MRI) [1]. Such Gd^{III}-complexing zeolite system represents a versatile tool to overcome sensitivity issues by delivering high payload of active species with each single particle.

Aqueous suspensions of lanthanide exchanged LTL have been investigated by ^1H, ^{17}O NMR, and EPR relaxivity studies. Both the longitudinal (r_1) and the transverse (r_2) relaxivity of these Gd^{III} complexing materials are strongly pH dependent and therefore, have great potential as pH responsive contrast agents. LTL-nanocrystals complexing 3.5 wt% Gd, show a dramatic decrease of r_1 from 32 to 7 $s^{-1}mM^{-1}$ (7.5 T and 25° C) when going from pH 4 to 9. ^1H and ^{17}O NMR suggest that this phenomenon can be rationalized by a decrease in proton mobility between the zeolite interior and the exterior due to a change from a fast prototropic exchange to a 3 orders of magnitude slower water exchange mechanism. The same material also has a high transverse relaxivity (98 $s^{-1}mM^{-1}$ at 7.5 T, 25° C, and pH 5 as measured with the CPMG pulse sequence), which is governed by proton exchange too, while water diffusion plays a minor role.

The high relaxivities and pH dependence render Gd-complexed LTL materials promising pH responsive contrast agents. Since the r_2/r_1 ratio of the designed probe strongly increases with the magnetic field strength, these materials are expected to be applicable for both T_1 and T_1 weighted imaging at low and high fields, respectively. An additional advantage is that compartmentalization of LTL interior can be used to complex ions in different framework environments that leads to increased performances of the single components and offers possibility to combine different imaging modalities in a single probe [2].

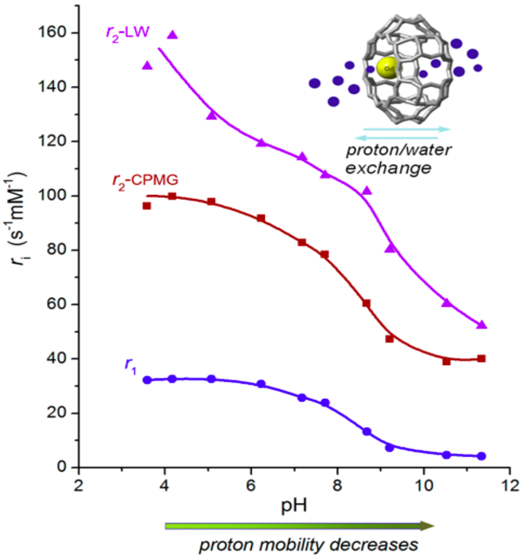

Figure 1. r_2 and r_2 relaxivity of Gd-LTL (inset) as a function of pH.

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Unexpectedly high kinetic inertness of a bis-hydrated Gd-complex formed with the cyclohexyl ring fused AAZTA-like ligand

Massimo VISIGALLI, [a)] **Zsolt BARANYAI**, [a,b)] **Adrienn VÁGNER**, [b)] **Lorenzo TEI**, [c)] **Alessando MAIOCCHI** [a)]

[a)] Centro Ricerche Bracco, Bracco Imaging Spa, Via Ribes 5, 10010 COLLERETTO GIACOSA, Italy
[b)] Department of Inorganic and Analytical Chemistry, University of Debrecen, Egyetem tér 1., 4032 DEBRECEN, Hungary
[c)] Dipartimento di Scienze ed Innovazione Tecnologica, Università del Piemonte Orientale "Amedeo Avogadro", Viale T. Michel 11, 15121 ALESSANDRIA, Italy
massimo.visigalli@bracco.com

Paramagnetic Gd(III)-complexes formed with the octadentate ligands are widely used as T_1 positive contrast agents (GBCAs) in Magnetic Resonance Imaging (MRI). In all the complexes commercially available, one coordination site of the Gd(III) ion is occupied by a water molecule which transfers the paramagnetic effect to the bulk via exchange reactions. Since the GBCA efficiency, expressed in terms of relaxivity, relies on the number of water molecules (q) coordinated to Gd(III) ion, the use of a heptadentate ligand, which allows the coordination of a second water molecule, leads to an increased efficiency. In this respect $[Gd(AAZTA)(H_2O)_2]^-$ has been developed and thoroughly investigated in terms of its solution properties showing excellent thermodynamic stability and T_1 relaxation enhancement of water protons, mainly as a result of the two coordinated water molecules in rapid exchange with the bulk water [1]. Nowadays, it is generally accepted that the *in vivo* kinetic inertness of metal complexes has to be considered together with its thermodynamic stability, to properly design metal-complexes exploitable as MRI contrast agents. $[Gd(AAZTA)(H_2O)_2]^-$ shows a kinetic inertness significantly lower than that reported for the macrocyclic GBCAs like $[Gd(DOTA)(H_2O)]^-$ [2].

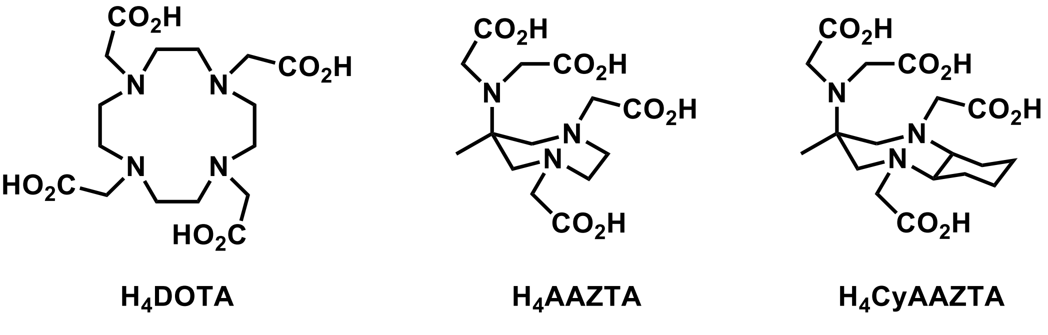

Figure 1. Structures of H_4DOTA, H_4AAZTA and $H_4CyAAZTA$ ligands.

It has been reported that the introduction of one or more cyclohexyl rings fused into the ligand backbone has enhanced the stability and kinetic inertness of the metal complexes [3]. Therefore the CyAAZTA ligand has been synthetized and the equilibrium, kinetic, structural and relaxation properties of CyAAZTA complexes formed with several divalent and trivalent metal ions, including lanthanides, have been investigated. In spite of the lower $\log K_{\mathrm{ML}}$ values of M(CyAAZTA) compared to the corresponding M(AAZTA) complexes, a remarkably high kinetic inertness of Gd(CyAAZTA) have been evidenced and highlighted by the dissociation half life of about 91 years at pH 7.4, which is more than two orders of magnitude higher than that of Gd(AAZTA).

Moreover, the structure stiffening of the ligand produced an increasing of the relaxivity of $[\mathrm{Gd(CyAAZTA)(H_2O)_2}]^-$ that is 8.3 $\mathrm{mM^{-1}s^{-1}}$ (20 MHz, 25 °C, pH 7.4), which is higher than that of $[\mathrm{Gd(AAZTA)(H_2O)_2}]^-$ (7.1 $\mathrm{mM^{-1}s^{-1}}$).

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Mn^{2+}-based magnetic resonance imaging contrast agent candidates: How far can we go with open-chain ligands in terms of inertness?

Gyula TIRCSÓ, [a] **Zoltán GARDA**, [a] **Ferenc K. KÁLMÁN**, [a] **Kristóf PÓTA**, [a]
Enikő MOLNÁR, [a] **Balázs VÁRADI**, [a] **Richárd BOTÁR**, [a] **Éva TÓTH**, [b]
Imre TÓTH [a]

[a] Department of Inorganic and Analytical Chemistry, University of Debrecen,
Egyetem tér 1, 4010 DEBRECEN, Hungary
[b] Centre de Biophysique Moléculaire, CNRS, Rue Charles-Sadron,
45071 ORLEANS Cedex 2, France
gyula.tircso@science.unideb.hu

Magnetic Resonance Imaging (MRI) has become one of the most important non-invasive and non-destructive diagnostic tools of modern medicine for imaging of soft tissues. In order to enhance the image contrast, stable Gd^{3+} complexes formed with polyaminocarboxylate ligands (DTPA, DOTA and their derivatives) are commonly used as contrast agents (CAs) in MRI. However, the direct link established between the progressive, potentially fatal disease called Nephrogenic Systemic Fibrosis (NSF) and the use of gadolinium based CAs in patients with renal failure has clearly marked the need for safer CAs. One possibility to obtain harmless CAs is to apply modifications to the structures of the ligands in order to increase the safety (e.g. improve the inertness) of their Gd^{3+} chelates. Another possibility is to reduce the toxicity of the CAs by replacing the paramagnetic metal ion with one that is better tolerated in the living systems (essential transition metal ions) such as Mn^{2+} (T_1 agents), Fe^{2+} (ParaCEST) or high spin Fe^{3+} complexes (T_1 agents). It should be reminded however that large amount of essential metal ions released form their complexes may also induce toxic effects (e.g. Parkinson like symptoms caused by overexplosure to uncomplexed Mn^{2+} or hemochromatosis provoked by the iron overload) and thus the kinetic inertness of the essential metal ion based MRI CA candidates has to be considered with extra care, too. Our efforts to find suitable ligand for Mn^{2+} complexation started from equilibrium, kinetic and relaxometric characterization of Mn^{2+} complexes formed with commercially available open-chain ligands [1]. This study revealed that the rigid *trans*-CDTA forms relatively inert complex with Mn^{2+} ion (the half-life of the dissociation is 12 hours near physiological conditions). To our surprise Mn^{2+} complexes of other rigid EDTA derivative ligands like *cis*-CDTA or PhDTA (Figure 1) turned out to be not well characterized in the literature. Therefore these ligands were re-synthesized and the stability constants of complexes formed with the most abundant essential metal ions (Ca^{2+}, Mg^{2+}, Zn^{2+} and Cu^{2+}) and Mn^{2+} have been determined in 0.15 M NaCl at 25 °C and compared to those of the corresponding EDTA and *trans*-CDTA complexes. The log *K* values of the Mn^{2+} complexes changes in the following order: *trans*-CDTA>*cis*-CDTA>EDTA>PhDTA whereas the order for the pMn values (calculated at pH = 7.4 by using 0.01 mM Mn^{2+} and ligand concentrations) indicates slightly different trend (*trans*-CDTA~PhDTA>EDTA~*cis*-CDTA) owing to the differences in the apparent stabilities of the complexes at pH = 7.4. The inertness of the complexes was studied by following the metal exchange reactions occurring between the complexes and Cu^{2+} as a function of pH. The results of the dissociation kinetic studies revealed that the $[Mn(PhDTA)]^{2-}$ complex possess somewhat better dissociation kinetic properties than the [Mn(*trans*-CDTA)]$^{2-}$ does whereas the [Mn(*cis*-CDTA)]$^{2-}$ dissociates slightly faster than the $[Mn(EDTA)]^{2-}$ itself. The relaxation enhancement data recorded for 1 mM paramagnetic metal complexes (termed as relaxivity) were found to be very similar (in the range of 3.2-3.7 mM^{-1} s^{-1}) indicating the formation of mono aquated ($q = 1$) complexes in all cases. Altogether, the $[Mn(PhDTA)]^{2-}$ complex possess the best features at near physiological pH as far as the stability, inertness and the relaxivity of the complex concerned.

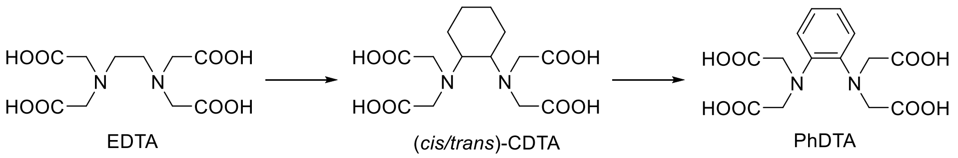

Figure 1. Formulae of the ligands studied.

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Novel class of Pt_2L_4 metallacages: Design, self-assembly and host-guest chemistry

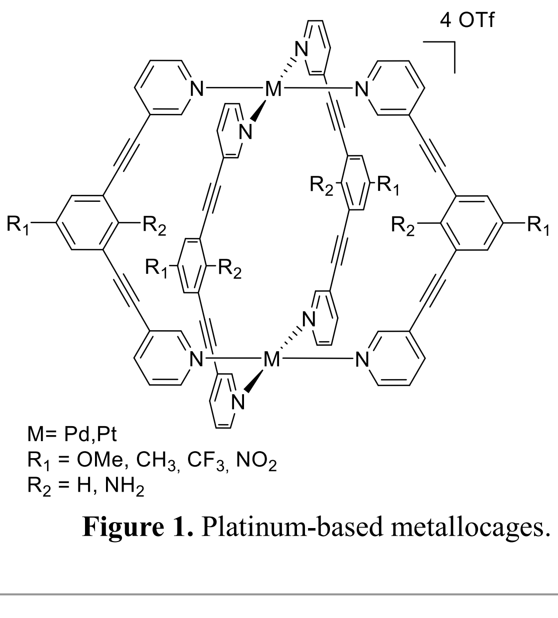
Emmanuel PUIG, [a] **Christophe DESMARETS**, [a] **Lise-Marie CHAMOREAU**, [a] **Hani AMOURI** [a]

[a] *Institut Parisien de Chimie Moléculaire de l'Université Pierre et Marie Curie Sorbonne Universités (IPCM, UMR CNRS 8232), 4 place Jussieu, 75252 PARIS Cedex 05, France*
emmanuel.puig@upmc.fr

The design and construction of discrete metal-organic architectures such as metal-organic polyhedra, cages, bowls or capsules continue to attract attention [1] because of their potential applications as containers for storage, recognition, delivery and catalysis [2]. Although much has been achieved in the field, there have been relatively few reports in endo-functionalized fluorescent metallocages. Moreover bis(ethynylpyridine)aniline based ligands, in which a simple modification of the para functional group to the aniline allows to tune photophysical properties, are good candidates to the construction of such assemblies [3]. Finally the formation of nanocages and especially of type Pt_2L_4 remains relatively unexplored [4].

In this context, our group has recently described the use of highly rigid bis(ethynylpyridine) based ligands which lead to Pd_2L_4 luminescent nanocapsules [5]. These nanocages are able to accommodate neutral organic molecules and also anionic organometallic complexes in its cavity.

In this communication, we describe the synthesis of novel bis(ethynylpyridine)aniline based ligands, with para functional R1-groups attached to the central aniline unit. Moreover the preparation and the X-ray molecular structures of new M_2L_4 (M=Pd, Pt) nanocapsules as well as their usage as inorganic receptors for host-guest chemistry will be presented and discussed (Figure 1).



M= Pd,Pt
R_1 = OMe, CH_3, CF_3, NO_2
R_2 = H, NH_2

Figure 1. Platinum-based metallocages.

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Extended metal compounds. From 1D metallophilic polymers to metallogels and coordination polymers

Matti HAUKKA

University of Jyväskylä, Department of Chemistry, P.O. Box 35, 40014 JYVÄSKYLÄ, Finland
matti.o.haukka@jyu.fi

Polymeric structures consisting of metal compounds as building blocks have attracted increasing attention because of their versatile and tunable magnetic, photophysical, conductive, and catalytic properties [1]. The unique features of the polymeric structures arise from the interplay between the building blocks. Bringing metal compounds together in a systematic structure may enhance the intrinsic chemical, physicochemical or optical properties of the metal compounds. On the other hand, building an extended structure with strong interaction between the structural units may generate completely new properties that don't exist in the building blocks. For example, electric conductivity throughout the polymer material and completely new catalytic properties can be obtained by such supramolecular approach.

Metal units can be brought together by using a variety of interactions ranging from non-covalent contacts to covalent bonds. In metallophilic polymers interactions between the metal centers are in principle non-covalent. However, in the extreme case direct metal-metal contacts can eventually become covalent. Ruthenium and osmium carbonyls of the type $[M(CO)_4]$ and $[M(L\text{-}L)(CO)_2]$ (L-L = polypyridyl ligand such as 2,2'-bipyridine, 1,10-phenathroline etc.) are among the most studied covalent 1D metal chains [2-5]. The metal contacts can be adjusted for example by using supporting multi-dentate ligands such as α-pyridyl amines [6], Schiff bases [7], or biimidazole derivatives to support the chain and to make so called EMAC systems [8]. Another option is to build coordination polymers where metal centers are separated by ligands. Depending on the supramolecular interactions between the polymeric chains, the physical properties of the material can also vary from amorphous or crystalline solid to metallogels.

We have studied a series of square planar Rh complexes as building material for metallophilic Rh-Rh chains (Figure 1) [9, 10] and use of single-atom and multi-atom nitrogen and sulphur linkers for synthesizing coordination polymers of Cu, Ag and Au [11]. We have also shown that bipyridine-based ligand can be used for silver metallogels (Figure 1) [12]. By simple reduction procedure silver can be reduced to silver nanoparticles attached to the polymer fibers [12].

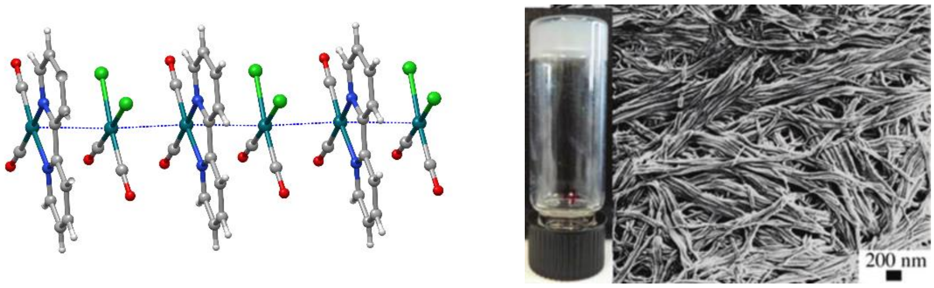

Figure 1. Left: Chain of cationic and anionic Rh-complexes with metallophilic Rh-Rh contacts [10]. Right: Polypyridine-based Ag-metallogel [12].

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Kojic acid derivatives as sensors for phosphate anions. Complex stability, DNA binding and cellular study.

Joanna I. LACHOWICZ, [a] **Valeria M. NURCHI**, [a] **Guido CRISPONI**, [a]
Claudia CALTAGIRONE, [a] **Sergio MURGIA**, [a] **Giuseppina PICHIRI**, [b]
Pierpaolo CONI [b]

a) University of Cagliari, Department of Chemical and Geological Sciences, Cittadella Universitaria, 09042 MONSERRATO-CAGLIARI, Italy
b) University of Cagliari, Department of Surgical Sciences, Section of Pathology, Cittadella Universitaria, 09042 MONSERRATO-CAGLIARI, Italy
lachowicz@unica.it

Anions play a crucial role in biological, environmental and industrial fields [1-3]. In particular, phosphates are among the most important anions in biological systems as they play the central role in the building of two fundamental molecules in living systems, DNA and RNA. Phosphates are also involved in various cellular processes such as energy storage, signal transduction and gene regulation, while phospholipids are essential constituents of lipid membranes [4,5]. Moreover, phosphates are important components of medicinal drugs and fertilizers and their increasing presence in natural water sources leads to eutrophication of the aquatic ecosystems [6]. For all these reasons, a great effort has been made to design highly selective receptors for phosphorylated species [7–9].

This communication deals with four new kojic acid derivatives synthesized as phosphate anion receptors [10-12]. Their binding properties toward different phosphate anions (PO_4^{3-}, $P_2O_7^{4-}$, $P_3O_{10}^{5-}$, ATP, ADP and AMP) have been studied by potentiometry, ^1H and ^{31}P-NMR, UV-Vis and fluorescence spectroscopy. In addition, mixed metal-anion-ligand complexes have been studied by ^1H, ^{27}Al and ^{31}P-NMR, and single crystal X-ray diffraction. In addition, cellular assays and DNA-ligand and DNA-metal-ligand complex formation studies have been performed.

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New bis-cyclometalated iridium and rhodium complexes coordinated to heteroaromatic ancillary ligands: Photoreactivity and selective binding to G-quadruplexes

Matteo LARI, [a] **Natalia BUSTO**, [a] **Gustavo ESPINO**, [a] **Francesco MANOLI**, [b]
Hector J. LOZANO, [a] **Marta MARTINEZ-ALONSO**, [a] **José M. LEAL**, [a]
Ilse MANET, [b] **Begoña GARCIA** [a]

*[a] Facultad de Ciencias, Universidad de Burgos, Plaza Misael Bañuelos s/n,
09001 BURGOS, Spain*
[b] ISOF - CNR Area della Ricerca di Bologna, Via P. Gobetti 101, 40129 BOLOGNA, Italy
mlari@ubu.es

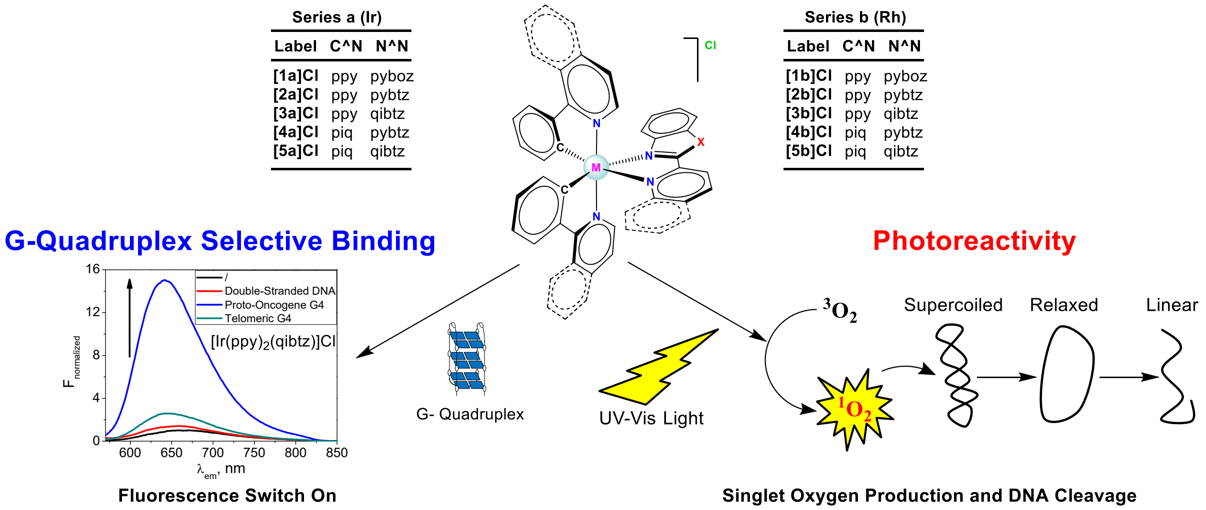
Rh(III) and Ir(III) bis-cyclometalated complexes are a valuable type of compounds applied in different fields due to their promising photophysical properties [1]. Concerning to biological applications, they have been studied as labelling reagents [2] and as drugs in Photodynamic Therapy (PDT) [3]. This work aims to understand the contribution of the bis-cyclometalated complexes moieties, namely the metal centre (M), the ancillary and the cyclometalated C^N ligands, on two reactivity aspects: their photoreactivity and interaction with nucleic acids.

Dimeric $[M(C^{\wedge}N)_4Cl_2]$ (M = Ir, Rh) precursors were synthesized by reaction of MCl_3 and the 2-phenylpyridine (ppy) and 2-phenylisoquinoline (piq) HC^N pro-ligands. Then, the bis-cyclometalated complexes of general formula $[M(C^{\wedge}N)_2(N^{\wedge}N)]Cl$ were obtained by reaction of the dimers with three different heteroaromatic ancillary N^N ligands, 2-2'-pyridylbenzoxazole (pyboz), 2-2'-pyridylbenzothiazole (pybtz) and 2-2'-quinolinylbenzothiazole (qibtz). Characterization of the complexes was carried out by NMR and ESI-MS techniques. The spectroscopic analysis showed that the emission spectra can be tuned varying the metal centre and the C^N and N^N ligands, with shift of the maximum (λ_{em}) from 530 to 670 nm.

Photoreactivity was evaluated by cleavage of pUC18 plasmid DNA via electrophoretic assay detection. Efficient DNA breakage was found irradiating at UV (365 nm) and Visible (435 nm) wavelengths. The rhodium complexes exhibit higher cleavage activity compared to iridium complexes, explained by the larger production of singlet oxygen measured by phosphorescence at 1270 nm. Thus, a predominant oxygen-dependent pathway is involved in the reaction mechanism.

Furthermore, light-switch behaviour of the iridium complexes was detected in the presence of nucleic acids. Interestingly, the effect resulted more pronounced for G-Quadruplexes, especially for the parallel-stranded folding of the *c-myc* proto-oncogene, whereas only minor effects were observed for the duplex structure. Stabilisation proofs by FRET assays demonstrated high stabilisation of G-Quadruplexes in the presence of the metal complexes, proving the selectivity towards various G-Quadruplex conformations. Both the light-switch behaviour and the stabilisation effect depend on the aromatic extension of the N^N and C^N ligands.

In conclusion, the study of this new synthesized family of metal complexes reveals that the nature of the ligands concurs with reactivity aspects; in particular, rhodium complexes seem to be very efficient for PDT, whereas iridium complexes can be a valuable tool to investigate labelling reagents (Figure 1).



Series a (Ir)

Label	C^N	N^N
[1a]Cl	ppy	pyboz
[2a]Cl	ppy	pybtz
[3a]Cl	ppy	qibtz
[4a]Cl	piq	pybtz
[5a]Cl	piq	qibtz

Series b (Rh)

Label	C^N	N^N
[1b]Cl	ppy	pyboz
[2b]Cl	ppy	pybtz
[3b]Cl	ppy	qibtz
[4b]Cl	piq	pybtz
[5b]Cl	piq	qibtz

Figure 1. Synthesized bis-cyclometalated complexes and their properties: singlet oxygen production and G-Quadruplex selective binding.

Acknowledgements: this work was supported by Obra Social "la Caixa" (OSLC-2012-007), MINECO, Spain (CTQ2014-58812-C2-2-R, FEDER Funds) and Junta de Castilla y Leon (BU042U16).

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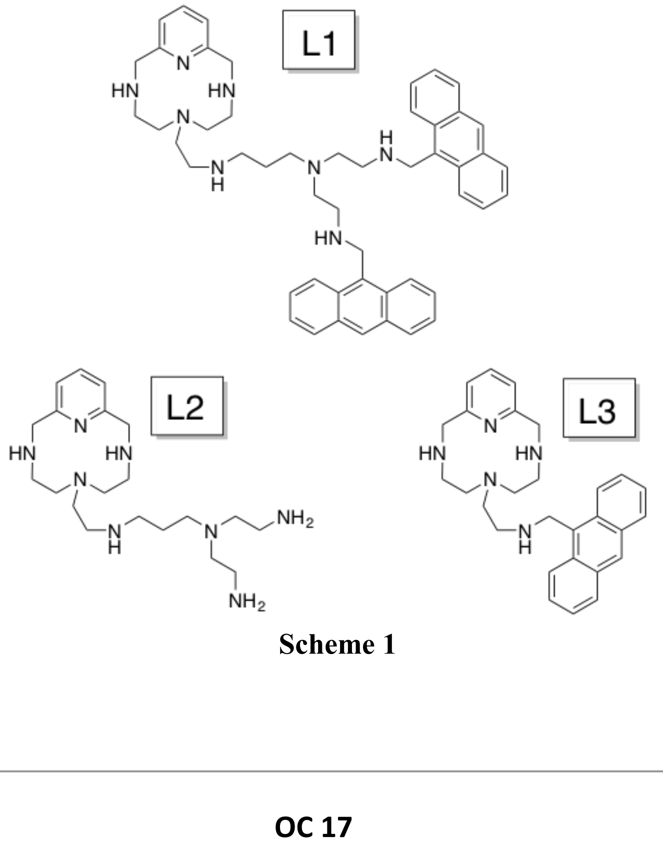
DNA interaction studies of new bis-anthracene polyaza macrocyclic derivatives

Lluís GUIJARRO, Mario INCLÁN, Begoña VERDEJO, Àlvar MARTINEZ, Enrique GARCÍA-ESPAÑA

Molecular Science Institute (ICMol), Department of Inorganic Chemistry, University of Valencia, Catedrático José Beltran 2, 46980 PATERNA - VALENCIA, Spain
lluis.guijarro@uv.es

Great efforts have been made in order to understand the interaction of polyamines with nucleic acids since it was found, in the 1960s, that they were bound to various cellular anions, including DNA and RNA [1]. In this line, we have previously prepared a polyamine compound based on a macrocyclic core appended with an arm containing extra donor atoms. The pendant arm has been further functionalized with an aromatic unit. Anthracene was the choice for this aromatic moiety (Scheme 1) (**L3**), for several reasons: other anthracene derivatives show antitumor activity; it has good absorption in the near-UV region and strong fluorescence; and the planar anthracene ring is suitable for intercalation [2]. Recent studies performed in our group, showed that **L3**, and similar compounds, bind efficiently and selectively to mononucleotides [3], as well as to calf thymus DNA (ctDNA). We also showed how the metal-induced conformational changes of these compounds could be used to modulate their interaction with ctDNA, by hampering the intercalation of the aromatic unit, and how this allosteric effect had an important impact on the in vitro cytotoxicity of the compounds [4].



Scheme 1

In this regard, a new poly-aza macrocycle derivative presenting two antrhacene units at the end of the central chain has been synthesized (**L1**), with the main aim to go deeper into the study on the influence of the presence of an extra aromatic ring to the interaction towards DNA. Once synthesized, its acid base behavior has been determined by potentiometric and spectroscopic UV-Vis and fluorometric studies.

Four specific 29-mer oligonucleotides were selected in order to perform the study about the interaction with the selected polyamines (Scheme 1) towards different sequences. An A-T rich sequence (AAAATT), G-C rich sequence (GGCCC), the intermediate A-T rich with G-C base pairs (AAGCTT) and the G-C rich with A-T base pairs (GAAGGC).

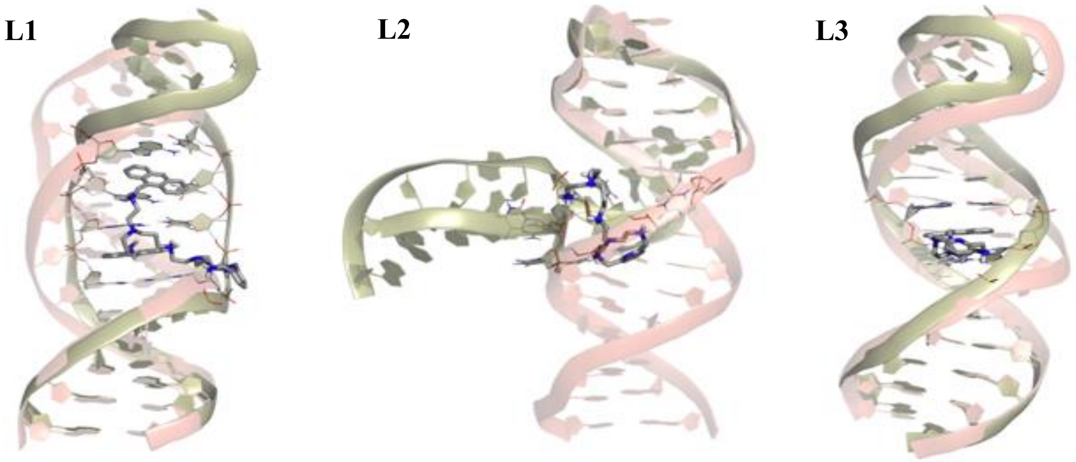


Figure 1. Cartoon-sticks representation from molecular dynamic studies for the interaction of **L1**-**L3** towards *AAAATT* 29-mer oligonucleotide, overlapped to free sequence conformation.

Ligand-oligonucleotide interactions have been studied by means of fluorometric titrations, melting point displacement assays, circular dichroism and molecular dynamic studies. The results lead to the conclusion that while interaction of **L2** towards the four sequences under study is mainly driven by electrostatic interactions, **L1** and **L3** interact not only by electrostatic forces but also by interacalation of the antracene towards the base-pairs (Figure 1).

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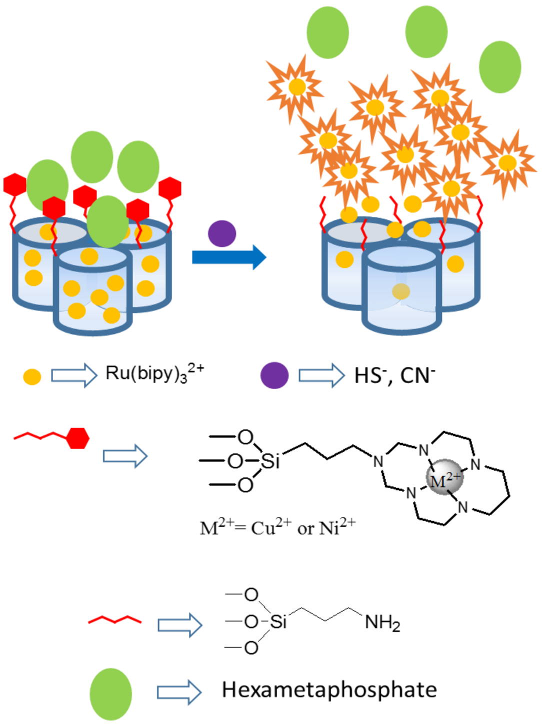
Selective and sensitive detection of cyanide and sulfide in water by metal-macrocycle-based capped silica mesoporous nanoparticles

Sameh EL SAYED, [a,b] Maurizio LICCHELLI, [c] Ramón MARTÍNEZ MÁÑEZ, [a,b] Félix SANCENÓN [a,b]

[a] CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Departamento de Química, Universidad Politècnica de Valencia Camino de Vera s/n, 46022 VALENCIA, Spain
[b] Instituto Interuniversitario de Investigación de Reconocimiento Molecular y Desarrollo Tecnológico (IDM), Universitat Politécnica de València-Universitat de València
[c] Dipartimento di Chimica, Università di Pavia, via Taramelli 12, 27100 PAVIA, Italy
saelsa@upvnet.upv.es

Organic-inorganic hybrid materials based on functionalised mesoporous silica nanoparticles (e.g. MCM-41) have been recently applied in the optical detection of different substrates [1]. These materials are obtained by combining the inorganic nanometric mesoporous scaffold with organic fragments that are anchored on its external surface. The new sensing strategy is based on a gate-like behaviour of the hybrid materials, which are able to modulate the mass transport at the nanometric level (closed /opened) depending on the presence of certain chemical species [2].



Scheme 1. Schematic representation of the sensing mechanism of **NP1** and **NP2**.

Dealing with that, in this work mesoporous silica nanoparticles MCM-41 was loaded with $[Ru(Bipy)_3]^{2+}$ dye and the external surface were functionalised by two different complex, Cu^{2+}-macrocyclic complex to obtain **NP1** and Ni^{2+}-macrocyclic complex to form **NP2**. In fact these metal macrocyclic complexes efficiently interact (electrostatic interaction) with multiply charged anionic species (e.g Hexanetaphosphate), which, as a consequence block the pores and inhibit the dye release ("closed gate" behaviour). The sensing features of **NP1** and **NP2** were studied in the presence of different anionic species. In particular, it was suspended in buffered solution (pH 7.5, HEPES 10 mM) and dye release was monitored by measuring the emission intensity of $[Ru(Bipy)_3]^{2+}$ (610 nm) at different time intervals. The relative fluorescence intensity values determined after 5 h in the presence of various anionic species where in case of **NP1** allow a fast dye release only in the presence of sulphide while with **NP2** only CN^- induce dye release as shown in Figure 2. Moreover these two nanoparticles show no response towards other common anions, amino acids and bio-thiols that may interfere (e.g. GSH, Cys, Homo-cys). These high selectivity can be ascribed to the interaction of anion HS^- with Cu^{2+} in **NP1** or CN^- with Ni^{2+}in **NP2** accompanied with destroying the macrocyclic-Hexametaphosphate interaction (the gate) [2]. As a consequence, Hexametaphosphate is no longer held close to the pores and dye release is allowed [3]. Taking into account these results, it seems that the selectivity of the hexametaphosphate-capped nanoparticles can be directed by changing the metal ion in the grafted macrocyclic subunits. When the complexed cation is Cu^{2+} nanoparticles respond selectively to hydrogen sulphide, whereas on changing to Ni^{2+} the uncapping process is only observed with cyanide.

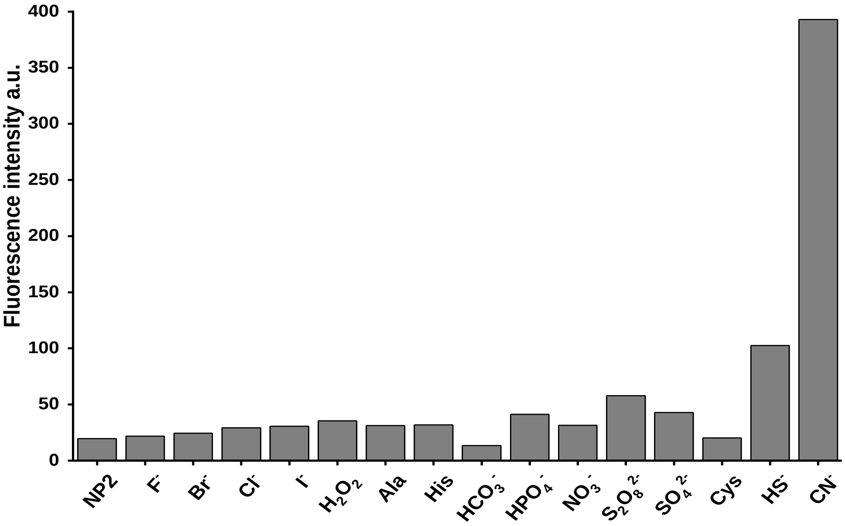


Figure 1. Fluorescence intensity at 610 nm of $[Ru(bipy)_3]^{2+}$ dye released from **NP2** (HEPES 10 mM at pH 7.5) after 5 h of adding 1 mM of selected anions, amino acids and oxidants.

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Luminescent lanthanide(III) complexes for anions sensing: Spectroscopy, speciation and modelling studies

Andrea MELCHIOR, [a] **Fabio PICCINELLI,** [b] **Lorenzo DI BARI,** [c]
Georgina FAURA, [a] **Marco LEONZIO,** [b] **Francesco ZINNA,** [c]
Marilena TOLAZZI, [a] **Marco BETTINELLI** [b]

[a] *Chemical Technologies Laboratory, DPIA, Università di Udine, via Cotonificio 108, 33100 UDINE, Italy*
[b] *Luminescent Materials Laboratory, DB, Università di Verona, and INSTM, UdR Verona, Strada Le Grazie 15, 37134 VERONA, Italy*
[c] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13, 56124 PISA, Italy*
andrea.melchior@uniud.it

Lanthanide complexes (Ln^{3+} = Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Yb^{3+}) have been extensively studied as luminescent sensors [1] and optical sensors for cell imaging [2]. The long emission lifetimes of Ln^{3+} ions are favourable for reducing interference from light scattering or autofluorescence in complex microenvironments such as cells, tissue or animals [3] *via* time-gated detection. Complexes of Ln^{3+} ions present an efficient intramolecular energy transfer from a donor state (usually triplet) of the coordinated organic ligand (*antenna*) to the acceptor excited states of Ln^{3+} ion giving rise to an efficient Ln^{3+} excitation, bypassing the Laporte-forbidden nature of the f-f transitions. The large energy shift between absorbed and emitted radiations and very narrow emission bands allow the discrimination between Ln^{3+} luminescence and short-lived background fluorescence.

In this framework, Eu^{3+} complexes with a new family of imine- and amine-based ligands containing an heteroaromatic (pyridine or furan) ring (Figure 1) have been studied in anhydrous acetonitrile Figure 1 [4,5]. These ligands have been synthesized by an easy synthetic protocol which allows to systematically tune the nature (σ-donor ability) of the heteroaromatic ring which demonstrated to have a strong effect both on the species formed in solution and on the optical sensing response towards the nitrate anion. Furthermore, the ligand stereochemistry can be easily defined. In a following study, the effect of water present in non-anhydrous acetonitrile was investigated [6]. Indeed, water dissolved in an organic solvent in significant amounts was demonstrated to greatly affect the stability and the sensing ability of Eu^{3+} complexes.

The addition of two acetate moieties to the amino-pyridinic scaffold allows to obtain stable Ln^{3+} complexes in water. The dissymmetric environment imposed by the ligand stereochemistry is able to solicit strong chiroptical features, while at the same time leaving free coordination sites available to dock of an analyte molecule. Potentiometric and spectrophotometric studies show that Ln^{3+} complexes have a relatively good stability and that at pH = 7 the 1:1 species is largely dominant. DFT calculations carried out on the Y^{3+} analogue indicate that the two *trans*-O,O and *trans*-N_{py},N_{py} configurations are equally stable in solution and present 2 or 3 coordinated water molecules (Figure 2), in agreement with the hydration number ~2.6 determined by luminescence lifetime measurements. A detailed optical and chiroptical spectroscopic characterization has been carried out and reveals that complexes display an efficient luminescence in the visible spectral range and a strong CPL activity [7].

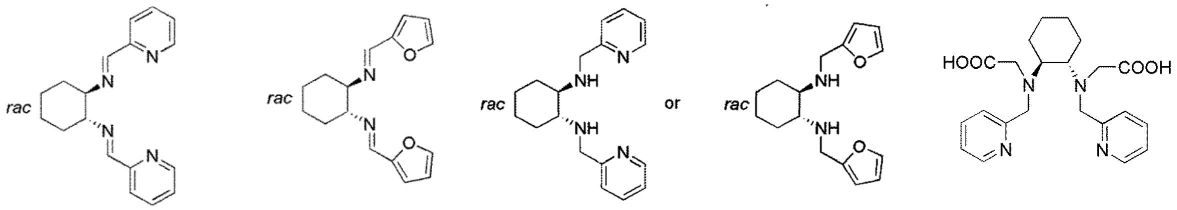

Figure 1. Structures of the ligands studied in organic solvent and water.

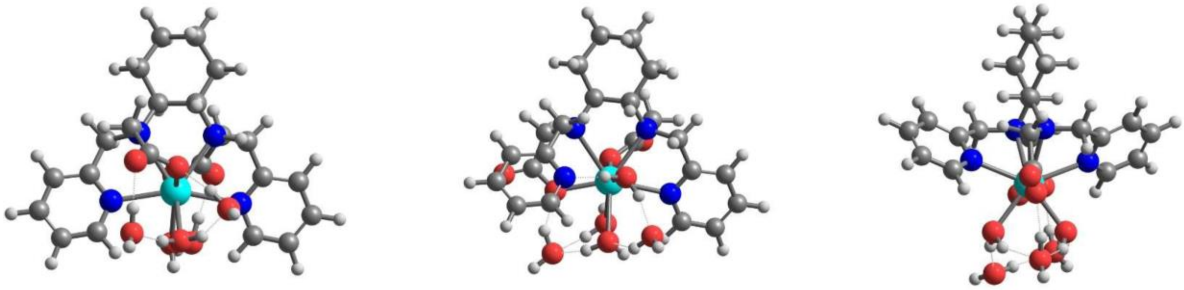

Figure 2. DFT optimized geometry of the possible isomers of the Y^{3+} analogue of the Eu^{3+}.

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Multifaceted coordination ability of phytate: Unprecedented structural data

Nicolás VEIGA, [a] **Delfina QUIÑONE**, [a] **Julia TORRES**, [a] **Carla BAZZICALUPI**, [b] **Antonio BIANCHI**, [b] **Carlos KREMER** [a]

[a] *Química Inorgánica, Departamento Estrella Campos, Facultad de Química, Universidad de la República, CC 1157, MONTEVIDEO, Uruguay*
[b] *Department of Chemistry "Ugo Schiff", Universitá degli Studi di Firenze, FIRENZE, Italy*
nveiga@fq.edu.uy

The most abundant *myo*-inositol phosphate in nature is phytate (InsP_6, L^{12-}, Figure 1), whose biological roles are still not completely understood. InsP_6 interacts strongly with divalent and trivalent cations in a complicated chemistry encompassing solution complexation and precipitation reactions. The lack of detailed structural information concerning these systems is a significant hurdle for studying InsP_6 biology. The structural data available so far have been mostly obtained through molecular modeling combined with data from NMR spectra in solution, while crystallographic data for InsP_6 compounds are still very scanty. The formation of highly insoluble and amorphous complexes has been a major obstacle for the obtaining of single crystals and then for getting a full structural characterization.

In this work we present our so far findings on the chemical and structural characterization of the phytate multifaceted coordination ability (partly reported in [1, 2]). We carried out the synthesis and structural characterization by X-ray diffraction of four new InsP_6 metal complexes with Cu(II) or Mn(II) (Figure 1). These compounds were obtained by the use of an aromatic rigid amine (terpyridine, phenanthroline), which acts as an auxiliary ligand, satisfying some of the metal coordination sites and promoting the crystallization of the solid phases. In conjunction with potentiometry (0.15 M NMe_4Cl at 37.0 °C) and DFT computational calculations, we unveiled the structural parameters of the soluble M(II)-phytate complexes and the molecular assembling processes that leads to the solids.

When phytate competes for the Cu^{2+} ions with a bidentate ligand like phenanthroline (phen), it is allowed in acidic media to bind the metal center mostly through two coordination sites (Figure 1). This gives rise to a set of stable polynuclear complexes, considerably abundant under the experimental conditions applied, which self-assemble in aqueous solution to produce the neutral complex $[Cu_5(H_7L)_2(H_2O)_2(phen)_5]\cdot 23H_2O$. When tridentate terpyridine (terpy) is present, the phytate anion is capable of producing highly stable ternary 1:1:1 complexes with Cu(II), being the polynuclear complexes less abundant in acidic media that those for phenanthroline under the same conditions. In this regard, more phosphate groups became available to coordinate, and at low pH values the self-assembling of the ternary mononuclear $[Cu(H_8L)(terpy)]^{2-}$ species with $[Cu(terpy)]^{2+}$ cations leads to the formation of infinite double tapes with a low nuclearity $[Cu_2(H_8L)(terpy)_2]\cdot 7.5H_2O$. The phosphate groups involved in the coordination scheme are those at C1/C3, C2, and C4/C6, while P5 remains mostly protonated.

When pH is increased to neutrality, P5 is deprotonated enough to start binding the copper cations bidentately, and the nuclearity of the system increases again. An isolated tetranuclear complex is obtained, $K[Cu_4(H_3L)(terpy)_4]·26H_2O$, in which a potassium cation is, for the first time, crystalized bound to a phytate molecule. Finally, when Mn(II) is present at acidic pH, the complex $(H_2terpy)_2[Mn(H_6L)(terpy)(H_2O)]·17H_2O$ is isolated, being the first reported structure containing Mn(II) and phytate. Interestingly, the axial phosphate group remains free and does not participate in the coordination. The connection between [Mn(terpy)] units is sustained through contiguous equatorial phosphate groups acting as monodentate ligands. According to the species distribution and the computational results, a possible assembling mechanism involves the reaction of $[Mn(H_6L)(terpy)]^{4-}$ mononuclear species, where Mn(II) cations are coordinated through the phosphate group at position 1 or 6.

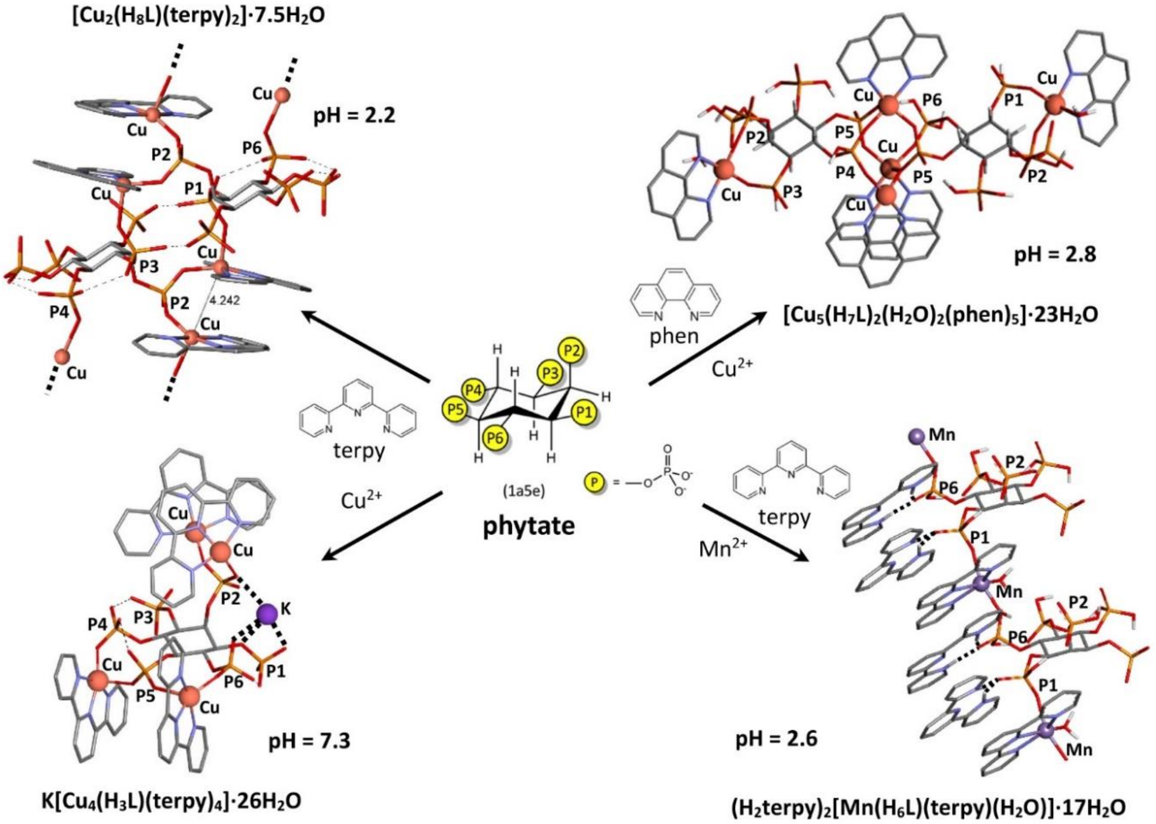

Figure 1. Structure of InsP_6 metal complexes with Cu(II) and Mn(II).

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Solution synthesis, structure and properties of bioctahedral rhenium clusters with mixed inner ligands

Yakov M. GAYFULIN, [a] **Anton I. SMOLENTSEV**, [a,b] **Yuri V. MIRONOV** [a,b]

[a] Nikolaev Institute of Inorganic Chemistry SB RAS, 3, acad. Lavrentiev ave.,
630090 NOVOSIBIRSK, Russia
[b] Novosibirsk State University, 2, Pirogova st., 630090, NOVOSIBIRSK, Russia
gayfulin@niic.nsc.ru

Rhenium chalcogenide clusters, being typical examples of so-called high-valence clusters and the most characteristic of Groups 5−7 4d- and 5d-metals, take a special place in the family of cluster compounds because of their extensive and rich chemistry [1]. During the past decade, the family of molecular rhenium chalcogenide clusters has been supplemented by compounds based on the bioctahedral anions $[Re_{12}(\mu_6\text{-}C)(\mu_3\text{-}S)_{14}(\mu\text{-}S)_3(L)_6]^{n-}$ ($L = CN^-, OH^-, Br^-$, $n = 6$; $L = SO_3^{2-}$, $n = 12$) [2]. These anions are usually represented as two octahedral cores connected face-to-face through one $\mu_6\text{-}C^{4-}$ and three $\mu\text{-}S^{2-}$ ligands. The remaining faces of $\{Re_6\}$ octahedra are capped by $\mu_3\text{-}S^{2-}$ ligands, while three outer Re atoms of each $\{Re_6\}$ octahedron additionally bear the terminal ligands L (Figure 1). In general, the bioctahedral anion closely resemble the well-known octahedral clusters $[Re_6(\mu_3\text{-}S)_8L_6]^n$; however, the presence of two types of inner ligands, $\mu\text{-}S^{2-}$ and $\mu_3\text{-}S^{2-}$, clearly distinguishes the bioctahedral clusters from their structurally related octahedral counterparts.

The structure, physical and chemical properties of cluster compounds are known to strongly depend on the ligand shell bound to the metal centers. The inner chalcogenide μ- and μ_3-bridging ligands are relatively strongly bound to the metal scaffold and their replacement is a non-trivial task. With regard to the $\{Re_{12}CS_{14}(\mu\text{-}S)_3\}$ core, it was assumed that the $\mu\text{-}S^{2-}$ ligands possess a higher chemical activity as compared to $\mu_3\text{-}S^{2-}$ ones because of their lower bonding energy with the rhenium atoms and high steric accessibility. The detailed study revealed that $\mu\text{-}S^{2-}$ ligands can be selectively oxidized to form the $\mu\text{-}SO_2^{2-}$ groups by reaction of $[Re_{12}CS_{14}(\mu\text{-}S)_3CN_6]^{6-}$ with aqueous H_2O_2 [3]. Oxidation process is characterized by a sharp change in the profile of electronic absorption spectrum. Further investigations revealed that $\mu\text{-}SO_2^{2-}$ ligands of the $[Re_{12}CS_{14}(\mu\text{-}SO_2)_3(CN)_6]^{6-}$ anion are very labile. Particularly, in the presence of light irradiation, $\mu\text{-}SO_2^{2-}$ ligands are oxidized in solution by air oxygen forming $\mu\text{-}SO_3^{2-}$ groups without destruction of the cluster core. On the other hand, $\mu\text{-}SO_3^{2-}$ were reduced by chalcogenide ions yielding $\mu\text{-}SO^{2-}$ and $\mu\text{-}S^{2-}$ ligands, generating a mixture of isotypic cluster anions with common formula $[Re_{12}CS_{14}(\mu\text{-}S/SO/SO_2)_3(CN)_6]^{6-}$ [3, 4].

Recently, a useful synthetic approach was developed for selective substitution of $\mu\text{-}SO_2^{2-}$ groups by O^{2-} or Se^{2-} ions in relatively soft conditions. As a result, several new bioctahedral clusters with $[Re_{12}CS_{14}(\mu\text{-}Q)_3]^0$ cores (Q = O, Se) were synthesized. It was found that type of inner ligand dramatically changes chemical and physical properties of new compounds. In particular, characteristic bond lengths, spectroscopic characteristics, redox and chemical activity of $[Re_{12}CS_{14}(\mu\text{-}Q)_3(CN)_6]^{6-}$ cluster anions change regularly in the row of Q = O, S, Se. Note that all $[Re_{12}CS_{14}(\mu\text{-}Q)_3]^0$ clusters with mixed inner ligands are particularly interesting because, unlike $[Re_{12}CS_{14}(\mu\text{-}S)_3]^0$ analogues, they cannot be obtained using classic high-temperature synthesis from simple precursors. We anticipate that investigation of reactivity of inner chalcogenide ligands within the bioctahedral rhenium clusters can be applied to other transition metal clusters, enlarging a number of convenient tools used for modification of their ligand environment.

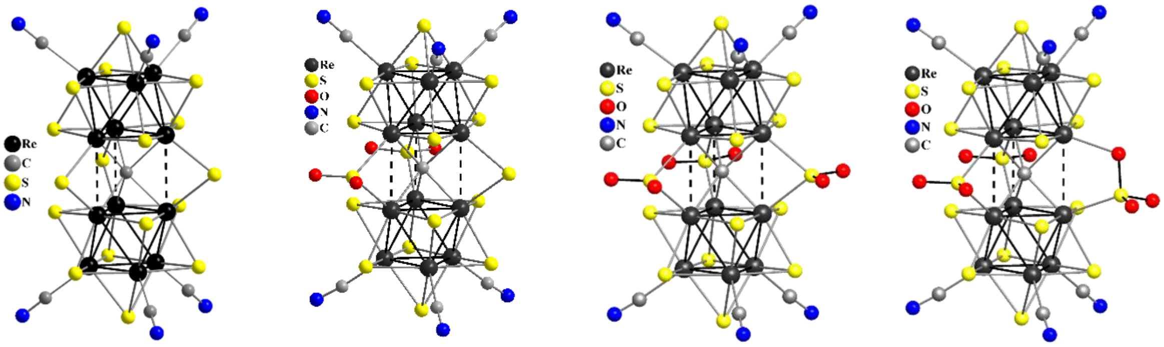

Figure 1. A series of structurally characterized bioctahedral cluster anions of $[Re_{12}CS_{14}(\mu\text{-}Q)_3(CN)_6]^{6-}$ type, from left to right: $[Re_{12}CS_{14}(\mu\text{-}S)_3(CN)_6]^{6-}$, $[Re_{12}CS_{14}(\mu\text{-}SO_2)_2(\mu\text{-}S)(CN)_6]^{6-}$, $[Re_{12}CS_{14}(\mu\text{-}SO_2)_3(CN)_6]^{6-}$ and $[Re_{12}CS_{14}(\mu\text{-}SO_2)_2(\mu\text{-}SO_3)(CN)_6]^{6-}$.

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Designing an aromatic oligoamide foldamer based artificial second coordination sphere for a biologically inspired [2Fe–2S] hydrogenase cluster

Antoine MEUNIER, Michael SINGLETON, Thierry GRANIER, Ivan HUC, Yann FERRAND

Université Bordeaux, CBMN, UMR 5248, Institut Européen de Chimie Biologie,
2 rue Escarpit, 33607 PESSAC, France
y.ferrand@iecb.u-bordeaux.fr

The ability to replicate enzymatic activity with a synthetic molecule is a highly sought after goal in modern chemistry. The well-ordered arrays of functional groups that give rise to the reactivity of enzymes are difficult to replicate in synthetic systems. In the recent years, our group has developed helical foldamers [1,2] – oligomers that adopt stable helical folded conformations – derived from a large toolbox of aromatic amino acids. In the current work, we show that cavities can be designed within such synthetic molecules that can enable them to serve as a scaffold around a tethered, hydrogenase inspired, 2Fe2S cluster. Several stages of inclusion based on oligomer length and folding have been observed with X-ray crystallography and NMR. Additionally, spectroscopic studies (NMR and IR) have been used to show the effect of the aromatic oligoamides on the structural and dynamic processes of the metal cluster. Finally, attempts have been made to post-modify the first coordination sphere of the complexes.

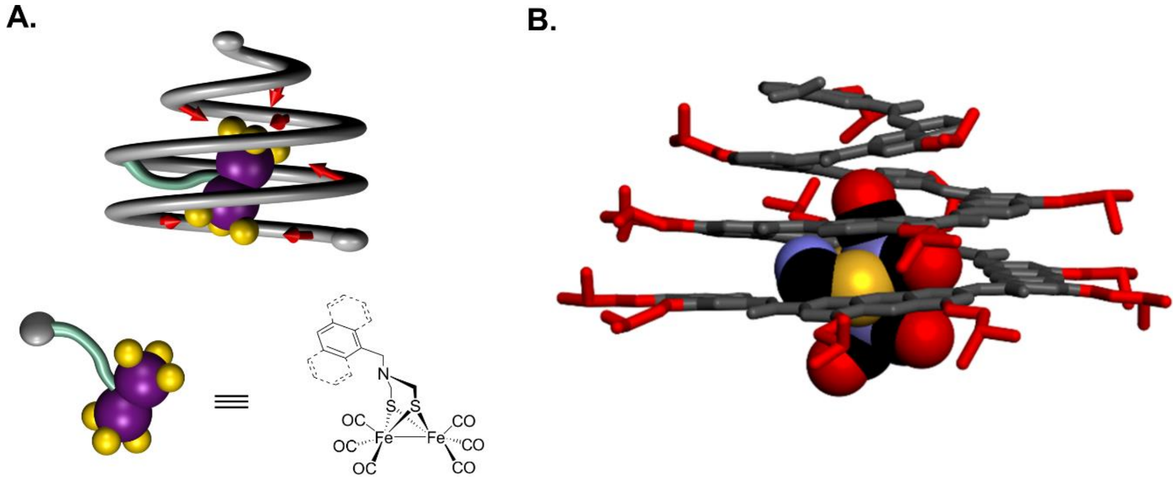

Figure 1. (A) Schematic representation of a helical foldamer "cone" or "half-capsule" (grey tube) surrounding a covalently attached (light blue tube) metal complex (purple and yellow sphere). The red arrows indicate designed interactions from the helical backbone to the complex (top). Schematic representation and developed structure of the metal complex (μ-SCH_2NRCH_2S-)$[Fe(CO)_3]_2$ attached to a benzylic monomer model (bottom). (B) Crystal structure of a (μ-SCH_2NRCH_2S-)$[Fe(CO)_3]_2$ metal complex surrounded by a foldamer cone acting as a second sphere of coordination.

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Electronic interactions in transition metal linked oligoporphyrins

Hervé DEKKICHE, [a] **Mary-Ambre CARVALHO,** [a] **Romain RUPPERT,** [a]
Laurent RUHLMANN, [a] **Sébastien RICHETER,** [b] **Adam LANGLOIS,** [c]
Paul-Ludovic KARSENTI, [c] **Pierre D. HARVEY** [c]

[a] *Institut de Chimie, UMR CNRS 7177, Université de Strasbourg, 4 rue Blaise Pascal, 67000 STRASBOURG, France*
[b] *Institut Charles Gerhardt, UMR CNRS 6253, Université de Montpellier 2, CC1701, 34095 MONTPELLIER, France*
[c] *Université de Sherbrooke, Département de Chimie, PQ J1K 2R1, SHERBROOKE, Canada*
dekkiche@unistra.fr

Energy and electron transfers are key photophysical events in photosynthetic bacteria and plants. Synthetic models for these processes often use covalent linkers between the individual chromophores. Several metallo-bridged homo- and hetero-oligoporphyrins are reported in the literature and some of them showed significant electronic communication between the subunits [1]. In our group, metalloporphyrins bearing one or two external chelating groups were used to build porphyrin dimers or higher oligomers by complexation with a cationic metal (see Figure 1). Strong electronic interactions were found in these architectures, as evidenced by electronic spectroscopy and electrochemical studies.

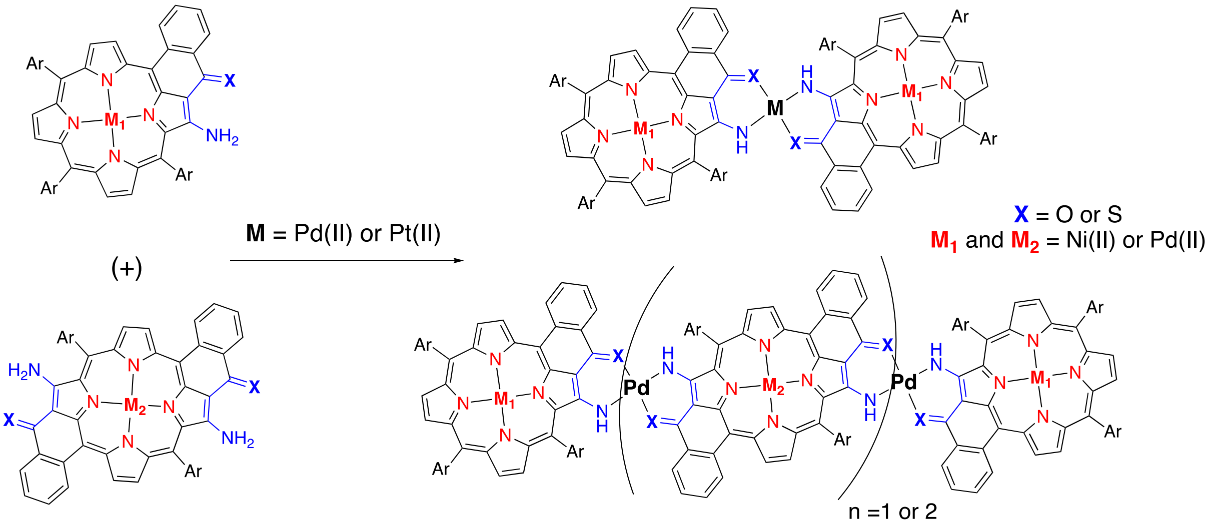

Figure 1. Synthesis of porphyrin dimers, trimers and tetramers.

Porphyrin dimers and dyads (see Figure 2) showed stronger electronic interactions when replacing O by S in the external coordination site and substituting the linking ion Ni(II) by Pd(II) or Pt(II) [2,3]. An increase in the energy transfer rate measured in the zinc(II)porphyrin-freebaseporphyrin dyads, a larger bathochromic shift and an increase of the first oxidation potentials splitting in the homo-dimers were observed. This tendency was correlated with an increase in the molecular orbital overlap through the linking atom between the porphyrin units. Porphyrin trimers and tetramers were also synthesized, by introducing a doubly functionalized porphyrin moiety in the assemblies. Near-infrared absorption bands were observed which express the strongly delocalized nature of their π-system.

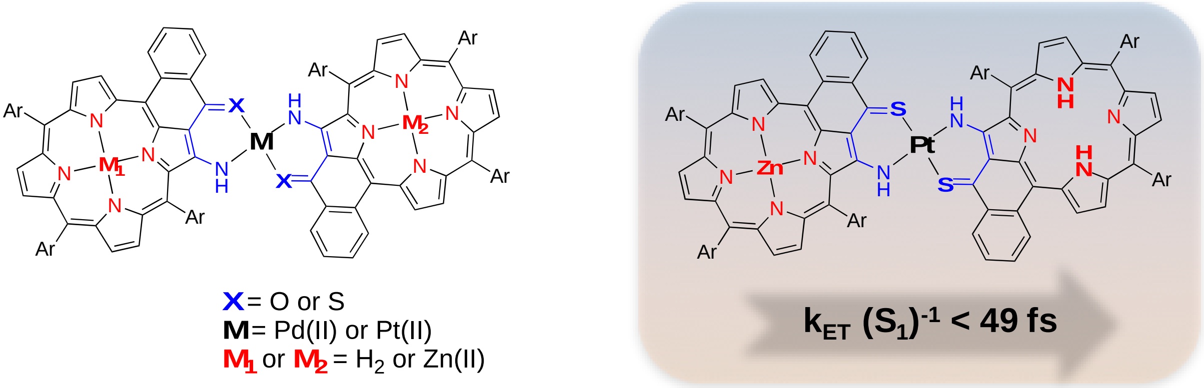

Figure 2. Porphyrin dyads studied.

These molecules, along with their building blocks were characterized by routine measurements (^{1}H NMR, mass spectroscopy) and their properties studied with electro- and photo-chemical techniques (cyclic voltammetry, spectroelectrochemistry, UV-Vis absorption, transient absorption spectroscopy, fluorimetry). Some of the results could also be corroborated by DFT calculations.

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Phosphorescent metal complexes and their bioconjugates in imaging using one- and two-photon excitation and PLIM technology

Sergey TUNIK, Pavel CHELUSHKIN, Anastasiya SOLOMATINA

St. Petersburg State University, Institute of Chemistry, Universitetskii pr., 26,
198504 ST. PETERSBURG, Russia
sergey.tunik@spbu.ru

Phosphorescent metal complexes attract increasing attention due to their potential application in biology and medicine as bioimaging probes and selective sensors for molecules of biological importance. These fields of research are rapidly growing because of some critically important advantages provided by heavy metal complexes compared to traditionally used fluorescent dyes based on small organic molecules. The metal complexes display large Stokes shift (up to 400 nm) and lifetime in microsecond domain that make possible to avoid luminescence self-quenching and to cut-off background fluorescence in imaging experiments thus increasing resolution of luminescent microscopy. Sensitivity of phosphorescence parameters to the presence of molecular oxygen provides another useful tool to analyze physiological status (oxygen distribution) of cells and tissues using phosphorescent intensity and lifetime (PLIM) measurements.

To completely exploit the positive photophysical features of the phosphorescent metal complexes in bio-medical applications including *in vivo* imaging it is necessary to additionally make these compounds water-soluble and to improve their bio-availability. This can be done either by introduction of bio-compatible functions in the ligand environment or by preparation of covalent and non-covalent conjugates with biomolecules, e.g. with peptides and/or proteins. In our studies we used both approaches and in the present communication we present the synthesis and characterization of the phosphorescent Pt(II), Au(I)-Cu(I), Au(I)-Ag(I) complexes and their conjugates with proteins (human serum albumin (**HAS**), ubiquitin) as well as the application of these species in one- and two-photon imaging and in PLIM experiments. It was also shown that ortho-metallated Pt(II) complexes (Figure 1, A) features switch-on phosphorescence upon interaction with histidine containing bio-molecules due to platinum coordination to imidazole moiety of histidine. The phosphorescent complexes and their bio-conjugates were studied by UV-vis and emission spectroscopy, multinuclear NMR, mass-spectrometry and X-Ray crystallography.

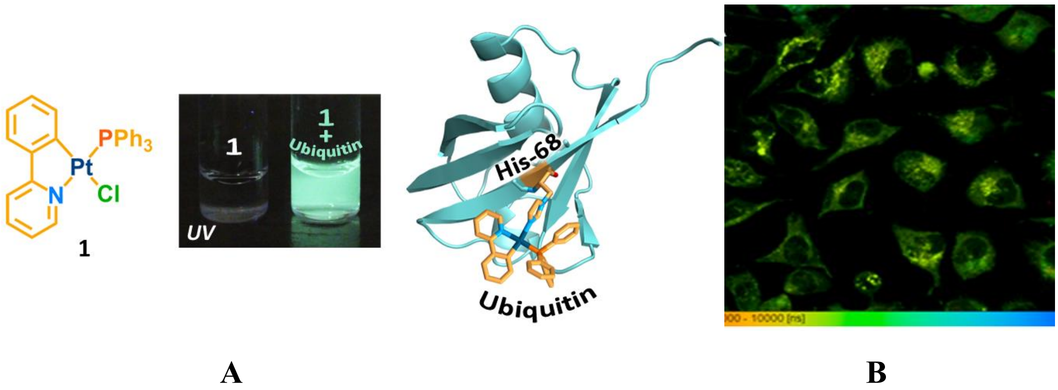

Figure 1. A. Regioselective labeling of histidine with ortho-metallated Pt(II) comples, **1**; B. PLIM image of live HeLa cells stained with **1-HSA** conjugates. Data from [1].

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Tailoring the local environment around metal ions by multidentate tripodal ligands

**Ferenc MATYUSKA, [a] Attila SZORCSIK, [b] Nóra V. MAY, [c] Éva KOVÁTS, [d]
Attila BÉNYEI, [e] Tamás GAJDA [a]**

*[a] Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7,
6720 SZEGED, Hungary*
[b] MTA-SZTE Bioinorganic Chemistry Research Group, Dóm tér 7, 6720 SZEGED, Hungary
[c] Research Centre for Natural Sciences HAS, Magyar tudósok krt. 2, 1117 BUDAPEST, Hungary
*[d] Institute for Solid State Physics and Optics, Wigner Research Centre for Physics HAS,
Konkoly Thege Miklós u. 29-33, 1121 BUDAPEST, Hungary*
*[e] Department of Pharmaceutical Chemistry, University of Debrecen, Egyetem tér 1,
4032 DEBRECEN, Hungary*
gajda@chem.u-szeged.hu

The favourable and preorganized spatial distribution of donor atoms in tripodal ligands has been long time recognised and applied to develop metal ion chelators for a variety of purposes. Here we report the metal complexes of some *cis,cis*-1,3,5-triaminocyclohexane (tach) and tris-(2-aminoethyl)amine (tren) derivatives (Figure 1). The substitution of these well-known tripodal platforms may provide additional donor site(s), may influence the steric environment around the metal centre or may help to introduce further metal binding site(s) in order to create polynuclear complexes. Accordingly, these polydentate tripodal ligands are proved to be versatile building blocks for metal-organic-frameworks, efficient metal sequestering agents or artificial enzymes.

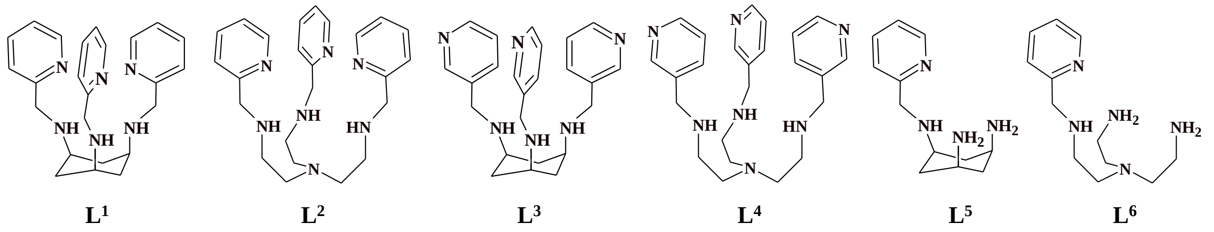

Figure 1. Schematic structures of the studied ligands.

L^1 and some of its derivatives are promising chelators of $^{64/67}$Cu for radiotherapeutic uses, moreover **L^1** and **L^2** are cytotoxic metal chelators with potential anti-tumor activity [1, 2]. Although **L^1**/**L^2** have been designed for efficient metal ion binding, no thermodynamic data on the stability of **L^1** is reported in the literature. The comparative evaluation of our solution chemical and spectroscopic data indicated that **L^1** and **L^2** offer high thermodynamic stability, and a variety of coordination environment/geometry for manganese(II), copper(II) and zinc(II). **L^1** is more efficient zinc(II) and similar copper(II) chelator than **L^2**. Considering the higher number of N-donors and conformational flexibility of **L^2**, as well as the energy demanding switch to the triaxial conformation required for metal ion binding of **L^1**, the above observation is surprising and is very likely due to the encapsulating effect of the more rigid tachpyr skeleton. This relative binding preference of tachpyr for zinc(II) may be related to the observation that zinc(II) is one of the principal metals targeted by tachpyr in cells. In contrast, trenpyr is considerably more efficient manganese(II) chelator, since it acts as a heptadentate ligand in the aqueous Mn(trenpyr) complex. The crystal structures of copper(II) and zinc(II) complexes of **L**^{1} indicated important differences in the ligand conformation, induced by the position of counter ions, as compared to earlier reports.

The closely related new ligands, **L**^{3} and **L**^{4} have been designed to form oligonuclear complexes. Indeed, we obtained a three dimensional polymer with copper(II)/**L**^{4}. Within this metal-organic framework (**1**MOF) three distinctly different copper geometries can be identified. Two square pyramidal and four trigonal bipyramidal copper centres create a hexanuclear subunit with a large inside cavity. These moieties are linked by tetrahedral copper(II) centres, constructing the three dimensional polymer structure (Figure 2).

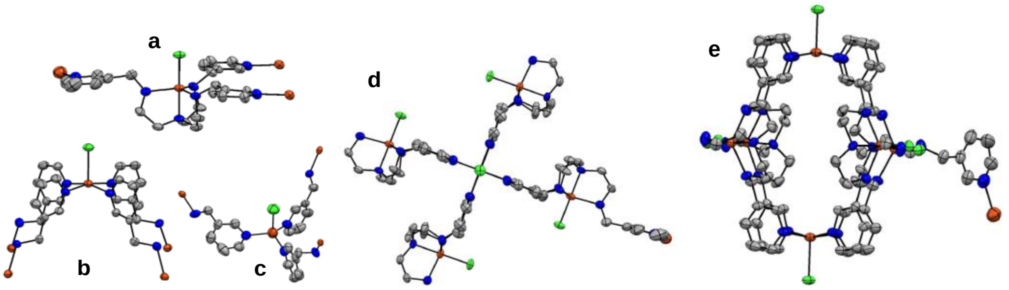

Figure 2. Structure of the three types of Cu(II) centres in the **1**MOF (a,b,c), as well as the top (d) and side view (e) of the $Cu_6(\mathbf{L}^4)_4$ subunit (for clarity, the third leg is shown only for one of the ligands, together with a tetrahedral copper which connects the hexanuclear subunits).

In solution only mononuclear complexes are formed with **L**^{3} and **L**^{4}. According to its facial donor set **L**^{3} forms square pyramidal complexes. The relatively open coordination sphere of Cu**L**^{3}(OH) results in efficient hydrolytic activity against phosphodiesters. The absence of pyridine nitrogens in chelatable positions allows the tren-subunit to enforce trigonal bipyramidal geometry in **L**^{4} complexes. **L**^{5} and **L**^{6} form highly stable 4N/5N complexes with manganese(II), iron(II), copper(II) and zinc(II). According to our X-ray and spectroscopic data Cu**L**^{5} has strongly distorted square pyramidal, Cu**L**^{6} has distorted trigonal bipyramidal geometry. Since the fifth coordination of Cu**L**^{5} is easily exchangeable, this complex also shows enzyme mimicking, *i.e.* catalase-like activity, with ligand-centered (imine/secondary amine) redox reactions.

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Versatility of coordination modes in complexes of monohydroxamic acids with some half-sandwich type cations

Etelka FARKAS, **Péter László PARAJDI-LOSONCZI,**
Linda BÍRÓ, Norbert LIHI, Péter BUGLYÓ

Department of Inorganic and Analytical Chemistry, University of Debrecen,
Egyetem tér 1, 4032, DEBRECEN, Hungary,
efarkas@science.unideb.hu

Hydroxamic acids ($R_CC(O)NR_N(OH)$, where R_C = alkyl or aryl; R_N = H in primary derivatives, alkyl or aryl in secondary ones) are important biomolecules and show a wide spectrum of biological activities. For example, they are, among others, building blocks of siderophores, known to uptake metal ions, mostly iron(III) [1] in microorganisms or act as inhibitors of various enzymes, including ureases, peroxidases, or matrix metalloproteinases [2]. There is no doubt that these diverse biological activities of hydroxamic acids are due to their complexation properties towards various metal ions. Half-sandwich type organometallic platinum group metal complexes with proven *in vivo* antiproliferative potential are also in the focus of intensive research in recent decades. Despite the numerous biological activities of hydroxamate-based compounds and also the high interest towards the complexes of platinum metals, only a few results have been published on monohydroxamate complexes with half-sandwich type Ru(II) [3] and Os(II) cations [4] and, to the best of our knowledge, no results were published previously on hydroxamate complexes of Rh(III)- or Ir(III)-containing cations.

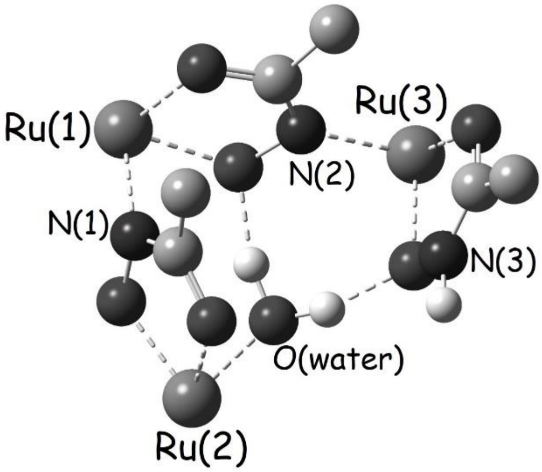
Complexation of the secondary N-methyl-acetohydroxamic acid (HMeaha) with $[(\eta^6\text{-}p\text{-cym})Ru(H_2O)_3]^{2+}$, $[(\eta^5\text{-Cp*})Rh(H_2O)_3]^{2+}$, $[(\eta^6\text{-}p\text{-cym})Os(H_2O)_3]^{2+}$or $[(\eta^5\text{-Cp*})Ir(H_2O)_3]^{2+}$ half-sandwich type cations and the primary acetohydroxamic acid (HAha) with the former two cations in solution have been studied in our present work with the combined use of pH-potentiometry, NMR and ESI-MS techniques supported by DFT calculations.

As it is well-known, the stable hexahapto bound arene (benzene(derivative)) or the pentahapto arenyl ((pentamethyl)cyclopendadienyl (Cp*/Cp)) ligands take three coordination sites of the metal ion and three sites in "piano-stool arrangement" remain free (occupied by aqua molecules in the formulas above) for interaction with additional ligand(s).

With the secondary HMeAha 5-membered O,O-chelate was found to be formed in all the four systems, showing the highest stability for the Ru(II)-containing complex, the lowest for the Rh(III)-containing one. The extent of interaction, however, depends very much also on the hydrolytic activity of the cation. For example, with the Os(II)-cation, where the tendency for hydrolysis is the highest, the extent of the complex formation with Meaha is the lowest, it is measurable only in the slightly acidic pH-range. On the contrary, the lowest stability Rh(III)-containing complex predominates even at neutral pH, because the competition by the hydroxide ion is quite moderate in this system.

The tendency for deprotonation of the aqua ligand at the third coordination site in the Meaha-containing ternary complexes follows completely the trend of the half-sandwich cations for hydrolysis.

The results support the significant role of R_N = H substituent of HAha on its complexation with the two investigated cations, especially with $[(\eta^6\text{-}p\text{-cym})Ru(H_2O)_3]^{2+}$ above pH ca. 4-5. The interpretation of the bonding mode in the very high stability trinuclear species, the formation of which is clearly supported be our results and the most likely calculated structure is shown below are planned to be presented at the conference.



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Copper complexation with tacn-based bifunctional picolinate ligands for potential PET application

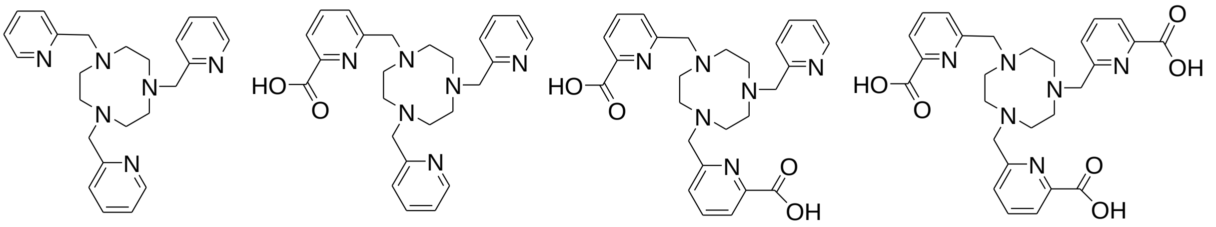
Amaury GUILLOU, [a] Luís M. P. LIMA, [b] Mélissa ROGER, [a]
David ESTEBAN-GÓMEZ, [c] Rita DELGADO, [b] Carlos PLATAS-IGLESIAS, [c]
Véronique PATINEC, [a] Raphaël TRIPIER [a]

[a] Université de Bretagne Occidentale, UMR CNRS 6521, UFR des Sciences et Techniques,
6 avenue Victor le Gorgeu, C.S. 93837, 29238 BREST Cedex 3, France
[b] Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa,
Av. da República, 2780-157 OEIRAS, Portugal
[c] Universidade da Coruña, Centro de Investigacións Científicas Avanzadas (CICA) and Departamento de Química Fundamental, Facultade de Ciencias, 15071 A CORUÑA, Spain
veronique.patinec@univ-brest.fr

Metallic radioelements are attracting a growing interest from the scientific community because of their continuously increasing applications in radiochemistry and in nuclear medicine. Among them, ^{64}Cu presents an interesting biologically viable half-life decay (12.7 h) and a low β^+ energy suitable for positron emission tomography (PET). Various ^{64}Cu radiolabeled pharmaceuticals have thus been used in preclinical PET trials of several cancers [1,2] and already in clinical studies [3].

In radiopharmaceuticals, ^{64}Cu radiotracer is sequestrated by a bifunctional chelating agent (BCA) conjugated to a targeting antibody or peptide. In order to avoid the release of the radioelement in the body, it is mandatory that the ^{64}Cu/BCA chelate presents the following features: rapid complexation, high thermodynamic stability, high kinetic inertness and stability of the chelate towards potential reductive bioagents that could reduce ^{64}Cu(II) into ^{64}Cu(I) leading to the irremediable metal dissociation. In the aim to improve the effectiveness and expand the applications of PET imaging, new chelates are currently developed by designing new ligands and studying their “cold” Cu(II) complex properties, prerequisite for further bioapplications.

Our group currently develops new chelates based on tri- and tetra-azamacrocycles presenting appropriate physico-chemical properties for radiopharmaceutical applications in imaging and therapy [4, 5]. Among them, new tetraazamacrocycle derivatives with picolinate pendant arms have exhibited expected behaviours with natural Cu(II) chelates and ^{64}Cu radiolabeling corroborated these promising results [6]. In order to widen the study to the tri-azamacrocycle derivatives and to evaluate the contribution of the number of picolinate pendants to the Cu(II) complexes stability, the following tacn (1,4,7-triazacyclononane) -based chelators with picolinate and/or picolyl arms have been synthesized (**no3py**, H**no1pa2py**, **H$_2$no2pa1py** and **H$_3$no3pa**: scheme 1) and their corresponding Cu(II) complexes studied.



no3py **Hno1pa2py** **H_2no2pa1py** **H_3no3pa**

Scheme 1

The synthesis of the chelates, the thermodynamic stability of their complexes with Cu^{2+}, the EPR and UV-vis spectroscopies, cyclic voltammetry, DFT calculations studies and the developments will be discussed in the presentation.

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Tacrine-hydroxypyridinone hybrids as anti-acetylcholinesterase agents with metal ion binding capacity

Rajeshwari RAJESHWARI, Karam CHAND, Sílvia CHAVES, M. Amélia SANTOS

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa,
Av. Rovisco Pais 1, 1049-001 LISBOA, Portugal
masantos@ist.utl.pt

3-Hydroxy-4-pyridinones (3,4-HP) have been intensively explored in drug design, as chelating drugs for metal overload therapy. However, more recently, they have been also investigated as *multi-target ligands*, in which one chelating unity is extra-functionalized (hybridized) to enable the interaction with other relevant biological sites associated with some specific diseases, namely neurodegenerative disorders [1-3].

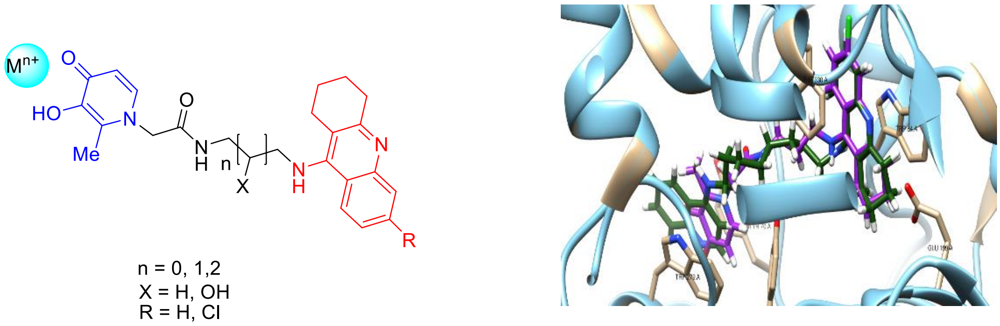
Alzheimer´s disease (AD) is an age-dependent neurodegenerative disease which main hallmarks are the accumulation of amyloid plaques and the loss of neurotransmitters (e.g. acetylcholine) in the brain synapses leading to severe memory impairments [4]. On the other hand, it is known that brain patients present metal dyshomeostasis, i.e. accumulation of redox-active metal ions. They can lead to production of detrimental reactive oxygen species (ROS) implicated in several neurodegenerative processes, including AD; also the metal ions are associated to increased toxicity of amyloid protein aggregates [5].

In spite of the intensive research along the last two decades on drug development for combating the main pathological hallmarks of AD, the FDA approved drugs can only alleviate the symptoms, as they are mainly inhibitors of acetylcholinesterase leading to some short-medium recover of acetylcholine loss and memory deficits. The absence of disease modifying agents and cure so far, has been mainly attributed to the multifactorial nature of AD. Therefore, quite an amount of recent research on anti-AD drugs has been focused on the development of multi-target compounds, assuming that for such complex disease hitting more than one disease target can have advantages over a mono-target strategy [6].

Thus, as part of our interest on that strategy, we have developed a series of hybrid molecules which contain a tacrine (TAC) group and a 3,4-HP moiety to guarantee both the inhibition of AChE and the chelation (modulation) of metal ions, respectively. The linkers between those two main moieties were selected based on molecular modeling for the improvement of the ligand interactions within the enzyme active site.

The results obtained for this set of hybrids showed a very good AChE inhibitory activity, namely sub μM range for the compounds with 3-methylene linker sizes, attributed to potential dual binding within the enzyme active site according to the docking simulations (see Figure 1b). For the evaluation of the metal chelating capacity of these hybrids, one compound, TAC-HP12 (see Figure 1a; R = H, n = 1, X = OH), was selected and studied in terms of acid-base properties, as well as metal complexation towards redox-active (Fe^{3+}, Cu^{2+}) and Aβ-binding (Cu^{2+}, Zn^{2+}) metal ions. Besides the 3,4-HP group, this compound has also another potential chelating moiety involving the tacrine amine, the hydroxyl group and the amide nitrogen. However, in stoichiometric conditions or even under excess of ligand and for the physiological pH, the results indicate a clear predominance of the HP chelating effect over the formation of polynuclear metal complexes. In fact, the metal chelating capacity of TAC-HP12 follows the expected trend (pFe > pCu > pZn at pH = 7.4) and the range of values reported for bidentate hydroxypyridinones such as Deferiprone, the marketed iron-chelating drug.

Furthermore, these compounds showed very high capacity (85-90%) for inhibition of the self-induced Aβ-aggregation. This may be attributed to the chelating effect of residual amounts of Cu(II) which induce fibril aggregation. Interestingly, in some cases, copper reduces the effect of the ligand as anti-Aβ aggregator, due to eventual competition of the ligand for the copper in solution and subsequent inactivation upon complex formation. Overall, although further studies are still needed, namely in cell environment, these new hybrids appear as potential anti-AD drugs.



a) b)

Figure 1

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Structural investigation of bioactive metal complexes with coumarin derivatives using X-ray absorption spectroscopy

Marcin KLEPKA, [a] **Aleksandra DRZEWIECKA-ANTONIK**, [a] **Anna WOLSKA**, [a]
Paweł REJMAK, [a] **Marta STRUGA** [b]

[a] Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46,
02668 WARSAW, Poland
[b] Medical University of Warsaw, Żwirki i Wigury 61, 02091 WARSAW, Poland
mklepka@ifpan.edu.pl

Metal complexes of coumarin-based ligands are being widely investigated due to their biological activity. Among reports about the activity of complexes there is little information concerning metal - organic ligand binding mechanism. It concerns especially complexes which were not obtained in a crystalline form. In such a case diffraction techniques are inapplicable and structural information can rather be speculated than experimentally determined. On the other hand, detailed knowledge about structure is extremely important in studies of bioactive coordination complexes.

In order to overcome an obstacle with non-crystalized complexes X-ray absorption spectroscopy (XAS) technique can be applied. X-ray absorption spectrum can be divided into two regions which provide complementary information about local atomic order around absorbing atom. These regions are: (*i*) X-ray absorption near edge structure (XANES) and (*ii*) extended X-ray absorption fine structure (EXAFS). The great advantage of XAS technique over other experimental techniques is that it can be used for crystal as well as amorphous materials at different states: (*i*) solid, (*ii*) liquid or (*iii*) gaseous.

In order to resolve molecular structure of the metal-organic ligand complexes we have developed the methodology which is a combination of experimental techniques and theoretical calculations [1-2]. We have successfully applied this methodology to describe molecular structure of bioactive Cu(II) complexes with hydroxycoumarins [3-4] as well as Ag(I) complexes with coumarin acids. The microbiological activity of studied complexes are comparable with commercially available drug.

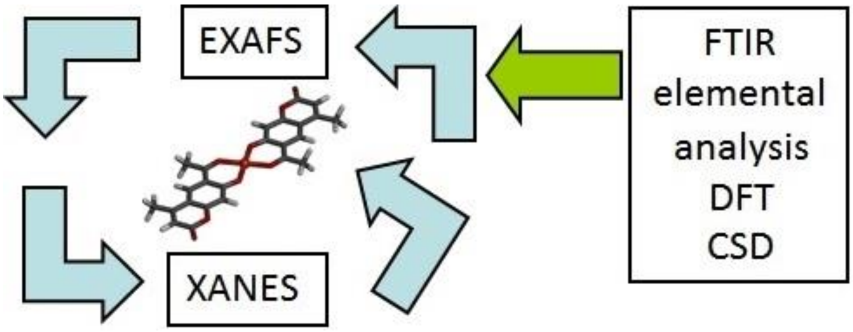

Figure 1. Scheme of the analysis methodology.

Results obtained for various metal complexes with coumarin derivatives, in both solid and liquid phase, as well as the basics of the XAS technique will be described during the presentation.

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HypCal, a versatile program for the determination of standard reaction enthalpy and equilibrium constant values from calorimetric data

Giuseppe ARENA, [a] Peter GANS, [b] Carmelo SGARLATA [a]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Catania, V. Andrea Doria 6, 95125 CATANIA, Italy*
[b] *Protonic Software, 2, Templegate Avenue, LEEDS, LS15 0HD, UK*
sgarlata@unict.it

HypCal is a new general-purpose computer program that has been developed for the simultaneous determination of both standard enthalpy of reaction and binding constant values from data obtained by isothermal titration calorimetry. The program does not impose limits on the complexity of the chemical systems that can be treated, including competing ligand systems, or on the quantity of experimental data to be analyzed. The chemical system is defined in terms of species of given stoichiometry rather than in terms of binding models (e.g. independent, cooperative, etc.) [1,2]. The parameter refinement procedure is robust and efficient and the program is fully protected against hard-failure. Many titration curves may be treated simultaneously. HypCal can also be used as a simulation program for the experiment design. The program is able to process data from both partially filled and overfilled calorimeters. Typical applications are for the study of ligand protonation, host-guest reactions, metal-ligand complexation and competition reactions.

The use of the program is illustrated with sample data obtained with nicotinic acid [3]. Preliminary experiments were used to establish the different titration conditions for the two sets of titration curves that are needed to determine the thermodynamic parameters.

The same advantageous experimental procedure has been used for the determination of species as well as standard enthalpy and log β values for the binding of pyridinium-based gemini guests to a *p*-sulfonato-calix[4]arene ligand in aqueous solution at physiological pH [4]. Results obtained showed that guests having different size, shape and flexibility are able to form water-soluble homodimeric supramolecular capsules in solution. The molecular recognition process is driven by different and often opposing forces including hydrophobic and electrostatic interactions.

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Monoamide vs TBP: A comparative study of uranium and plutonium mass transfer in solvent extraction

Romain BERLEMONT, [a)] **Anne LELIAS-VANDERPERRE,** [a)] **Christian SOREL,** [a)]
Jean-Pierre SIMONIN [b)]

[a)] CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes, SPDS / LCPE, BP 17171, 30207 BAGNOLS-SUR-CÈZE, France
[b)] PHENIX Laboratory, Paris VI University, 4 Place Jussieu, 75252 PARIS, France
anne.lelias@cea.fr

For many years, *N*,*N*-dialkylamides have been identified as interesting extractants for the reprocessing of spent nuclear fuels [1-2]. To develop an advanced solvent extraction process for plutonium multi-recycling from Generation IV reactors, many equilibrium data have been collected. However little is known on the mass transfer kinetics. Indeed, the knowledge of the mass transfer coefficients and the understanding of the implied phenomena are essential to simulate the process in contactors with short residence time and for its scale-up in industrial contactors.

To supplement kinetic data related to a process using a mixture of DEHBA-DEHiBA as extractant, mass transfer coefficients of uranium(VI) and plutonium(IV) between nitric acid and the monoamide based solvent have been acquired using the single drop method [3]. This experimental technique based on a 1.5 meters height column allows the determination of global mass-transfer coefficients K_g ($m.s^{-1}$) for cations of interest. It involves the formation of single drops of one phase rising or falling through the continuous phase. The variation of the element (U or Pu) concentration in the drop is measured in the feed and in the raffinate for different travel times.

The influence of temperature, solute concentration, interfacial area (drop size), viscosity of the organic phase and emulsion nature (continuous aqueous or organic phase) on the kinetics of uranium and plutonium extraction has been studied. The results have been exploited to determine either the chemistry or the diffusion process controls the kinetic. These data are compared with results obtained in similar conditions with TBP solvent currently used in the PUREX process in order to estimate the difference of kinetics between these two solvents.

Acknowledgment: this work was co-founded by AREVA-NC through the PRONG project.

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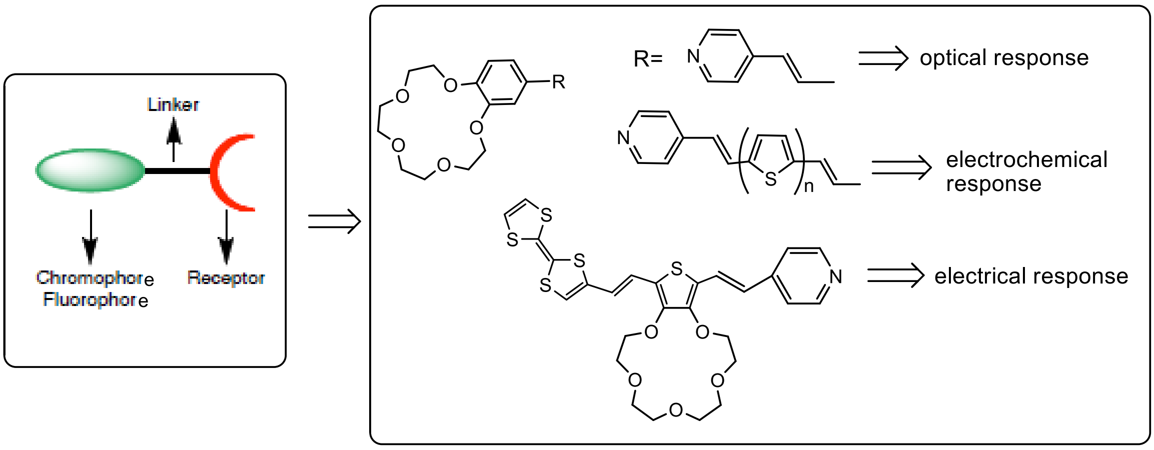
Organic and inorganic-organic hybrid systems for chemical sensing in liquid and gas media

Olga FEDOROVA, **Elena GULAKOVA, Nikolai SCHEPE**, **Pavel PANCHENKO, Yuri FEDOROV**

A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), Vavilova St. 28, MOSCOW, Russia
fedorova@ineos.ac.ru

Sensors belong to the modern world like the mobile phone, the compact disc or the personal computer. A chemical sensor is a device that transforms chemical information, ranging from concentration of a specific sample component to total composition analysis, into an analytically useful signal. The sensor element in such device contains receptor group for recognition of analyte and transducer group providing the type of observed signal. Based of signal transduction the sensor groups could be defined as optical sensors, electrochemical sensors, electrical sensors, mass-sensitive sensors, magnetic sensors, etc. [1-3].

In the present research, we show the ways of the applying of proper design to obtain the molecular sensors demonstrated different types of sensor signals.



Donor-acceptor systems, either molecules or supramolecular assemblies such as compounds presented at scheme, have been identified as ideal chemosensors, i.e. components which translate the presence of the analyte into an appropriate optical response, in some cases also into an electrical response. The system is designed such that it is highly modular, i.e. receptor units, linker and chromophore may be exchanged and combined, and even different chromphores may be employed. The chemical, optical and conductive properties of these systems depend strongly on the extent of the donor-acceptor interplay because of charge-transfer, charge-shift, or charge-separation processes. Thus, if either the donor or the acceptor unit interacts with the analyte, in most cases upon complexation, this recognition event leads to a significant change of the optical properties or electrical conductivity, allowing to monitor the process by absorption or emission spectroscopy, conductivity measurements or even by the determination of molecular electronics or photodynamics.

Acknowledgment: this work was supported by RFBR № 15-03-04705.

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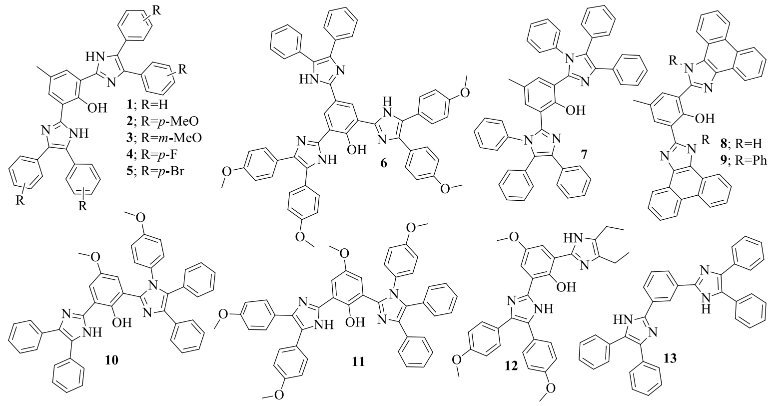
Metal coordination with ESIPT-enabled 2,6-di(1H-imidazol-2-yl)phenols in turn-on fluorescent chemosensing for Cr(III), Zn(II) and Cd(II): Studies on molecular tuning for sensor selectivity

Abiodun O. ESEOLA, [a,b] **Helmar GÖRLS**, [b] **Winfried PLASS** [b]

[a] *Materials Chemistry group, Department of Chemical Sciences, Redeemer's University,*
EDE, Osun State, Nigeria
[b] *Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena,*
Humboldtstr. 8, 07743 JENA, Germany
biodun.eseola@uni-jena.de

A series of structurally and electronically varied derivatives of 2,6-di(1H-imidazol-2-yl)phenols (**1**–**12**) and the corresponding meta-phenylene bridged derivative 4,5-diphenyl-2-(3-(4,5-diphenyl-1H-imidazol-2-yl)phenyl)-1H-imidazole (**13**) [1,2] have been synthesized and comparatively evaluation for molecular effects on sensitivity and selectivity characteristics in metal ion sensing. Ligands **1**–**12** are composed of two imidazole moieties at both *ortho*-positions of a phenol hydroxyl function. These ligands are either symmetric or unsymmetric with respect to the substitution pattern of the two imidazole moieties. X-ray crystal structure data were obtained for the unsymmetric ligand 2-(4,5-bis(4-methoxyphenyl)-1H-imidazol-2-yl)-6-(4,5-diethyl-1H-imidazol-2-yl)-4-methoxyphenol (**12**) and the self-assembled complex species **7**-$CoCl_2$ containing the symmetric ligand 4-methyl-2,6-bis(1-phenyl-4,5-bis(4,5-diphenyl)-1H-imidazol-2-yl)-phenol (**6**).

Quantum yields for all ligands have been determined and which revealed that ligands with the symmetric 4-methyl-2,6-bis(1-H-4,5-bis(4,5-diphenyl)-1H-imidazol-2-yl)-phenol backbone (**1**–**6**) possess low quantum yields in acetonitrile (0.01 – 0.07), while the remaining ligands generally give higher quantum yields (0.20 – 0.61). The ligands **1**–**5** were observed to give fluorescence turn-on behaviour in the presence of Cr^{3+} and Zn^{2+} ions while also having weak sensitivity for Cd^{2+} ions. The methoxy-substituted compound **2** shows an impressive fluorescence sensitivity and selectivity for Cr^{3+} ($F/F_o = 106$) while the unsubstituted counterpart compound **1** also exhibits a remarkable potential for Zn^{2+} at a blue-shifted emission band. Job plot analysis obtained for the fluoro-substituted compound **4** shows 1:1 fluorophore to metal ion stoichiometry for the fluorescence-enhanced species formed in solution. The compounds that possess promising fluorescent turn-on behavior have something in common, which are (i) symmetric substitution pattern on both azole rings and (ii) the presence of multiple active protons engaged in intramolecular hydrogen bonding relays. It is also concluded that subtle molecular modifications could serve as tools for tuning and improving selectivity of chemosensors. Possible metal to ligand interactions leading to fluorescence turn-on were also discussed on the basis of preserved ESIPT in the presence of Cr^{3+} or loss of ESIPT in the presence of Zn^{2+}.



Scheme 1. Studied 2,6-di(1H-imidazol-2-yl)phenol derivatives (1–12) and 4,5-diphenyl-2-(3-(4,5-diphenyl-1H-imidazol-2-yl)phenyl)-1H-imidazole (13).

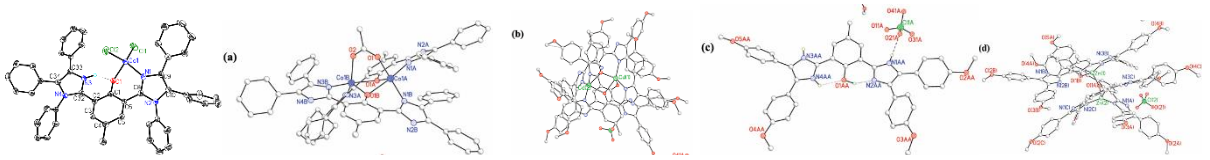


Figure 1. (i) Molecular structure of metal complex species obtained for the studied ligands drawn at 50% probability level. Some atomic labels and protons have been omitted for clarity.

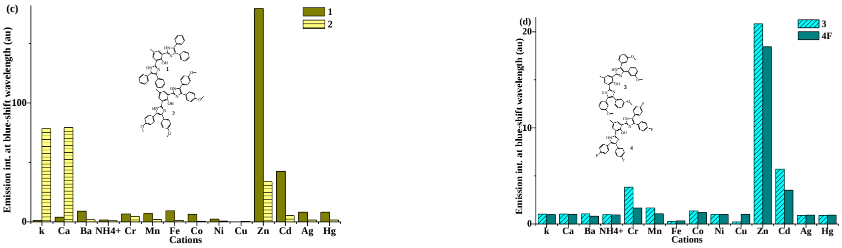


Figure 2. Bar charts showing *F/F*$_o$ values derived from response emission intensities in the presence of various cations. (a) **1** and **2** studying selectivity for Cr^{3+} and Cd^{2+} at ~485 nm; (b) **3** and **4** studying selectivity for Cr^{3+} and Cd^{2+}at ~485 nm; (c) **1** and **2** for studying Zn^{2+} selectivity at ~440 nm and (d) **3** and **4** for studying Zn^{2+} selectivity at ~440 nm.

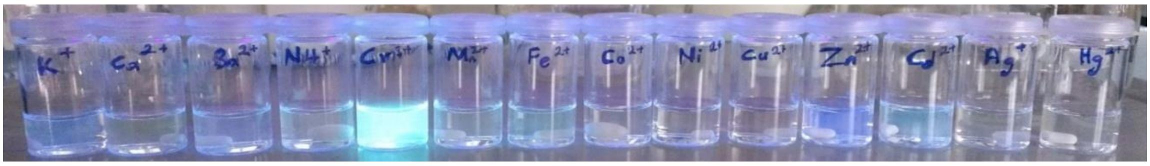


Figure 3. Fluorescence of **4F** in the presence of various cations showing visible sensor strength for Cr^{3+} and the weakness of interference from other cations (note that some brightness seen in vial near the Cr^{3+}vial come from the Cr^{3+} vial).

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Solvent extraction: Structure of the liquid/liquid interface containing a diamide ligand

Ernesto SCOPPOLA, [a)]Thanh PHAM, [a)]Luc GIRARD, [a)]
Jean-Francois DUFRECHE, [a)]Giovanna FRAGNETO, [b)]Olivier DIAT [a)]

[a)] *Institut de Chimie Séparative de Marcoule, UMR 5257 CEA/CNRS/UM/ ENSCM,*
30207 BAGNOLS-SUR-CEZE, France
[b)] *Institut Laue Langevin, 38000 GRENOBLE, France*
olivier.diat@cea.fr

Among the many solvent extraction technologies, those used for metal recovering are quite challenging due to the poor solubility of inorganic ions in oils. Metal extraction thus requires the use of lipophilic extractant molecules to complex the cations and solubilize the complex in the oil phase. In practice, there is a trade-off between selectivity, kinetics and efficiency, in keeping with cost constraints. Despite all the attention solvent extraction has received, however, the molecular structure of the Liquid/liquid (LL) interface remains quite elusive and, as a result, the mechanisms of complexes (ion + extractant molecules + counterions) formation and transfer, that influence the kinetics of extraction, are not well understood. Ion-extraction can be referred to as a diffusion-limited or a reaction-limited process depending on how high is the energy barrier at the LL interface. To tackle this highly challenging problem, we will buckle down by seeking for coherent structural information of the interface at the nanometer scale, at equilibrium in a first step. X-ray AND neutron reflectivities (see figure) were used to show for the first time the evolution of the interfacial structure and to determine the ion potentials at the LL interface [1,2].

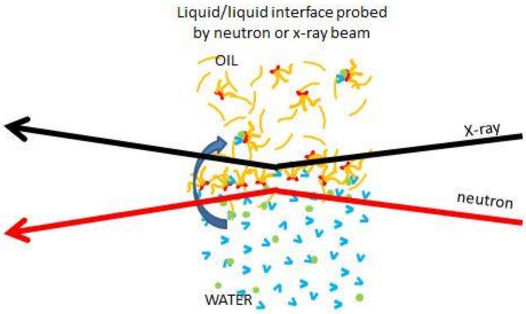

Figure 1. LL interface probed using x-ray or neutron beam.

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In vitro studies of dermally absorbed Cu(II) tripeptide complexes as potential anti-inflammatory drugs

Graham JACKSON, Ahmed HAMMOUDA, Fatin ELMAGBARI

Department of Chemistry, University of Cape Town, PBag Rondebosch,
7701 CAPE TOWN, South Africa
graham.jackson@uct.ac.za

Rheumatoid Arthritis (RA) is a chronic inflammatory disease that leads to the destruction of joints. During the inflammatory stage of the disease, serum copper levels are significantly elevated and evidence in the literature suggests that there is a deficiency in the concentration of serum albumin copper associated with RA patients [1]. Previously, we have shown that injected Cu(II) complexes are effective in reducing the inflammation associated with RA [2]. Recently Alcusal [3], a salicylate complex of copper, became available for over the counter, human use to alleviate arthritic pain, however, dermal absorption is the preferred route for drug administration.

In this paper we have used glass electrode potentiometry to investigate the potential of different peptides and peptide mimetic to improve dermal absorption. NMR, ESR and UV/Vis spectroscopies have been used to investigate the solution structure of the different species. Partition coefficients and membrane permeability studies have been used to assess the bioavailability of the different complexes. These results, together with some bio-distribution studies will be presented.

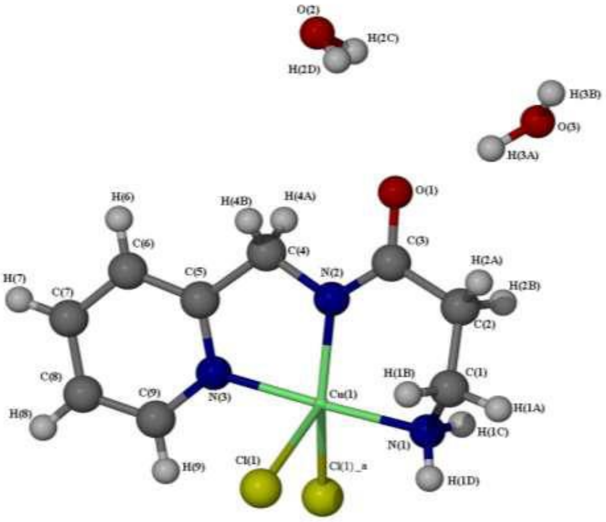

Figure 1. Crystal structure of Cu(II)-[H(56)NH_2Cl]H_{-1}.

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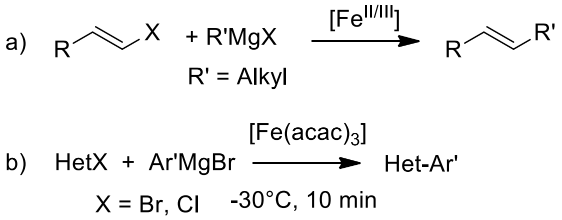
Structural analysis and quantitation of low-valent iron species in Fe-catalyzed Kumada cross-coupling: Insights from Mössbauer and EPR spectroscopies

Martin CLEMANCEY, a) Thibault CANTAT, b) Geneviève BLONDIN, a)
Jean-Marc LATOUR, a) Pierre DORLET, c) Guillaume LEFEVRE b)

a) University of Grenoble Alpes, LCBM/PMB - CEA, BIG/CBM/PMB - CNRS, LCBM UMR 5249, PMB, 38000 GRENOBLE, France
b) NIMBE, CEA, CNRS, Université Paris-Saclay, GIF-SUR-YVETTE, France
c) Institute for Integrative Biology of the Cell (I2BC), CEA, CNRS, Univ. Paris-Sud, Université Paris-Saclay, GIF-SUR-YVETTE, France
guillaume.lefevre@cea.fr

Iron chemistry is an inexpensive and non-toxic alternative to the noble-metal-based systems used in organometallic catalysis. The field of iron-catalyzed C—C bond formation, which was discovered by Kochi in the 1970s, is still in its infancy, and witnessed recent improvements thanks to the work of Fürstner, Nakamura and Bedford during the two last decades [1]. One of the main advantages of Fe-mediated Kumada cross-coupling is that no additional ligand is required, and simple salts such as $FeCl_2$, $FeCl_3$ or $Fe(acac)_3$ exhibit excellent catalytic performances (Scheme 1).

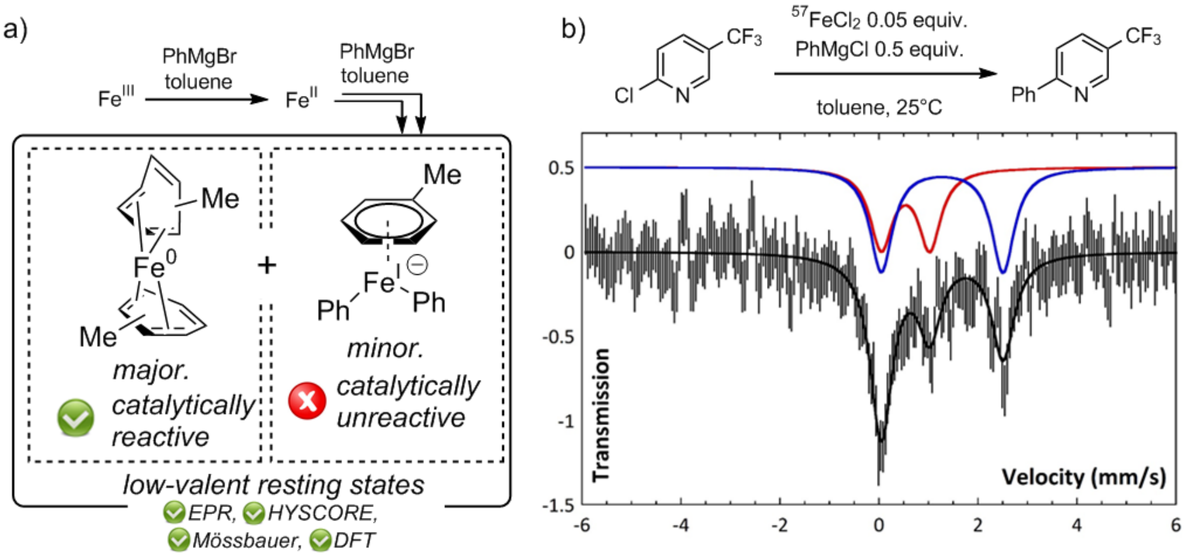


Scheme 1. Representative examples of Fe-catalyzed C–C cross-couplings.

However, the mechanistic features of such transformations are still unclear, since numerous oxidation states can be reached by iron upon reduction by Grignard reagents. The absence of stabilizing co-ligand moreover leads to the formation of short-lived active species, thus making *in-situ* mechanistic investigations challenging. An illustrating example of these difficulties is the very recent structural elucidation of the paramagnetic cluster $[Fe_8Me_{12}]^-$ by Neidig. This allowed the identification of a species whose EPR spectrum had first been reported by Kochi in the context of the reduction of $FeCl_3$ by MeMgBr almost 40 years earlier [2,3].

By means of Mössbauer, cw-EPR and pulsed-EPR spectroscopies, we demonstrated that the reduction of FeX_n salts (X = $acac^-$, halide, n = 2 or 3) by aryl Grignard reagents in toluene led to the formation of two low-valent arene-stabilized resting states (Scheme 2a). A major bis-arene-ligated diamagnetic Fe^0 species $(\eta^4\text{-}C_6H_5Me)_2Fe^0$ (accounting for ca. 85% of the overall iron quantity), and a homoleptic organoferrate low-spin Fe^I minor complex $[(\eta^6\text{-}$

$C_6H_5Me)Fe^I(Ph)_2]^-$ (S = 1/2, ca. 15% of the overall iron quantity) could therefore be characterized.



Scheme 2. a) low-valent resting states obtained by reduction of FeX_n (X = $acac^-$, halide, n = 2 or 3) by PhMgBr in toluene; b) *In-situ* “Mössbauer snapshot” of the iron distribution during a aryl-heteroaryl Kumada cross-coupling process (recording conditions: frozen solution; 80 K – blue lines: $FeCl_2$, red lines: $(\eta^4\text{-}C_6H_5Me)_2Fe^0$).

The reactivity of these low-valent Fe^I and Fe^0 species in aryl-heteroaryl Kumada cross-coupling conditions was also investigated. Mössbauer analysis showed that the zerovalent Fe^0 species can be used efficiently as a catalyst in this reaction. However, the Fe^I oxidation state does not exhibit any reactivity, as attested by EPR spectroscopy. In-situ Mössbauer analysis of the reaction bulk reveals that both Fe^0 and Fe^{II} oxidation states coexist during the cross-coupling process (Scheme 2b), suggesting that a Fe^0/Fe^{II} redox cycle can be operative in such systems [4].

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Modelling the dependence on medium, ionic strength and temperature of N-Acetyl-L-cysteine acid-base properties, and its interactions with Na^+, Mg^{2+}, Ca^{2+}, and Zn^{2+}

Clemente BRETTI, [a] **Concetta DE STEFANO,** [a] **Gabriele LANDO,** [a]
Demetrio MILEA, [a] **Alberto PETTIGNANO,** [b] **Silvio SAMMARTANO** [a]

[a] *Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali,*
Università degli Studi di Messina, V.le F. Stagno d'Alcontres, 31, 98166 MESSINA, Italy
[b] *Dipartimento di Fisica e Chimica, Università di Palermo, V.le delle Scienze,*
90128 PALERMO, Italy
dmilea@unime.it

N-acetyl-L-cysteine (NAC) is the acetylated precursor of L-cysteine, and it is strictly related to glutathione activity. NAC is used in medicine since more than 30 years, primarily as a mucolytic, though its properties are exploited in the treatment of many diseases, such as acute poisoning by acetaminophen (restoring protective levels of glutathione), HIV, contrast-induced nephropathy, type-2 DM (diabetes mellitus), and it also looks promising in the treatment of several psychiatric disorders [1]. This resulted in a huge number of scientific contributions published during the years on NAC (searching in some scientific databases, more than 10000 papers appear).

As expected, most of them are focused on the biological and therapeutic activity of NAC, while relatively few data are reported on the solution chemistry of this molecule, despite the thorough knowledge of its acid-base and coordination behaviour are of fundamental importance for the understanding of its properties in aqueous solution, as biological fluids are. Moreover, the relatively few thermodynamic data available (necessary to assess the speciation of this ligand in the system under study) are reported in single, specific conditions, while it is well known that the most of biological fluids (and natural waters) are, from a chemico-physical perspective, multielectrolyte aqueous solutions of very variable composition, ionic strength, and temperature [2].

Therefore, in this contribution we report the results of an investigation on the modelling of the acid-base properties of NAC in different ionic media (sodium and tetramethylammonium chlorides and tetraethylammonium iodide) at different ionic strengths ($0 < I$ / mol dm$^{-3} \leq 3.0$) and temperatures ($283.15 \leq T$ / K ≤ 318.15). Due to their importance from a biological perspective, we also report the results on the binding ability of NAC towards Na^+, Mg^{2+}, Ca^{2+} and Zn^{2+} in $NaCl_{aq}$ at $T = 298.15$ K and different ionic strengths ($0 < I$ / mol dm$^{-3} \leq 2.0$).

Surprisingly, despite the importance of these cations and their involvement in many biological mechanisms strictly connected with NAC activity, to our knowledge almost no data (only some for Zn^{2+}) are present in literature on these interactions. The dependence on medium, ionic strength and temperature of the protonation and complex formation constants obtained has been modelled by classical approaches, such as the Extended Debye-Hückel (EDH), Specific ion Interaction Theory (SIT), Pitzer, and by the van't Hoff equation.

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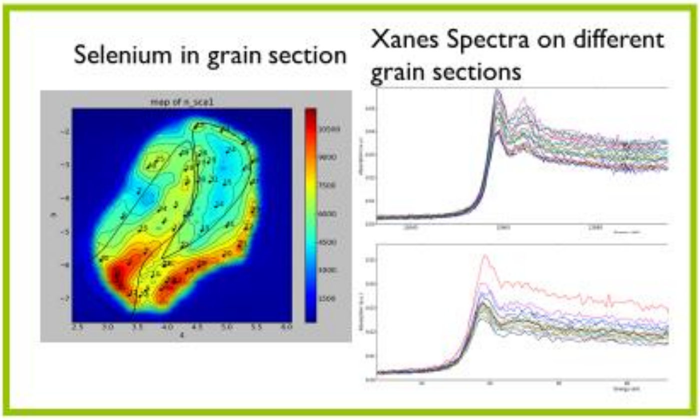
Mapping chemical species of selenium in wheat plants under various nutrient conditions

M. Angels SUBIRANA, [a] **Mercè LLUGANY,** [b] **Gordon E. BROWN,** [c]
Samuel M. WEBB, [d] **Laura SIMONELLI,** [e] **Carlo MARINI,** [e] **Manuel VALIENTE** [a]

[a] *Univ Autònoma de Barcelona, Dept Química. Centre GTS, BELLATERRA, BARCELONA, Spain*
[b] *Univ Autònoma de Barcelona, Dept BABVE, Unit Fisiologia Vegetal, BELLATERRA BARCELONA, Spain*
[c] *Stanford University, Department of Geological Sciences, School of Earth, Energy & Environmental Sciences, STANFORD, USA*
[d] *Stanford Synchrotron Radiation Lightsource, STANFORD, USA*
[e] *Synchrotron ALBA, CLAESS beamline, Cerdanyola del V, BARCELONA, Spain*
Manuel.Valiente@uab.cat



X-Ray Absorption Spectroscopy on mature wheat plants

Wheat (Triticum aestivum) is a major source of dietary intake of selenium in humans that is mandatory because of its presence in vital enzymes. Se antioxidant role has resulted in the popularity of agronomic biofortification practices in Se deficient areas. Control of Se uptake, metabolism, translocation and accumulation in plants is important to decrease healthy risk of toxicity and deficiency and to help selecting adequate methods for biofortification. In this concern, it is important to indicate the key role of selenium chemical forms, in particular selenoaminoacids bearing proteins.

It is known the role of selenate and selenite as the main inorganic Se forms available in soil behave differently, so selanate is taken up faster and interferes with selenite uptake and transport, having a dual effect on wheat plants [1].

Special interest is paid to the distribution of Se species along the plant and in particular in the wheat grain, closely related to human consumption. In this concern, the present study deals with the characterization of selenium species (mostly selenoanimoacids) produced under different conditions of the inorganic selenium in the nutrient solution and how these species are distributed along the plant and in the grain. The work includes the hydroponic cultivation of wheat plants under different Se(III)/Se(V) conditions of the nutrient solution. Selected samples of the plants have been analysed to ascertain selenium speciation by direct observation using Synchrotron light source techniques. Conventional HPLC-MS methods have been employed to confirm the obtained results. Remarkable differences on the obtained chemical species have been observed along the plant for the different selenite to selenate relationships in the nutrient hydroponic solution. In particular, a mapping of the grain will be presented where the non-homogeneous distribution of the selenium species is clearly depicted.

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Complexation of two divalent cations with a multisite flavonoid ligand

Aurélien MONCOMBLE, **Diksha Jani THAVILIGADU**, **Jean-Paul CORNARD**

Univ. Lille, CNRS, UMR 8516 - LASIR - Laboratoire de Spectrochimie Infrarouge et Raman,
59655 VILLENEUVE D'ASCQ, France
aurelien.moncomble@univ-lille1.fr

Flavonoids are compounds that are involved in the secondary metabolism of several higher vegetables. Then their presence in the environment is very common and their interaction with others species such as cations is likely.

In previous studies, we have developed a methodology that deeply associates the electronic spectra measurements and quantum chemistry computations. Using it, we have studied several equilibria in solutions involving flavonoids and cations, for instance between quercetin (Figure 1a) and Pb^{II} [1] or a more complex one between quercetin and Mg^{II} [2].

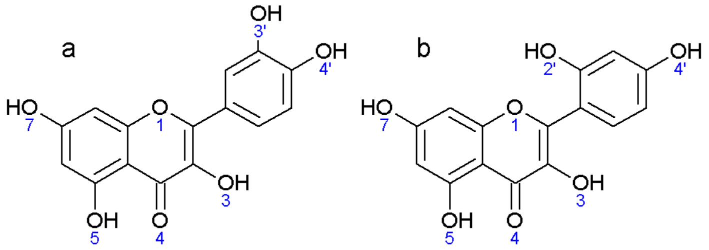

Figure 1. Structure and oxygen atom numbering of (a) quercetin and (b) morin.

Quercetin has three conceivable binding sites: α-hydroxyketo (O3,O4), β-hydroxyketo (O4,O5) and catechol (O3',O4'). This last binding site is not present in morin (Figure 1b). Instead, the existence of O2' leads to two other potential sites: a chelate involving O2' and O1 and a chelate involving O2' and O3. Therefore, a small change in the structure could affect the complexation properties of such ligands.

In this study, we focused on the reactivity of morin with zinc (II). This system had been previously studied but no consensus was obtained on the binding site. Among a dozen of publications, the (O1,O2') site [3], the (O3,O2') site [4] and the (O3,O4) one [5] were proposed, and even the stoichiometry is a matter of debate. Then we applied our methodology to this system to determine more precisely the stoichiometry of the actual complex and its binding mode.

More precisely, titrations of the ligand by the cation were carried out and electronic spectra were carried after each addition. Chemometric treatments of the acquired spectra resulted in the computation of the spectra for each pure species involved in the equilibrium. In parallel, quantum chemistry computations were processed. Density functional theory (DFT) based optimizations of conceivable structures, followed by time dependent computations of the electronic transitions, lead to UV spectra that were compared with the experimental.

An important aspect of these computations was the precise description of the solvent. Indeed, the solvent is both a ligand and a solvent that needs a hybrid model associating microsolvation around the cation with an implicit model at larger distance [6] (Figure 2).

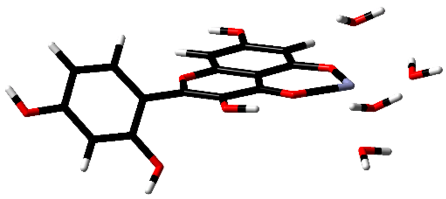

Figure 2. Solvation sphere around zinc cation bound to morin.

This methodology associating experiments and computations shed light on the morin-zinc (II) system and determined the nature of the actual complex formed in theses conditions. With this success, the study of the morin-manganese (II) system was initiated and preliminary results will be presented.

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Thermodynamic and kinetic study of lead(II) complexes with tetraazamacrocyclic ligands

Viktorie REICHOVÁ, [a] **Přemysl LUBAL,** [a,b] **Petr HERMANN** [c]

[a] *Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2,*
61137 BRNO, Czech Republic
[b] *Central European Institute of Technology (CEITEC), Masaryk University, Kamenice 5,*
62500 BRNO, Czech Republic
[c] *Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030,*
12840 PRAGUE, Czech Republic
lubal@chemi.muni.cz

Lead radioisotopes ($^{203/212}$Pb) have potential to be utilized in nuclear medicine and, therefore, their complexes should exhibit a high thermodynamic stability and a kinetic inertness under physiological conditions [1,2]. Thus, it is necessary to know the thermodynamic and kinetic properties (dissociation/formation rate constants) of the Pb(II) complexes to design macrocyclic bifunctional ligands for possible *in vivo* applications of their complexes. Here, thermodynamic and kinetic properties of Pb(II) complexes with cyclen-based macrocyclic ligands having two (*trans*-H_2do2a), three (H_3do3a) or four (H_4dota) acetic pendant arms, and H_4dota monophosphonic (H_5do3ap) or -phosphinic (H_5do3ap^{PrA}, H_4do3ap^{ABn}) acid derivatives were studied. Thermodynamic stability of the Pb(II) complexes follow the order H_4dota ~ H_4do3ap^{ABn} ~ H_5do3ap^{PrA} < H_5do3ap. The formation kinetics study showed that lead(II) complexation is significantly influenced by a number but not by the type of pendant arms attached to the DO3A skeleton. The kinetic inertness of Pb(II) complexes in an acidic medium is reasonably high. Therefore, the introduction of phosphorus acid pendant arms does not have a significant impact on the kinetic properties of the Pb(II) complexes. The results will be compared with other values of thermodynamic and kinetic constants obtained for Pb(II) complexes of other tetraazamacrocyclic ligands [2-4]. In addition, the thermodynamic and kinetic properties of Cu(II) and Pb(II) complexes of the same macrocyclic ligands [5,6] will be compared.

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Heavy metal complexes in recycling and waste disposal: Application of the PSI Chemical Thermodynamic Database

Wolfgang HUMMEL, [a] **Gisela WEIBEL** [b]

[a] *Laboratory for Waste Management, Paul Scherrer Institut, 5232 VILLIGEN PSI, Switzerland*
[b] *Institut of Geological Sciences, University of Bern, Baltzerstr. 1+3, 3012 BERN, Switzerland*
wolfgang.hummel@psi.ch

The PSI Chemical Thermodynamic Database [1] is designed and periodically updated for application in general waste management problems. Its recent update and application will be exemplified by two rather different tasks involving the same heavy metal: lead.

In Switzerland around 75’000 tonnes of fly ash are generated annually from the 30 municipal waste incineration plants. According to the recently revised Swiss waste legislation recovery of metals from fly ash is required from 2021 onwards. Within the scope of a PhD project [2] an effective method of very high recovery of 90% lead from fly ash was investigated: Leaching of lead in highly concentrated NaCl solutions, which is based on the strong affinity of Pb^{2+} to chloride by formation of aqueous $PbCl_x$ complexes [3].

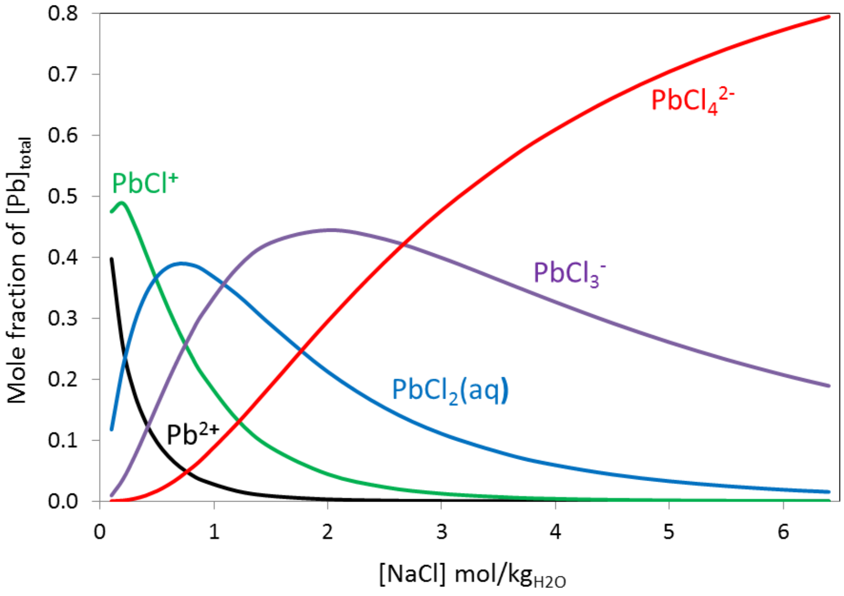

Figure 1. Speciation diagram for the $Pb^{2+} – Na^+ – Cl^-$ system at 25°C. The activity coefficients of aqueous species in concentrated NaCl solutions were calculated using the Specific ion Interaction Theory (SIT) [4]. The uncertain stability constant of $PbCl_4^{2-}$ was optimised using experimental data at 6.4 mol/kg_{H2O} NaCl solution [3].

The dissolved Pb^{2+} is forming Pb-chloride complexes with increased chloride content ($PbCl_3^-$, $PbCl_4^{2-}$) with increasing NaCl concentration (Figure 1), which significantly increases the solubility of the metal. The existence of the 1:4 lead chloride complex in filtrates from fly ash leaching has been proven using UV-VIS spectroscopy.

Spallation induced neutron sources, like the facility SINQ at PSI, not only produce high neutron fluxes for research purposes but also generate radioactive isotopes in their lead or lead/bismuth targets like the long-lived isotopes Pb-202 (53’000 years half-life) and Pb-205 (15’300’000 years half-life). No recovery or re-use of this radioactive contaminated material is envisioned; it has to be disposed of in a radioactive waste repository.

In contrast to the above described lead recovery method by high solubility, radioactive lead disposal requires (geo)chemical conditions minimising dissolution and migration of contaminants. This is favoured by low solubility of lead solids and strong sorption of dissolved lead to mineral surfaces. In both cases aqueous lead complexes play a crucial role.

In order to reliably estimate the very low solubility of galena (PbS), for example, it is not sufficient to determine its solubility product, $PbS(cr) + H^+ \Leftrightarrow Pb^{2+} + HS^-$. Knowledge of the existence and stability of possibly forming aqueous complexes like $PbHS^+$, PbS(aq), $Pb(HS)_2(aq)$ are a prerequisite to calculate reliable Pb solubility values.

Likewise, the dominating aqueous Pb species expected in the pore water of a radioactive waste repository need to be known in order to estimate sorption effects: Pb^{2+} and positively charged complexes may strongly sorb to negatively charged clay mineral surfaces, while negatively charged Pb complexes may not sorb and thus migrate without retardation.

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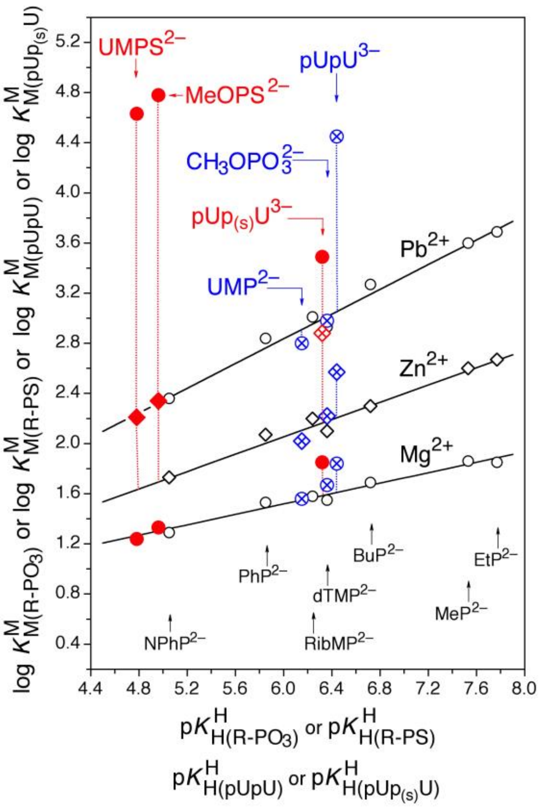
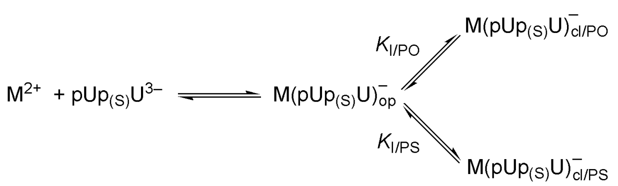
The ambivalent properties of lead(II) and related metal ions in complexes of nucleoside phosphorothioates

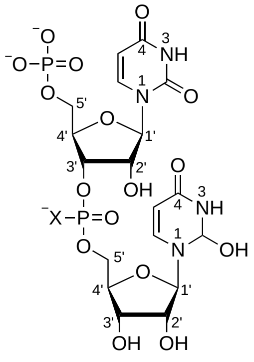
Astrid SIGEL, Bert P. OPERSCHALL, Helmut SIGEL

Department of Chemistry, Inorganic Chemistry, University of Basel,
Spitalstrasse 51, 4056 BASEL, Switzerland
Helmut.Sigel@unibas.ch

In the phosphorothioate group (PS) a phosphate O is replaced by a S atom giving the $–OP(O)_2^-(S)^-$ residue. This popular alteration in mononucleotides leads to nucleoside phosphorothioates, which are widely applied [1], e.g., as therapeutics [2], as small interfering RNAs (siRNA) [3], and as tools to study the chemistry of ribozymes [4, 5]; yet, quantitative information on the metal ion-binding strength to the $–OP(O)_2^-(S)^-$ residue is relatively scarce [1]. In the Figure the stabilities of several M(PS) complexes, where $M^{2+} = Pb^{2+}$, Zn^{2+} Mg^{2+} and PS^{2-} = uridine 5'-*O*-thiomonophosphate ($UMPS^{2-}$) or methyl thiophosphate ($MeOPS^{2-}$), are plotted, and these data can be compared with those of the parent ligands, that is, UMP^{2-} and $CH_3OPO_3^{2-}$. The data pairs, ($\log K$ *vs* pK_a) for the parent ligands fit on the reference lines, demonstrating that the uridine residue does not participate in metal ion binding and that the stability of these complexes is simply determined by the basicity of the phosphate group. This is in contrast to the Zn(PS) and Pb(PS) complexes which show a large stability enhancement, despite the reduced basicity of $UMPS^{2-}$ and $MeOPS^{2-}$, proving that sulfur coordination with the $–OP(O)_2^-(S)^-$ residue is very important, whereas this is not the case with the Mg(PS) complexes, the data pairs of which fit on the reference line [6]. The fact that the data points for the two Zn(PS) complexes (◆) fall on the reference line for the $Pb(R\text{-}PO_3)$ species is by accident and of no relevance. Yet, the indicated results allow to calculate the ratio *R* of S *versus* O coordination in the $–OP(O)_2^-(S)^-$ residue, i.e., $R = [(PS\cdot M)]/[(PO\cdot M)]$. These *R* values are about 268 for Pb^{2+}, 3.2 for Zn^{2+}, and zero for Mg^{2+}, and from these data it follows for Pb(PS) that about 99.6% of Pb^{2+} are S-coordinated, for Zn(PS) the value is 76%, and for Mg(PS) it is about zero [1, 6]. -- What is the effect of a terminal sulfur atom in the phosphodiester linkage on metal ion coordination? Does the following equilibrium, where $pUp_{(s)}U^{3-}$ equals *P*-thiouridylyl-(5'→3')-5'-uridylate, exist?







$\mathrm{pUpU^{3-}}$: X = O
$\mathrm{pUp_{(s)}U^{3-}}$: X = S

In the $\mathrm{M(pUp_{(s)}U)}^{-}_{\mathrm{cl/PO}}$ isomer $\mathrm{M^{2+}}$ is coordinated to the terminal O atom of the phosphodiester bridge, whereas in the $\mathrm{M(pUp_{(s)}U)}^{-}_{\mathrm{cl/PS}}$ isomer S binding occurs. For the $\mathrm{M(pUp_{(s)}U)^{-}}$ and $\mathrm{M(pUpU)^{-}}$ complexes of $\mathrm{Pb^{2+}}$, $\mathrm{Zn^{2+}}$, and $\mathrm{Mg^{2+}}$ the data [5] are also plotted in the Figure shown above. It needs to be noted that the small stability enhancement, log Δ, observed for both $\mathrm{Mg^{2+}}$ complexes corresponds to the charge effect which the negative charge of the phosphodiester bridge exercizes on $\mathrm{M^{2+}}$ coordinated at the terminal phosphate group; on average log $\Delta = 0.24 \pm 0.04$ [1,5]. Hence, $\mathrm{Mg(pUpU)^{-}}$ and $\mathrm{Mg(pUp_{(s)}U)^{-}}$ do not form 10-membered macrochelates. For $\mathrm{Zn^{2+}}$ a stability enhancement for both complexes is observed, which is beyond the charge effect, but which is larger for $\mathrm{Zn(pUp_{(s)}U)^{-}}$; indeed, a detailed evaluation shows that for this complex about 12% exist as the $\mathrm{Zn(pUp_{(s)}U)}^{-}_{\mathrm{cl/PO}}$ isomer and about 55% occur as the $\mathrm{Zn(pUp_{(s)}U)}^{-}_{\mathrm{cl/PS}}$ isomer, which also means that the open isomer with a phosphate coordination reaches a formation degree of 33%. This is a nice example which demonstrates the adaptability of $\mathrm{Zn^{2+}}$ to different coordination environments. This contrasts with $\mathrm{Cd(pUp_{(s)}U)^{-}}$ (data not shown), which forms only the $\mathrm{Cd(pUp_{(s)}U)}^{-}_{\mathrm{cl/PS}}$ isomer with 64%, the remaining 36% being present in the open form. However, the most surprising result is that the stability enhancement for the $\mathrm{Pb(pUp_{(s)}U)^{-}}$ complex is not very pronounced (see the Figure); furthermore, with Pb(II) only the $\mathrm{Pb(pUp_{(s)}U)}^{-}_{\mathrm{cl/PO}}$ isomer forms having 45 ± 18% [5] and thus about 55% are present as the open isomer; no indication for a sulfur interaction is found. This result is very surprising in view of the observations made with Pb(UMPS) and Pb(MeOPS) (see also the Figure). Evidently, once Pb(II) coordinates to a strong primary O-donor site, its affinity for S-donor sites is strongly reduced. In other words, Pb(II) is a chameleon-like metal ion because its binding properties depend on the first strongly coordinating site.

Acknowlegements: this work was supported by the Department of Chemistry of the University of Basel, Switzerland.

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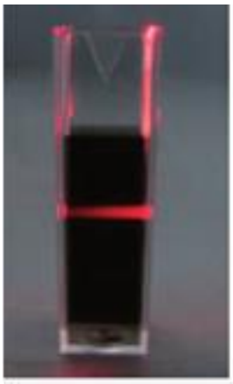
Posters

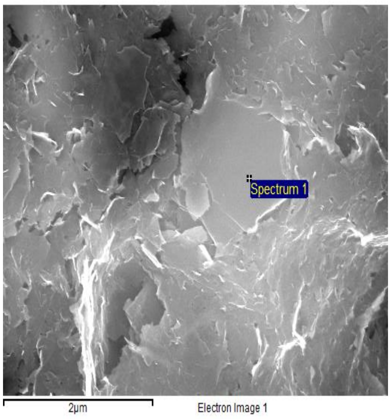
Aqueous-phase exfoliation of graphite in the presence of a histidine/pyrimidine conjugate

Paloma ARRANZ-MASCARÓS, [a)] **Maria Dolores GUTIÉRREZ-VALERO**, [a)]
Manuel MELGUIZO-GUIJARRO, [a)] **Maria DOMINGO-GARCÍA**, [b)]
Irene MENA-CRUZ, [a)] **Maria Luz GODINO-SALIDO** [a)]

[a)] *Department of Inorganic and Organic Chemistry, Faculty of Experimental Sciences, University of Jaén, 23071 JAEN, Spain*
[b)] *Department of Inorganic Chemistry, Faculty of Sciences, University of Granada, 18071 GRANADA, Spain*
parranz@ujaen.es

Single layer and few layer graphenes exhibit a two dimensional carbon lattice structure with exceptional properties including high surface area as well as strong electronic, mechanical, thermal and chemical properties [1]. Several chemical and physical routes have been developed to produce graphene, for example, epitaxial grown by chemical vapor deposition of hydrocarbons on metal substrates, mechanical exfoliation, and heat treatment of silicon carbide wafers [2] between others. As liquid-phase exfoliation of graphene is recognized to be one of the most satisfactory methods, in the present work, we made an 18 hours treatment of crystalline graphite fine power with an aqueous solution of an auxiliary agent, a histidine-pyrimidine derivative, under sonication, resulting in graphene of few functionalized layers. The adsorbed derivative stabilized the graphene dispersion in water. The dispersed particles were obtained by precipitation with a mixed solvent system. The lustrous grey precipitate was isolated by precipitation. The obtained solid product was characterized by SEM, Raman, XRD and FTIR techniques.





Acknowledgements: the support of the MINECO (Projects MAT2014-601404-C2-1-R and MAT2014-60104-C2-2-R), the Autonomous Regional Government (Junta de Andalucía, Groups PAIDI FQM273 and RNM342) and the University of Jaén (EI-FQM6_2017) is acknowledged.

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Study of the protonation of tannic acid and of its influence on iron speciation

Silvia BERTO, [a] **Valeria SCHETTINI**, [a] **Marco MINELLA**, [a] **Marco GINEPRO**, [a] **Pier Giuseppe DANIELE** [a]

[a] *Dipartimento di Chimica, Università di Torino, Via P. Giuria, 7, 10125 TORINO, Italy*
silvia.berto@unito.it

Tannic acid (TA) is a macromolecule containing a glucose, as central core, esterified by hydroxybenzoic acids. It belongs to hydrolysable tannins class, natural polymers derived from vegetable kingdom that show antioxidant and antibacterial properties [1], that can be dispersed in surface waters and have similarities with humic substances [2,3]. They can interact with both organic molecules [3] and metal cations. The presence of catechol groups leads to the formation of chelates with metals, but the complex formation tends to favour precipitation process [4] and redox reactivity [5]. Considering the different and interesting aspects of these polymeric molecules, it could be interesting to identify chemical models that explain properly their protogenic capacity, and to characterize the redox behaviour and the coordination capability towards metal cations.

In this work, pH-metric and spectrophotometric titrations were performed in aqueous solutions of TA in order to evaluate the protonation of the macromolecule. The data obtained were elaborated with the BSTAC [6] and HypSpec® programs. The data reveal the occurrence of gallic acid in solution with TA (outcomes confirmed by HPLC analysis) and the elaboration of titrations indicates the presence of two protogenic sites quite acid with respect to those of other polyphenols. The redox behaviour of TA with iron cations, as a function of pH, was then evaluated in order to elucidate the role of this molecule with respect to the iron speciation. Previous literature studies report that the complexation of polyphenols stabilises the Fe(III) cation, therefore, in presence of oxygen, the Fe(II) can be more easily oxidized if complexed by catechol functions [5]. On the other hand, these natural molecules have an antioxidant behaviour that can be evaluated by their capability to reduce Fe(III) to Fe(II) (Ferric Reducing Antioxidant Power – FRAP) [7]. The redox behaviour is strictly linked to the formation of iron complexes [5] and depends on the pH of the water solution. Experiments were conducted with the aim to clarify the dual redox feature of TA and to relate it with the stability of the iron complexes.

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Bioconjugated pyrazine-based cyclometalated (C^N^{pz}^C)Au(III) complexes: Synthesis and anticancer potential

Benoît BERTRAND, [a] **Morwen WILLIAMS**, [a] **Adam GREEN**, [a]
Julio FERNANDEZ-CESTAU, [a] **Mark SEARCEY**, [a,b] **Maria O'CONNELL**, [b]
Manfred BOCHMANN [a]

[a] *School of Chemistry, University of East Anglia, NORWICH, NR4 7TJ, United Kingdom*
[b] *School of Pharmacy, University of East Anglia, NORWICH, NR4 7TJ, United Kingdom*
b.bertrand@uea.ac.uk

Gold complexes are widely studied as potential new anti-cancer agents [1]. Biscyclometalated Au(III) complexes are particularly known for their stability under physiological conditions and their promising cytotoxic properties [2]. We have demonstrated the potential of a pyrazine-based (C^N^{pz}^C)Au(NHC) complex (A figure 1) as anticancer treatment. However, the compound suffered from a certain lack of selectivity for cancer cells [3]. We thus explored various strategies to conjugate our known pharmacophore to different biovectors to improve the selectivity of the drug. We have investigated the possibility to attach some amino acid derivatives to the (C^N^{pz}^C)Au(III) scaffold via an open chain carbene ligand. We have also explored the synthesis of a (C^N^{pz}^C)Au(NHC) platform bearing a pentafluorophenyl ester moiety for the conjugation with several vectors including biotin and estradiol derivatives. We measured the cytotoxicity of the complexes against a panel of different human cancer cell lines.

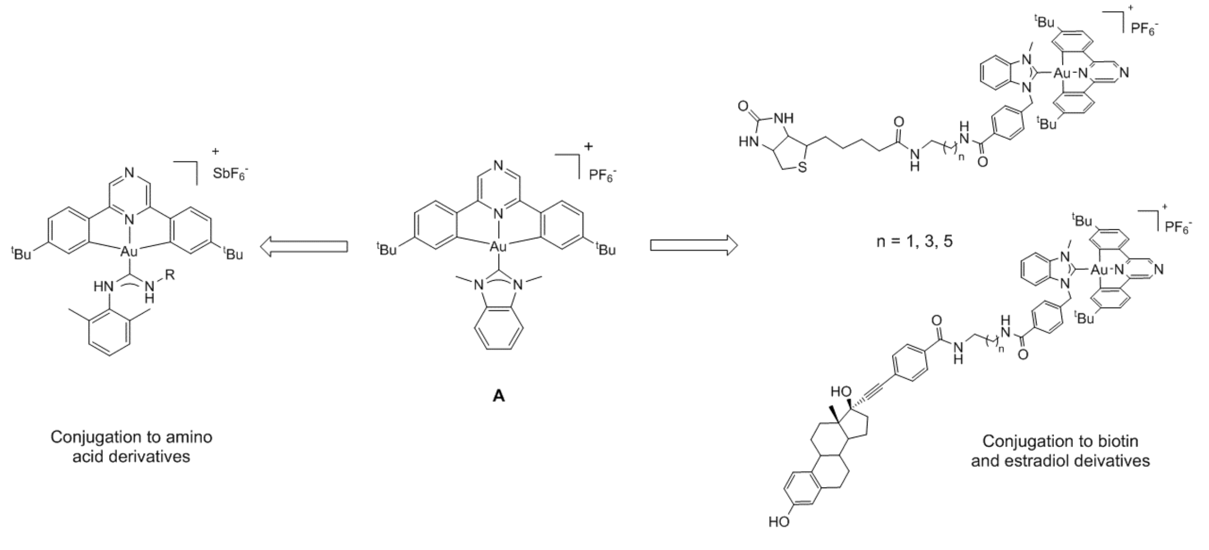

Figure 1. Scheme of the bioconjugated (C^N^{pz}^C)Au(III) carbene complexes.

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A differential Alizarine Red S-base receptor for Fe(III) and Al(III) determination

<u>Raffaela BIESUZ</u>, Chiara GIOBBIO, Giancarla ALBERTI

Dipartimento di Chimica, Università degli Studi di Pavia, via Taramelli 12,
27100 PAVIA,Italy
rbiesuz@unipv.it

A very cheap, disposable, differential sensor for the detection of Fe(III) and Al(III) is presented. The solid support selected for this project is more similar to a fabric, or a soft paper, than to a solid; it is insoluble in water and it lasts, under apparently unchanged conditions, in water solution for days. It is the so called "*Colour Catcher®"*, CC, a product of the detergents market, distributed, in Italy, by *Grey* a partner of the Henkel company, in England by Dylon. "Being able to prevent color run during washing, using its revolutionary anti-transfer technology to being dyes", it must exhibit sequestration properties towards molecules and ions, when released by clothes, even in the presence of surfactants, since it is used together with detergent substances during laundry. Since many dyes are anionic molecules we thought it could be used as good and cheap support for a proper ligand which constituted the detection unit of sensor. For several reasons we selected firstly Alizarine Red S, whose structure is reported in Figure 1, an old and well-known ligand for hard metal ions. The properties of this ligand for signalling metal ions was already applied successfully in the case of a device based on a triacetyl cellulose based film [1]. Here it is anchored on CC, and the obtained device is called Aliz-CC@. At the electronic microscope, the CC shows a fiber structure, as seen in Figure 2.

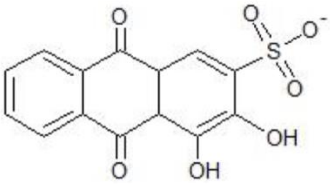

Figure 1. Chemical structure of Alizarine Red S.

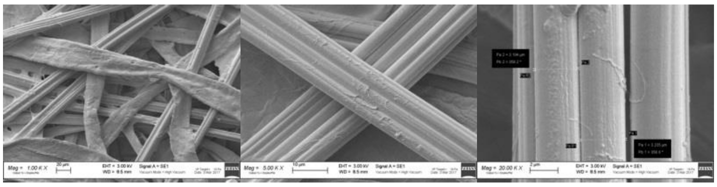

Figure 2. Electronic microscope imagines of *Colour Catcher®* at different magnification order.

The data obtained from IR spectra and EDX analysis of the pristine CC converge in a polymeric C based structure, with presence of COO^- OH^- and Na and Cl. The amount of Cl is in agreement with the sorption capacity towards Alizarine Red S, found to be 0.27(5) mmol/g, confirming the presence an anion exchange moiety.

Firstly, the behaviour of the device towards the anion Alizarine Red S was studied not only for its sorption capacity, but also for the kinetic, definitively quick for a biphasic system, and for competition towards other anions, such as chloride. The stability and the reproducibility of the device were tested and the product was selected as possible differential sensor. As an example in Figure 3 the colour of the Aliz-CC@ without any metal and after contact with Al(III) Fe(III) and Cu(II) solutions is shown.

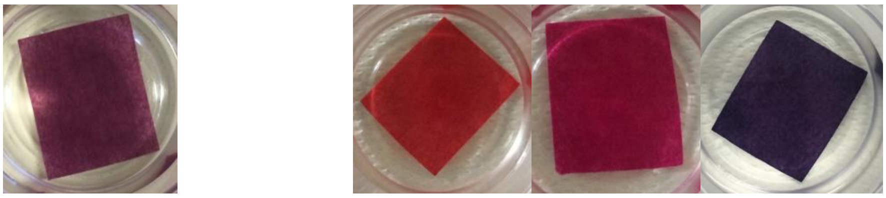

Figure 3. On the left, the aspect of Aliz-CC@ prior contact with metal ion solutions. On the right, the same after contact with Al(III), Cu(II), Fe(III) solutions at pH 5.5, respectively.

The Aliz-CC@ properties towards each of the metal ions was studied, based on the vis spectra of the solid phase, studying, also in this case, sorption isotherms and kinetics profiles. Under very mild stirring conditions, at pH 5.5 for acetate buffer, the sorption is quantitative after one hour.

To detect simultaneously the three cations, PLS (Partial Least Square Regression) has been used [2,3]. A training set of different solutions with known amounts of the three metal ions was analysed to build the calibration model. It was done according to a design of experiments and using the model proposed by Brereton, the multi partial factorial design. A test set of independent experiments was also employed to validate the model. Moreover a certificated sample (Sewage Sludge ERM®-CC136a) was also analysed as external set of data for validation.

To make easier the spectrophotometric analysis, in collaboration with 3D@UniPV Virtual Modelling and Additive Manufacturing for Advanced Materials, a prototype was developed to fix the Aliz-CC@ and to perform equilibration and spectrophotometric determination avoiding device manipulation and further improvement focused on the disposable device are going to be studied.

Finally, Aliz-CC@ is a promising solid support to realise disposable devices and further investigation are in progress to optimize the conditions for its applicability, in this and in other cases.

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Selective sensor design for Pd(II) determination from strongly acidic solutions

Raffaela BIESUZ, Marcello VANZULLI, Giancarla ALBERTI

Dipartimento di Chimica, Università degli Studi di Pavia, via Taramelli 12,
27100 PAVIA,Italy
rbiesuz@unipv.it

The aim of this research is the selective determination of palladium(II) from water samples at pH = 0. The analytical response is the change of the color, after contact with a solution containing Pd(II), of TazoC (2-(tetrazolylazo)-l,8 dihydroxy naphthalene-3,6,-disulphonic acid) impregnated on a commercial Macroporous Strong Anion Exchange Resin, Marathon® (Dow Chemical-USA).

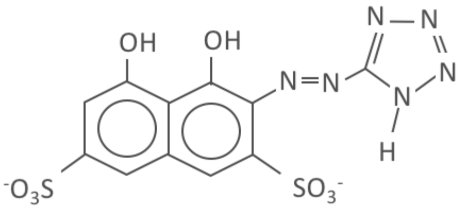

Figure 1. Chemical structure of TazoC.

Figure 2. On the left, Marathon® resin in HNO_3 1M, on the center, Marathon® resin with only 10% of its sites occupied by TazoC, on the right the same after contact with a concentrated solution of Pd(II).

The structure of Tazo C is reported in Figure 1. It belongs to a family of azo-ligands synthetized in the past by our group, proposed as spectrophotometer reagents for the individual determination of several metal ions [1-3]. The sorption of the ligand on the resin is extremely rapid and efficient, being based on a simple ion exchange. It is complete after 10 minutes, under mild stirring on a rotating plate.

For the practical development of the sensor, in the following called TazoC-Mar@, the amount of TazoC sorbed on the resin was always below the 10% of the total anionic sites, whose concentration is equal to 2 mmol/g. This guarantees a weak competition of other anions that may be present in a real sample and avoids colour saturation, i.e. too high absorbance values. The pictures of Figure 2 show the intense colour of TazoC-Mar@ before and after Pd(II) sorption. The change in the absorbance spectra as function of the amount of Pd(II) is the signal registered directly on the solid material, introduced with a Pasteur pipette in a 0.5 cm cuvette (as shown again in Figure 2) and reading the spectra versus a cuvette filled with the TazoC-Mar@, or simple Marathon®.

With the aim of using TazoC-Mar@ as a differential sensor as done elsewhere, at the beginning we thought to work at pH=4.5, hoping to obtain analytical response similar for different analytes. Unfortunately, the response of TazoC-Mar@ towards Pd(II) is definitively too strong, in term of the apparent molar absorptivity coefficient and stability of the complex. We succeeded to perform measurements of Pd(II) at pH 4.5 in solutions with Cu(II) and Ni(II), but the validation step was successful only for Pd(II). We also thought to carry out the external validation using the reference material, “Road Dust, trace elements, BCR 723”. In this sample Pd(II) was present at subtrace levels, several order of magnitude lower than Cu(II), Al(III), Mn(II), Fe(III), which are often 10^6 times more concentrated. All of these cations, at larger or lesser extension at pH = 4.5 are complexed by TazoC, making Pd(II) determination impossible. For these reasons, since the TazoC-Mar@ is stable for days in HNO_3 0.1M and also 1M, at a formal pH = 1 and 0, and the Pd(II) complex with the active sites results anyway formed, we definitively decided to use TazoC-Mar@ in these extreme conditions, as selective sensor for Pd(II). As shown in Figure 3a the signal is very disturbed, both for the measurement on a granular material and for the drastic condition. Nevertheless, since we do not use for calibration the univariate method, i.e. absorbance at λ_{max} vs Pd(II) concentration, but the multivariate method, where the whole absorbance curve from 560 to 800 nm is employed, a very satisfying model is obtained with 3 latent variables and more important, it is able to predict unknown sample concentrations. In Figure 3b the nominal concentrations of external data set are reported versus the concentrations predicted by the model. The empty circles refer to synthetic samples, while the asterisks to the reference sample “Road Dust, trace elements, BCR 723” after enrichment of the sample with Pd(II) performed before microwave assisted dissolution.

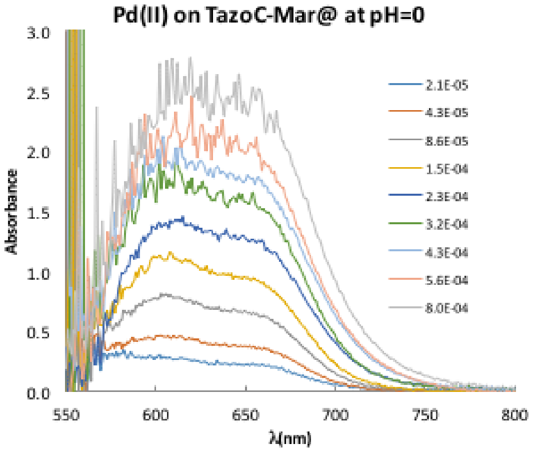

Figure 3. Spectra of TazoC-Mar@ of different Pd(II) solutions.

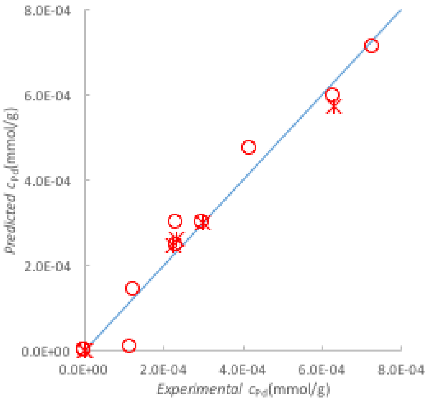

Figure 4. Nominal Pd(II) concentrations vs those predicted by the PLS regression model.

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Solution properties, cellular activity and DNA binding tests of a novel Zn(II)-bis-terpyridine metal complex

Tarita BIVER, [a] **Natalia BUSTO**, [b] **Sonia MONTANARO**, [a,b] **M. Carmen CARRIÓN**, [c,d] **Blanca R. MANZANO**, [c] **Felix A. JALON**, [c] **Begoña GARCIA** [b]

[a] Department of Chemistry and Industrial Chemistry – University of Pisa, Via G. Moruzzi 13, 56124 PISA, Italy
[b] Department of Chemistry – Universidad de Burgos, Plaza Misael Bañuelos s.n., 09001 BURGOS, Spain
[c] Departamento de Química Inorgánica, Orgánica y Bioquímica. Facultad de Ciencias y Tecnologías Químicas-IRICA, Universidad de Castilla-La Mancha, Avda. Camilo José Cela 10, 13071 CIUDAD REAL, Spain
[d] Fundación PCTCLM, Bulevar Río Alberche s/n, 45007 TOLEDO, Spain
tarita.biver@unipi.it

In recent years, the researchers have considered as possible anti-tumour agents metal complexes of bio-essential metal ions as Cu(II), Zn(II) and Fe(III) [1]. Among them, zinc is the second more abundant metal in cells (after iron) and it holds an important role in a plenty of enzymatic reactions that are essential for different biological functions.

The reactivity of a metal complex can, obviously, be tuned also owing to the particular ligand chosen. In the case of bio-systems, the ligand plays a fundamental role as for driving the interaction mechanism towards biomolecules as DNA or proteins. Studies on ter-pyridine and bis-pyridine complexes showed that these species are able to bind DNA with high affinity and also show high anti-tumour activity by promoting cell death [2,3]. Therefore, the combined action of a bio-essential metal and a ligand belonging to the above family could enhance the biological activity and/or activate new modes of action.

On this basis, we have studied the Zn(II)-bis-terpyrinide complex shown in Figure 1 (bis[4′-[4-(3-methylimidazol-1-ium)phenyl]-2,2′:6′,2″-terpyridine]zinc(II) diiodide dinitrate).

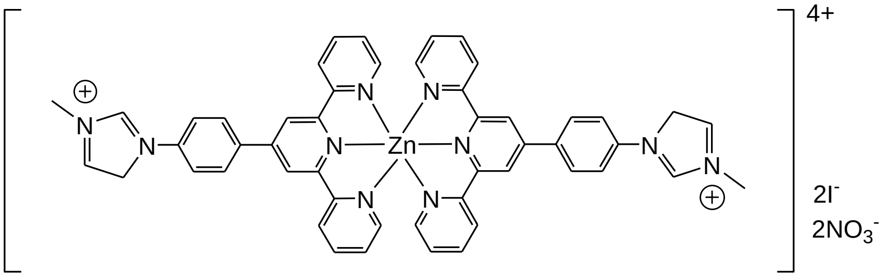

Figure 1. Molecular structure of the Zn(II) complex used in this study.

The MTT assay on the Zn(II) complex showed cytotoxicity towards colon tumour cell lines (SW480) with an $IC_{50} = 24.6 \pm 2.6$ μM. The bis-terpyridine complex is successfully internalized in the cells at 100 μM within 30 minutes and it seems to be localized mainly in the nucleus. Given these encouraging results and the ability to reach the cells' nuclei, possible interaction of the metal complex with double stranded DNA was analysed. This study can also help enlightening if DNA is the possible drug target.

First of all, the solution properties of the complex have been analysed, by means of spectrophotometric and spectrofluorometric measurements. The zinc complex was found to undergo auto-aggregation with $K_{aggr} = 2.9 \times 10^4$ M^{-1} and the monomer was found to be a fluorescent species with significant light emission properties and a lifetime of 6.3 ns.

Then, under conditions of high dilution so to ensure the presence of the dye monomer only, possible DNA interaction was investigated. To this aim, spectrophotometric and spectrofluorometric titrations, viscosimetric studies and thermal denaturation studies have been performed. The binding between the Zn(II) complex and double stranded DNA was indeed found to occur. However, the biphasic binding isotherms suggest a non-simple binding mechanism that needs to consider more than one binding mode.

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First design of titanocene-DOTA radiotrackable complexes

Océane FLORES, [a)] Francisco SILVA, [b)] Fernanda M. MARQUES, [b)]
Franck DENAT, [a)] Maria Paula C. CAMPELLO, [b)] Pierre Le GENDRE, [a)]
Christine GOZE, [a)] Ewen BODIO [a)]

[a)] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[b)] C²TN, Universidade de Lisboa, Estrada Nacional 10, 2695-066 BOBADELA LRS, Portugal
ewen.bodio@u-bourgogne.fr

Among the large variety of potential anticancer organometallic complexes, titanocene dichloride Cp_2TiCl_2 reached Phase 2 clinical trial. However, its poor solubility and stability in water lead to an uncertainty about the biologically active species and severely hampered its development as anticancer agents. Besides, the mechanism of action of such complexes is still unclear since the usual *in vivo* biodistribution studies and determination of metal uptake in organs by ICP-MS cannot be performed due to the natural occurrence of titanium in the human body. Scintigraphy appears then as a promising tool to visualize metal biodistribution and clarify the mechanism of action of titanocene derivatives.

To deal with the previously mentioned issues, Gansäuer and coworkers developed a synthesis of water-soluble and stable cationic titanium complexes (Figure 1) [1]. Seeking to synthesize new radiolabeled titanium based drugs, we decided to use this strategy to introduce a bifunctionnal chelating agent on the titanocene framework. The resulting titanocene-DOTA compound (Figure 2) proved to be relatively stable in water and serum up to 48 h and could handle radiolabeling-like conditions. Complexation of "cold" Lu, In, and Y has been performed successfully, as well as radiolabelling with ^{111}In. Biological assays such as determination of antiproliferative properties in cancer cells and *in vivo* biodistribution are currently under investigation.

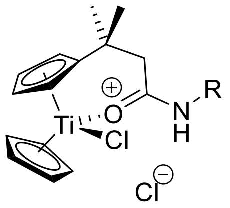

Figure 1. Structure of cationic titanium complexes.

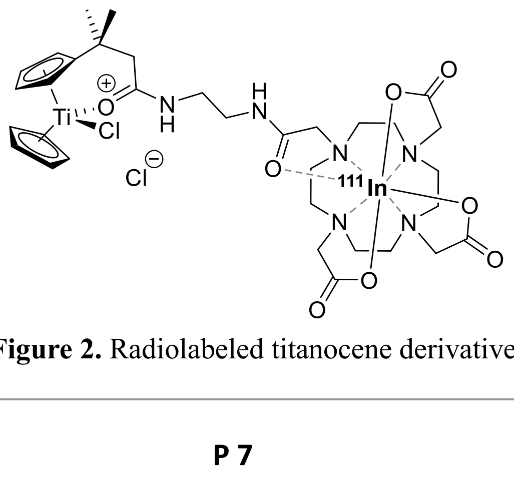

Figure 2. Radiolabeled titanocene derivative.

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Complexation of An(lll) and Ln(lll) with diglycolamides: Effect of the central chain length

N. BOUBALS, [a)]**C. BERTHON**, [a)]**L. BERTHON**, [a)]**C. CASTANO**, [a)]**S. CHAPRON**, [b)]
C. MARIE, [b)]**S. PETIT**, [a)]**N. ZORZ**, [a)]**M.-C. CHARBONNEL**, [c)]**P. GUILBAUD** [a)]

[a)]CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes SPDS/LILA; BP 17171, 30207 BAGNOLS-SUR-CÈZE, France
[b)]CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes SPDS/LCPE; BP 17171, 30207 BAGNOLS-SUR-CÈZE, France
[c)]CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes SPDS/DIR; BP 17171, 30207 BAGNOLS-SUR-CÈZE, France
nathalie.boubals@cea.fr

In the frame of the advanced nuclear fuel recycling studies, the EXAm solvent extraction separation process has been developed by the CEA to allow the recovery of Am alone from a PUREX raffinate [1]. In this process, TEDGA (tetraethyldiglycolamide, see Figure 1) a hydrophilic complexing agent is added to preferentially maintain Curium in the aqueous phase, while Americium is extracted in the organic phase by a synergistic system combining two extractants (DMDOHEMA and HDEHP). In order to improve the Am/Cm selectivity of the diglycolamide complexant in the aqueous phase, various ligands with different spacers between the two amide functional groups have been synthesized and tested. Among them, the TEDOODA complexing agent gave unexpected solvent extraction results: the addition of ether group spacers between the two amide functions (see Figure 2) led to an inversion of the Am/Cm selectivity with a better affinity for Am [2].

In order to better understand this difference of behavior, the aim of this study was to characterize the complex formed in the aqueous phase between the lanthanide and the actinide cations and the TEDGA (Figure 1) and TEDOODA (Figure 2) complexants.

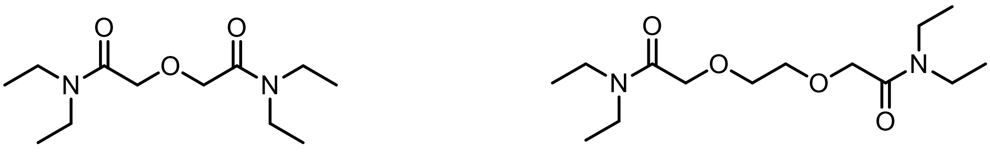

Figure 1. TEDGA (left) and TEDOODA (right).

The stoichiometry and the stability constants were determined using microcalorimetry, Time Resolved Laser Induced Fluorescence Spectroscopy (TRLIFS), UV/Vis spectrometry, Nuclear Magnetic Resonance (NMR), and Electrospray Ionization Spectrometry (ESI-MS). Molecular dynamics simulations were also performed to assess the TEDGA/lanthanide complexes stabilities for La, Nd, Eu and Dy as a function of their stoichiometry.

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Multimodal chelators against neurodegenerative diseases: Fighting metal accumulation and oxidative stress

Jérémy BRANDEL, [a] **Véronique HUBSCHER**, [a] **Frank W. LEWIS**, [b]
David TETARD [b], **James A. DUCE** [c]

[a] *Université de Strasbourg, IPHC, CNRS UMR 7178, 25 rue Becquerel,*
67087 STRASBOURG, France
[b] *Department of Applied Sciences, Faculty of Health and Life Sciences, Northumbria University, NEWCASTLE UPON TYNE, TYNE and WEAR NE1 8ST, UK*
[c] *School of Biomedical Sciences, The Faculty of Biological Sciences, University of Leeds, LEEDS, West Yorkshire LS2 9JT, UK*
jbrandel@unistra.fr

Recent research showed evidence that neurodegenerative diseases, and in particular Alzheimer disease (AD) and Parkinson disease (PD), are linked to two major factors, oxidative stress and protein misfolding in the brain. The two predominant neurodegenerative disorders, AD and PD are linked to the deposition within the brain of peptide aggregates, amyloid-β peptide and α-synuclein, respectively, which is considered as a key event in the pathogenesis of these diseases [1].

It has been observed that the toxicity of many aggregating peptides could be related to their ability to bind transition metal ions [2]. In particular, Cu(II) has been shown to facilitate the formation of aggregated α-synuclein [3]. Impaired copper and iron homeostasis has also been associated with AD and PD, with elevated levels of both metals being found in the senile plaques from AD patients and in the Lewy bodies and cerebrospinal fluid of PD patients [4]. On the other hand, the unhealthy accumulation of redox metals like iron and copper is involved in the formation of reactive oxygen species (ROS) which kill neurons. Moreover, similar to PD, iron dysregulation also occurs in Huntington's disease (HD) [5].

In this context, our objective is to develop novel therapeutic and/or alleviation strategies based on compounds able to hit both causative effects by combining coordination and antioxidant properties into a single active molecule. We present a detailed *in vitro* physicochemical study of ligands based on 1,2-hydroxypyridinone, showing promising Fe(III) and Cu(II) complexation and antioxidant properties.

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EPR study of copper(II) complexes with polyaza-macrocycles of interest for ^{64}Cu-based PET imaging

Stéphane BRANDES, Trong-Hung VU, Michel MEYER

Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
sbrandes@u-bourgogne.fr

Molecular imaging plays a steadily growing role in medical diagnosis and evaluation of therapeutic effects of new drugs. Among the widely used techniques, positron emission tomography (PET) is a non-invasive imaging modality providing insights into the physiological processes that occur within a living organism. ^{64}Cu is a particularly promising radionuclide for use in PET imaging. However, the use of ^{64}Cu-based radiotracers requires the development of high affinity chelators forming stable, inert, and non-reducible complexes under physiological conditions in order to prevent the release of the radioelement.

Among the variety of linear and cyclic chelators considered so far as potential ^{64}Cu-based radiotracers [1-3], researches evidenced high in-vivo performances of cyclic polyaminocarboxylates (Figure 1) [4,5]. In the present study, tri- and tetra-azamacrocycles (TACN, cyclam and cyclen) functionalized with three or four carboxylate ($NOTA^{3-}$, $TETA^{4-}$, $DOTA^{4-}$) as well as mixed derivatives bearing three acetate and one acetamide groups ($TE3AAM^{3-}$) were considered. The cross-bridged cyclam ligand CB-$TE2A^{2-}$ bearing two carboxylate arms was also studied.

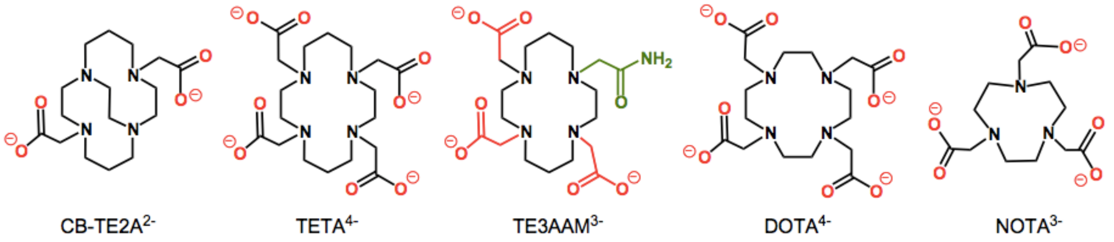

Figure 1. Ligands considered for EPR analysis of Cu(II) complexes.

Copper(II) binding has been monitored by electron paramagnetic resonance (EPR) spectroscopy, allowing us to unravel the speciation as a function of the solution composition and pH. EPR spectroscopy is certainly one of the most informative methods since characteristic signatures of the paramagnetic species are generally obtained in solid state or in frozen solution. The determination of the g factors as well as the hyperfin coupling constants provide valuable information about the coordination sphere around the metal center. In this study, we have established correlations between crystallographic and EPR data (H_2O, 100 K) for the $^{63/65}$Cu(II) complexes as a function of pH, which provide insights into the coordination geometry both in solution and in the solid state.

Acknowledgements: support was provided by the CNRS, the Université de Bourgogne, and the Conseil Régional de Bourgogne through the program PARI II "Pharmaco-imagerie et agents théragnostiques".

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Unusual intramolecular non-covalent platinum – iodine interaction: Computational and experimental study

Evgeny BULATOV, [a] **Peter TOLSTOY,** [b] **Alexander IVANOV,** [b] **Pipsa HIRVA,** [c] **Matti HAUKKA** [a]

[a] *University of Jyväskylä, Department of Chemistry, Survontie 9B, P.O. Box 35,*
40014 JYVÄSKYLÄ, Finland
[b] *St. Petersburg State University, Center for Magnetic Resonance, Universitetskij pr. 26,*
198504 ST. PETERSBURG, Russia
[c] *University of Eastern Finland, Department of Chemistry, Yliopistokatu 7, P.O. Box 111,*
80101 JOENSUU, Finland
evgeny.e.bulatov@student.jyu.fi

Transition metals in d^8 and d^{10} configurations are known to possess closed shell metallophilic interactions resulting in positively charged metal atoms approaching each other to a distance shorter than sum of their Van-der-Waals radii. These interactions are responsible for various photophysical properties and reactivity [1]. In this work, we demonstrate unusual similar to metallophilic intramolecular closed shell interaction between platinum and iodine atoms. Nature and effect of this interaction in cationic bis[(2-iodophenyl)methyldi(pyridin-2-yl)amine]platinum(II) complex on its conformation and properties in solid state and solution are studied computationally and by means of various spectroscopic techniques.

The studied complex was found to exist in two different conformations in solid state: with iodine atom oriented “out” from the molecule, or “in”, towards the metal center, as presented in Figure 1.

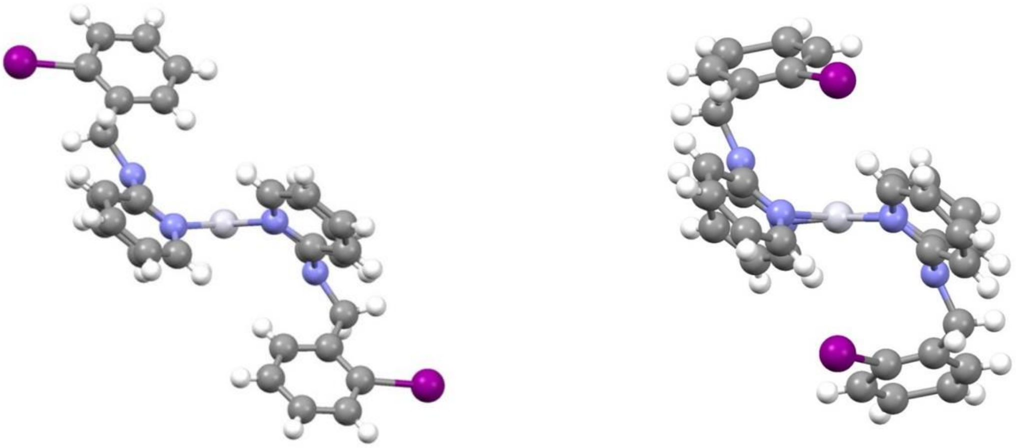

Figure 1. crystal structures of “out”- (left) and “in”- (right) conformations of the studied cationic complex (anions omitted for clarity).

It was found that “in”-conformation possesses short Pt…I contact, which could indicate attractive interaction between the atoms. C-I…Pt angle is close to 90°, and therefore iodine is oriented with its high electron density region towards platinum making this interaction very unusual [2]. According to computational results, Pt…I interaction is indeed attractive and non-covalent in nature, and is responsible for “in”-conformation being about 13 kJ/mol more stable than “out”-conformation in gas phase. In solution, however, additional interactions may result in more significant energy gap between the two conformations.

Various NMR spectroscopy techniques were applied to study equilibrium between the conformers in solution. Analysis of absorption and luminescence spectra revealed different photophysical properties of the complex depending on its conformation. Understanding and better control of such interaction may potentially give access to a new type of transition metal-based light-driven molecular switches [3].

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Novel hybrid material: Cubic unit cell of potassium iodide arranged by organic ligand into 1D coordination network

Margarita BULATOVA, Rajendhraprasad TATIKONDA, Matti HAUKKA

*University of Jyväskylä, Department of Chemistry, EMS research group, P.O. Box 35,
40014 JYVÄSKYLÄ, Finland
maminzar@student.jyu.fi*

Self-assembled potassium iodide-based hybrid material was synthesized and characterized; in the hybrid material ionic salt is wrapped with neutral organic ligand (Figure 1). Cubic KI units are arranged to linear 1D chains due to N-K binding of the ligand to potassium iodide. To the best of our knowledge this is the first crystal structure where potassium iodide is represented in a linear 1D chain of nearly cubic unit cells.

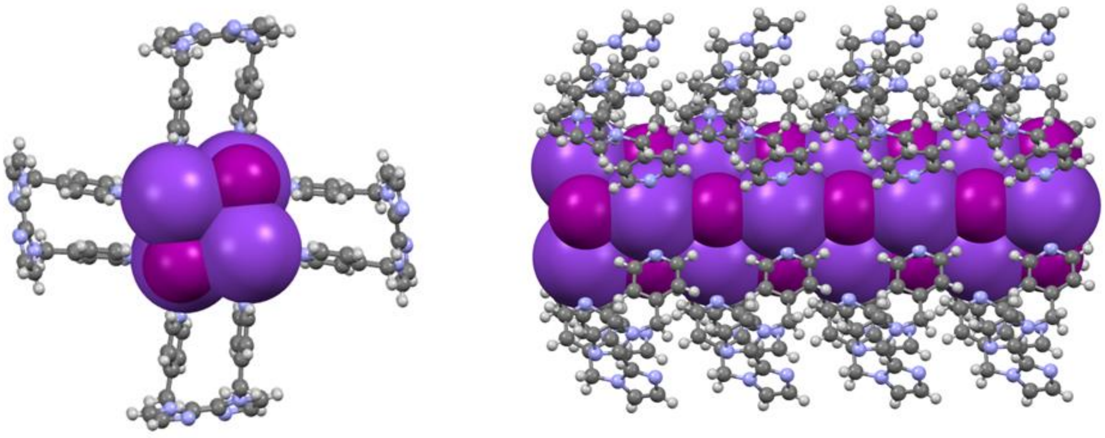
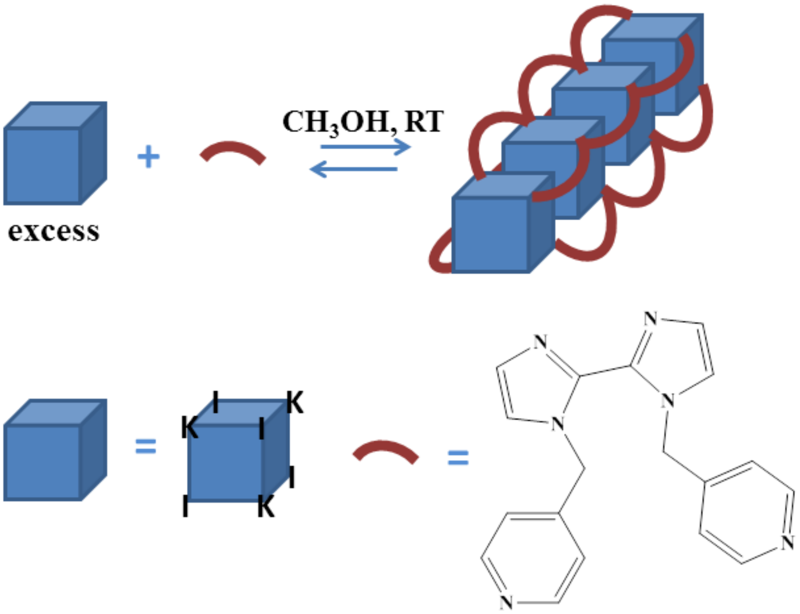


Figure 1. Top and side view of the polymeric potassium iodide-based coordination network. Color code: K – blue violet, I – purple, N – blue, C – gray, H – white.

To successfully design hybrid material one should properly choose starting materials. Right choice will lead to organized growth of a network and therefore desired structure can be obtained. Our group is interested in design of inorganic materials by controlling their growth with organic ones. In 2000 Sloan *et al.,* have shown it is possible to grow a 1D KI chain consisting of cubic K_2I_2 units within single wall carbon nanotube using capillary method [1]. However, single crystal structure has not been obtained. In 2006 Buttery *et al.,* have obtained complex under inert atmosphere, which contained the longest KI chain of 6 KI units, however units were not cubic anymore due to the steric hindrance [2]. In 2011 Martin *et al.,* have obtained under inert atmosphere adduct of imide–nitride complex which contained 2 KI units represented in a square-like shape [3]. Kruszynski *et al.,* have synthesized hybrid net compound, which contained only one unit of KI due to the robust ligand and crystal packing

[4]. Therefore modifying geometry and flexibility of N-donor ligand it is possible to design desired length of ionic salt of the hybrid material.

Acknowledging this idea novel potassium iodide-based coordination network was synthesized via reaction of ionic salt (potassium iodide) and organic ligand (1,1'-bis(pyridin-4-ylmethyl)-2,2'-biimidazole) under normal conditions (Scheme 1) and characterized by various methods (EA, NMR, SCXRD, IR and UV-VIS spectroscopy).



Scheme 1. Synthesis of potassium iodide-based hybrid material.

Biimidazole-based organic ligand is bound to an alkali metal part of the neutral ionic salt. The structure consists of nearly cubic potassium iodide units arranged as linear 1D chains. Moreover, a motif of potassium iodide retained the same representing a coordination polymer of potassium iodide wire surrounded by organic ligands. In the structure, pyridine fragments are coordinated to two different potassium atoms of the same potassium iodide wire through nitrogen atoms. Properties of the unusual network will be investigated further.

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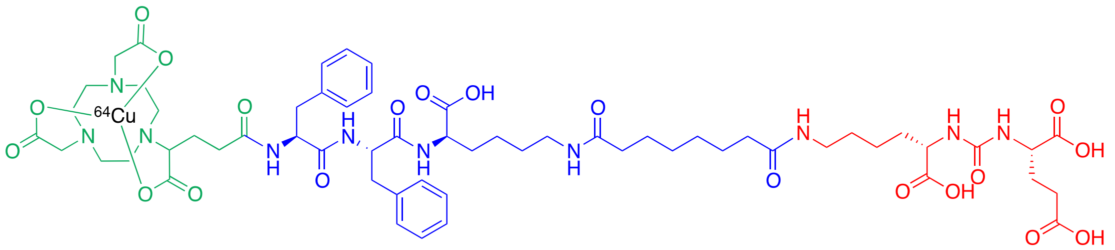
Synthesis and preclinical evaluation of a ^{64}Cu-labeled ligand of the prostate specific membrane antigen (PSMA): A promising radiopharmaceutical for prostate cancer imaging

Coline CANOVAS, [a] **Eleni GOURNI**, [b,c,d] **Franck DENAT**, [a] **Victor GONCALVES**, [a]
Phillip MEYER, [c] **Helmut MAECKE** [c]

[a] *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),*
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[b] *German Cancer Consortium (DKTK), 69120 HEIDELBERG, Germany*
[c] *Department of Nuclear Medicine, University Hospital Freiburg,*
79095 FREIBURG, Germany
[d] *German Cancer Research Center (DKFZ), 69120 HEIDELBERG, Germany*
coline.canovas@u-bourgogne.fr

Prostate cancer is the third most common cause of cancer in males in Europe and resulted in around 93,000 deaths in 2012. Great progress has been made in identifying appropriate targets that would enable efficient in vivo targeting of prostate tumors. One of the most promising targets is the prostate specific membrane antigen (PSMA), a type II integral membrane protein, which is overexpressed on prostate cancer as the stage and grade of the tumor progresses, especially in androgen-independent, advanced and metastatic disease [1].

The present study describes the development of a ^{64}Cu-labeled ligand of the PSMA for positron emission tomography (PET) imaging. A PSMA low-molecular weight targeting moiety, based on a lysine-urea-glutamate scaffold, was coupled to the spacer Phe-Phe-D-Lys(suberoyl) and further functionalized with the metal chelator (R)-1,4,7-triazacyclononane, 1-glutaric acid-4,7-acetic acid (NODAGA), to obtain (R)-NODAGA-Phe-Phe-D-Lys(suberoyl)-Lys-urea-Glu. (R)-NODAGA was selected for its ability to chelate ^{64}Cu rapidly and to form highly stable complexes in vivo [2]. The tracer was radiolabeled and evaluated in vitro and in vivo in LNCaP tumor xenografts by biodistribution and PET imaging studies.



^{64}Cu-(*R*)-NODAGA-Phe-Phe-*D*-Lys(suberoyl)-Lys-urea-Glu

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Synthesis, chemical and *in vivo* studies of a new tris-hydroxypyridinone chelating agent

**Rosita CAPPAI, [a)] M. Amélia SANTOS, [b)] Karam CHAND, [b)] Lurdes GANO, [c)]
M. Antonietta ZORODDU, [d)] Massimiliano PEANA, [d)] Joanna I. LACHOWICZ, [a)]
Valeria M. NURCHI [a)]**

[a)] Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, Cittadella Universitaria, 09042 MONSERRATO-CAGLIARI, Italy
[b)] Centro de Quimica Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais 1, 1049-001 LISBOA, Portugal
[c)] Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 BOBADELA LRS, Portugal
[d)] Dipartimento di Chimica e Farmacia, Università di Sassari, Via Vienna 2, 07100 SASSARI, Italy.
rositacappai@gmail.com

The behavior of a metal ion in physiological conditions depends on the different forms in which it is found in a given environment. Metal ions can exert conflicting roles in body physiology: some are essential, some are toxic and some essential metal ion can transform in a toxic one at increasing concentration. For example, iron, necessary for the normal metabolic functions, becomes toxic at high concentration, interfering with functions of various organs like the central nervous system, liver and kidneys.

The use of selective metal chelators as therapeutic agents for the prevention, diagnosis and treatment of cancer, diabetes, thalassemia, Alzheimer's, Parkinson's and Wilson's diseases, has received increasing attention [1-3].

The families of hydroxypyridinones and of close analogous hydroxypyrones are particularly useful classes of ligands. These easily functionalizable *O*,*O*-donor chelators allow the formation of a range of stable complexes with divalent and trivalent metal ions, and can include tissue molecular targeting features [4-9].

A new tripodal 3-hydroxy-4-pyridinone derivative has been synthesized and completely characterized by a number of spectroscopic techniques: ^{1}H NMR, ^{13}C NMR and ESI-MS. Its protonation and metal complex formation equilibria with Fe^{3+}, Al^{3+} and Ga^{3+} have been studied by potentiometry, UV-visible and ESI-MS spectroscopy. Moreover, biodistribution studies in mice with ^{67}Ga indicate that the ligand possess a high *in vivo* chelating ability promoting the rapid elimination of the radiometal from the animal body. The results are compared with reported data for homologous compounds [7].

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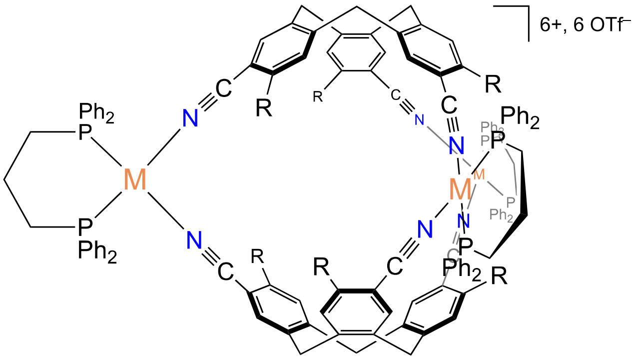
The stereoselective self-assembly of chiral metallo-organic cryptophanes

Astrid SCHALY, [a] Jean-Claude CHAMBRON, [a] Yoann ROUSSELIN, [a]
Emmanuel AUBERT, [b] Enrique ESPINOSA, [b] Marion JEAN, [c]
Nicolas VANTHUYNE [c]

[a] *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),*
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[b] *CRM2, Univ. Lorraine, CNRS UMR 7036, 54506 VANDŒUVRE-LES-NANCY, France*
[c] *ISM2, Aix-Marseille Univ., CNRS UMR 7313, 13397 MARSEILLE, France*
jean-claude.chambron@u-bourgogne.fr

Cryptophanes are macropolycyclic cyclophanes made from two triply-bridged concave cyclotriveratrylene analogues (CTV) that can encapsulate various molecular (alcanes, quaternary ammoniums) or monoatomic (Cs^+, Xe) substrates [1, 2]. They are generally obtained by multistep organic synthesis as separable mixtures of *meso* and chiral diastereomers, the latter showing chiral discrimination of guests [3]. Rare, however, are examples of cryptophanes obtained by metal-directed self-assembly [4, 5].

We report here the self-assembly of cryptophanes based on the M–N bond (M = Pd or Pt) from nitrile-functionalized CTVs [6]. The metallo-organic cryptophanes self-assembled in chlorinated solvents ($C_2H_2Cl_4$, $CHCl_3$, and CH_2Cl_2) at room temperature quantitatively and stereoselectively, the chiral *anti* diastereomers being observed in solution and in the solid state (X-ray crystallography), but in the case of Pt (and R = H, see Figure 1), the latter were accompanied by *ca.* 5% of the achiral *syn* diastereomer. Interestingly, variable temperature studies in CD_2Cl_2 showed that, in the case of the Pd-based metallo-organic cryptophane analogue, the major component switched to the *meso* form at low temperature. These findings were supported by self-assembly studies using optically pure CTVs, which were obtained by liquid chromatography on optically-active phases.



M = Pd, Pt ; R = H, OMe

Figure 1. Structural formula of the chiral *anti* form of the metallo-cryptophanes of this study.

The X-ray crystal structures of the Pd- and Pt-based metallo-organic chiral cryptophanes showed that they encapsulated a chloroform molecule. Gas-phase DFT calculations with the dispersion-corrected B97-D3 functional showed that this guest was stabilized in the molecular cage by 34.6 kJ mol^{-1}. However, in spite of the fact that its filling volume ratio was close to the ideal value of 0.55, the encapsulated chloroform molecule observed in the solid state could not be detected in solution, even at low temperature.

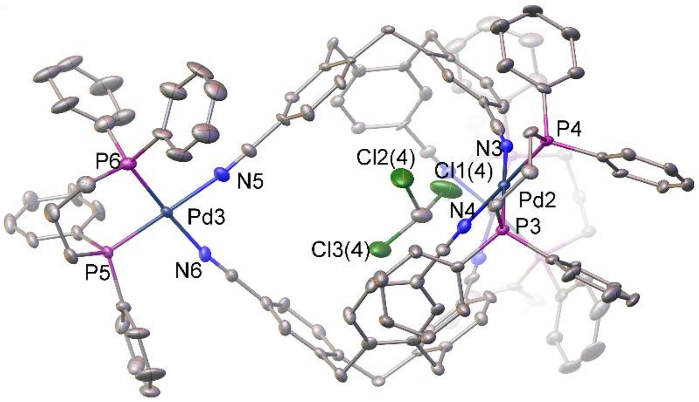


Figure 2. ORTEP representation of the X-ray molecular structure of the Pallado-cryptophane.

Dynamic combinatorial chemistry experiments were conducted by using palladium as assembling metal and two different nitrile-substituted CTVs. They showed that, whatever the starting compounds used (either a 3:1:1 mixture of [Pd(dppp)(OTf)$_2$] and the CTVs or a 1:1 mixture of the preformed trinuclear complexes), no heteroleptic metallo-organic cryptophane was formed. This suggests that a self-sorting process is involved in assembly formation.

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Silica-immobilized hydroxyquinoline as sorbent of metal ions from water resources

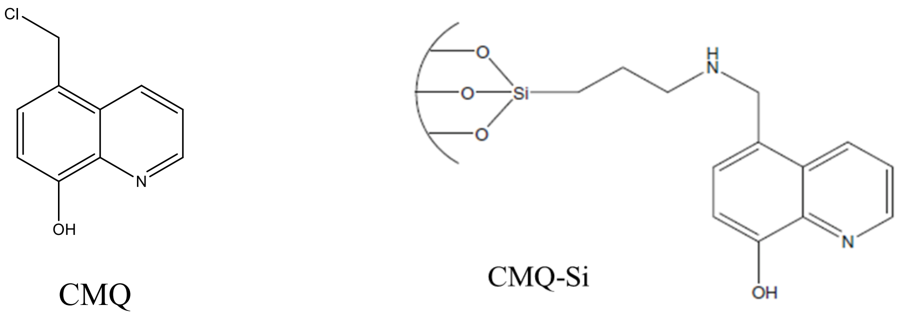
Sara CONCHINHAS, Karam CHAND, Sílvia CHAVES, Maria Amélia SANTOS

Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 LISBOA, Portugal
silvia.chaves@tecnico.ulisboa.pt

The decontamination of water streams from vestigiary amounts of metal ions is of utmost interest in environmental applications. In fact, the presence of metal ions in natural waters has diverse adverse consequences, namely due to the neurotoxicity of Al [1] and genotoxicity of gamma-emitting actinides associated to nuclear weapons or nuclear medicine [2], but also due to the possible appearance of dermatitis and cancer owing to Ni content increase, respiratory and reproductive disturbances in plants and fishes provoked by Cu excess or extreme development of bacteria such as Ferro bacteria.

The use of immobilized chelators in remediation techniques, for metal-contaminated watercourses, has several advantages over the use of water-soluble ones, such as avoiding the potential nephrotoxic effect of soluble chelators/complexes, higher capacity for removal of traces of metal ions, no need of a cautious control of experimental conditions and possible reusability of the solid matrix. Therefore, a number of research groups have been involved in the development of functionalized solid supports by establishing covalent bonding to specifically potent chelators. Regarding the choice of the chelators, although the first trials involved hydroxamates, other options, such as hydroxypyridinones [3] and hydroxypyrimidinones [4], were followed since fragile hydroxamates were not suitable ligands especially under the drastic conditions of solid support regeneration.

Herein we decided to immobilize 5-(chloromethyl)-8-quinolinol (CMQ, Figure 1), a derivative of a well-known potent chelator, 8-hydroxyquinoline, in a silica-based matrix.



CMQ

CMQ-Si

Figure 1

Silica-gel was chosen since it is a relatively low cost inorganic support, with good mechanical properties and stability in a wide range of pH, and also because it is easily derivatized by chemical coupling to several organic moieties. Thus, the present work reports the preparation of the functionalized silica, CMQ-Si (Figure 1), its physico-chemical characterization (FTIR, SEM, ligand density, stability in neutral/acidic medium), as well as its chelating capacity towards different metal ions in aqueous medium. It was found that the solid chelator is particularly stable during a 8 hours period and that it has a high chelating power towards Cu(II), Fe(III) and Th(IV), moderate towards Al(III) and low for Ni(II). These results are in accordance to the chelating properties of the ligand in aqueous solution. Th(IV) is a quite safe actinide that was selected for these studies as a plutonium model. The obtained results seem to point towards the interest in the development of this kind of solid chelating matrices for metal decontamination of natural waters.

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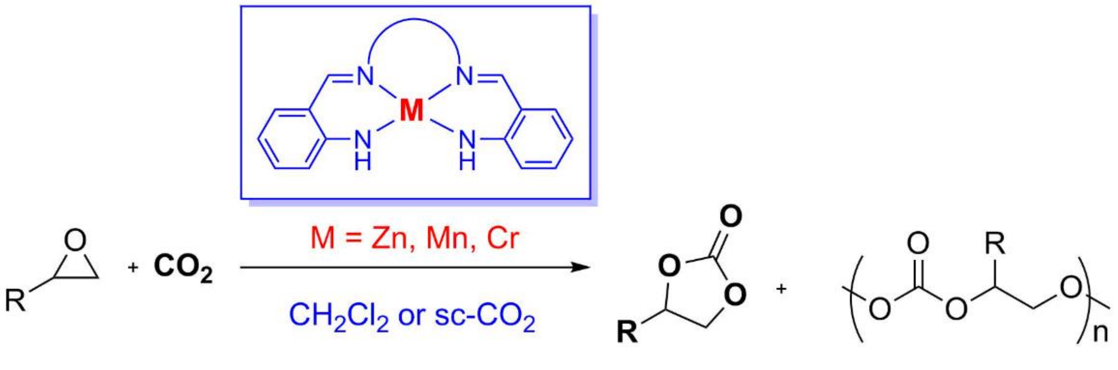
Nitrogen Schiff base complexes as selective catalysts for the valorization of CO_2

Walid LAMINE, [a,b] **Christophe MORELL,** [a] **Henry CHERLETTE,** [a]
Lorraine CHRIST [b]

[a] Institut de Sciences Analytiques, 5 rue de la Doua , 69200 VILLEURBANNE, France
[b] Institut de Recherches sur la Catalyse et Environnement de Lyon (UMR-CNRS 5256),
2 avenue Albert Einstein, 69626 VILLEURBANNE Cedex, France
lorraine.christ@univ-lyon1.fr

Our studies focus on nitrogen Schiff bases since these ligands are similar to porphyrins (N4 ligands) and Salen compounds (N2O2 ligands). Nitrogen Schiff bases are N4 ligands with an open structure that can be flexible and chiral, when prepared from the corresponding chiral diamine by a Schiff condensation with an aldehyde. Thus, we developed a series of nitrogen Schiff bases complexes using various metals (Ni, Co, Cu, Zn, Mn, Fe) and characterized them by spectroscopic methods (NMR, IR, Raman, Mössbauer) and X-Ray when suitable crystals were obtained [1-3]. These complexes should have interesting catalytic properties since many efficient catalysts are described with porphyrins and salen complexes.

The presentation will focus on the use of some nitrogen Schiff base complexes as catalysts for the carbon dioxide addition to epoxides and the optimization of experimental conditions to selectively form cyclic carbonates. The reactions were carried in liquid phase or supercritical conditions, thus having CO_2 as solvent and substrate [2-3]. A theoretical approach on the reaction mechanism will also be discussed [4].



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Nanohydrogels and gadolinium chelates: Seeking for hypersensitive T_1 probes in MRI

G. RIGAUX, [a] **V. GHERAN,** [b] **M. CALLEWAERT,** [a] **S. HUCLIER-MARKAI,** [c] **C. CADIOU,** [a] **J. MOREAU,** [a] **A. BERQUAND,** [d] **M. MOLINARI,** [d] **S. PETRACHE VOICU,** [b] **A. DINISCHIOTU,** [b] **C. HENOUMONT,** [e] **L. Vander ELST,** [e,f] **R. N. MULLER,** [e,f] **S. LAURENT,** [e,f] **C. PORTEFAIX,** [g] **F. CHUBURU** [a]

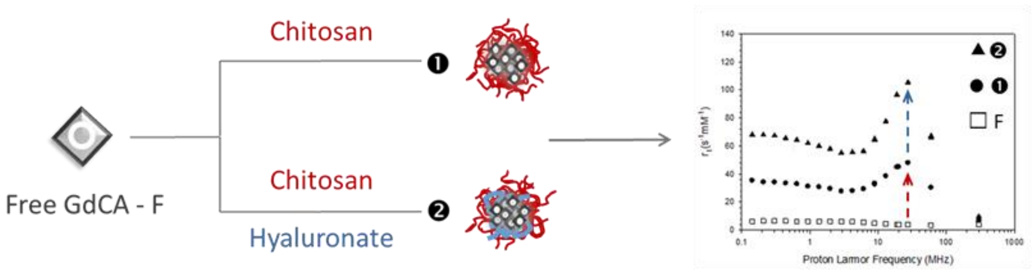
[a] URCA, ICMR, CNRS UMR 7312, Moulin de la Housse, 51687 REIMS, France
[b] Biochem. & Mol. Biol. Department, 91-95 Splaiul Independentei,
050095 BUCHAREST, Romania
[c] Subatech, CNRS UMR 6457 Ecole des Mines de Nantes / CNRS/IN2P3 / Université de Nantes, 4 Rue A. Kastler, BP 20722, 44307 NANTES Cedex 3, France and ARRONAX GIP, 1 rue Arronax, 44817 NANTES, France
[d] URCA, LRN, EA 4682, 21 rue Clément Ader, 51685 REIMS, France
[e] UMONS, NMR & Mol. Im. Lab., Boulevard Maistriau, 7000 MONS, Belgium
[f] CMMI, Rue Adrienne Bolland 8, 6041 CHARLEROI, Belgium
[g] CHU de Reims, Radiology Department, 45 rue Cognacq-Jay, 51092 REIMS, France

Gadolinium contrast agents (GdCAs) are widely used in MRI to distinguish healthy and diseased tissues. Recently, some alerts regarding the retention of Gd chelates in brain tissues have set off questions as to their use [1-2]. From a diagnostic point of view, the balance risk benefit is in question. From a chemical point of view the question is: how can be designed solutions in order to improve GdCA efficiency and to lessen the injected doses? The solution developed herein is based upon the encapsulation of GdCAs within nanohydrogels (GdCAs-NGs). After a careful morphological and toxicological characterization of these nanosystems, we will describe the effect of encapsulation on GdCA MRI efficiency.

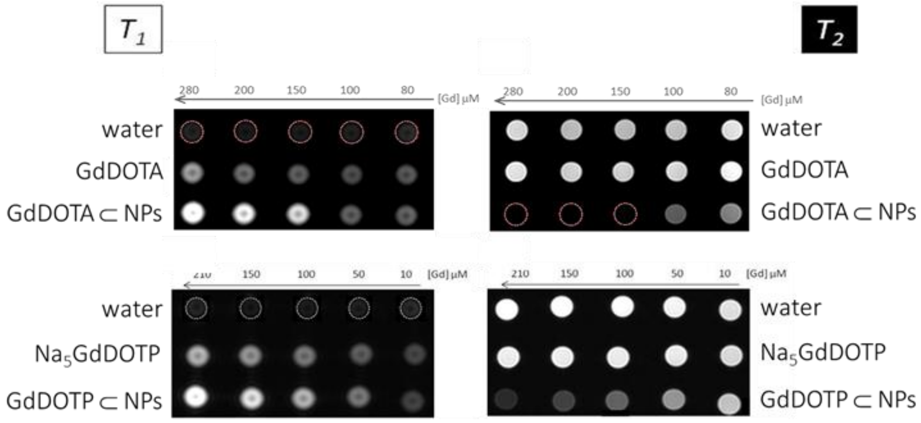
A series of GdCA-NGs were elaborated by an easy and robust ionotropic gelation process [3] involving chitosan (CS) and hyaluronan (HA). In this presentation, the synthesis of these nanohydrogels will be described and their characterizations will be presented.

Characterization of GdCA-NGs size distribution was performed by DLS, AF4 and AFM in liquid mode. The comparison of results obtained by DLS and AF4 showed discrepancies. Such a difference could be correlated to the presence of aggregates inherent to ionic gelation. This point was clarified by AFM in liquid mode which highlighted the main presence of individual NPs in nanosuspensions. The evaluation of their toxicity carried out by MTT, SRB and LDH tests will be also presented [3-4].

Finally, their MRI performance will be analyzed by relaxometric measurements and T_1- and T_2-weighted images at 3T. We will demonstrate that according to the nature of the polymer matrix and to the cross-linking ability of the GdCA, r_1 relaxivities per Gd ion as high as 100 s^{-1} mM^{-1} at 30 MHz can be reached. The NMRD profiles will confirm that molecular motions of Gd chelates are effectively restricted and water access to the inner core of these nanogels not limited. On T_1- and T_2-weighted images recorded at 3Teslas, we will show that this relaxation enhancement is clearly translated into a magnified contrast, demonstrating the powerful dual mode imaging capability of such nanosytems.



GdCA Nanohydrogels



Dual T_1/T_2 behaviour

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Structural diversity of palladium complexes with C,P- and O,P- chelating phosphine ligands

<u>Oleg M. DEMCHUK</u>, Barbara MIROSLAW, Katarzyna SZWACZKO

*Department of Chemistry, Maria Curie-Sklodowska University, pl. M. Curie-Skłodowskiej 2,
20-031 LUBLIN, Poland
Oleh.Demchuk@UMCS.Lublin.pl*

Electron rich sterically hindered phosphines constitute an important class of phosphorus ligands widely used in homogeneous catalysis as complexes with transition metals [1]. A series of unusual structures of palladium complexes of new *C,P-* and *O,P-* chelating phosphine ligand MeO*Sym*-Phos has been characterized. The presented here phosphine ligand was designed to be used in difficult cross-coupling reactions under the mild and sustainable reaction conditions. It may act as a monodentate ligand, coordinating through P atom, as well as a *C,P-* or *O,P-*chelating ligand, depending on the syntheses conditions.

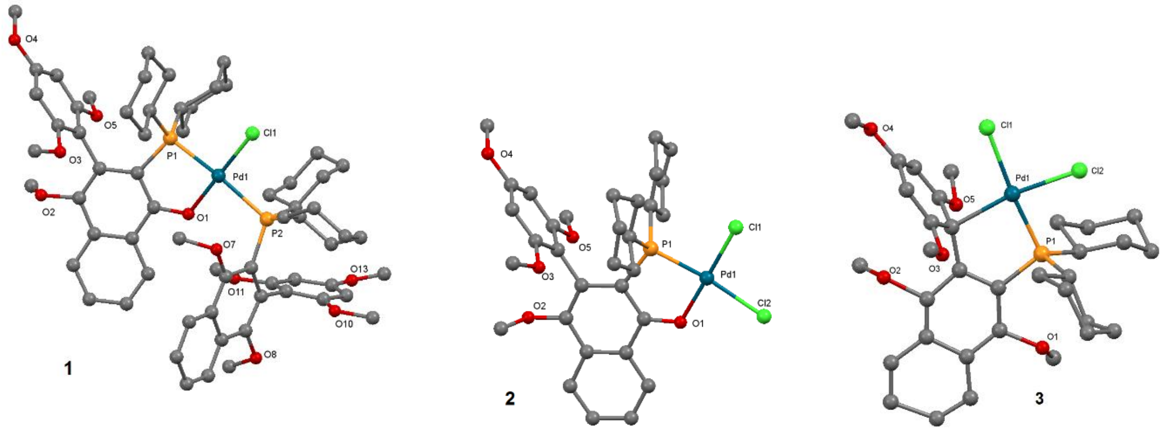

Figure 1. X-ray structures of the complexes **1-3**.

In all the studied structures, the palladium ion has a slightly distorted square planar environment. In **1** the Pd ion is coordinated by one Cl ion and two phosphine ligands. One of them is monodentate and the other one coordinates as a *O,P*-chelating ligand forming a five-membered metallacycle. The trans effect is observed and two phosphorus centers are in trans positions. It is worth to notice that the two large phosphine ligands are arranged mutually in a head-to-head fashion. In **1** is also observed a short intramolecular electrostatic interaction (anagostic) between Pd ion and methoxy C atom (d(M…H) = 2.79 Å, d(M…C) = 3.361(2) Å, ∠(M…H–C) = 119°).

In crystal **2** the phosphine ligand binds in a chelate fashion through O and P atoms. This coordination unit has a negative charge and crystallizes with a phosphonium cation formed *in situ* in an unusual alkylation reaction between free phosphine and activated methoxy group of monodentate palladium complex of MeO*Sym*-Phos.

In complex **3** the organic ligand behaves as a *C,P*-chelating ligand closing the five-membered ring. The remaining two cis positions are occupied by two Cl ions.

The structures of the complexes **1-3** are significantly different on the palladium complexes of monodentate MeO*Sym*-Phos sulfide (**4**) as well as *C,P*-bidentate *Sym*-Phos (**5**) ligands.

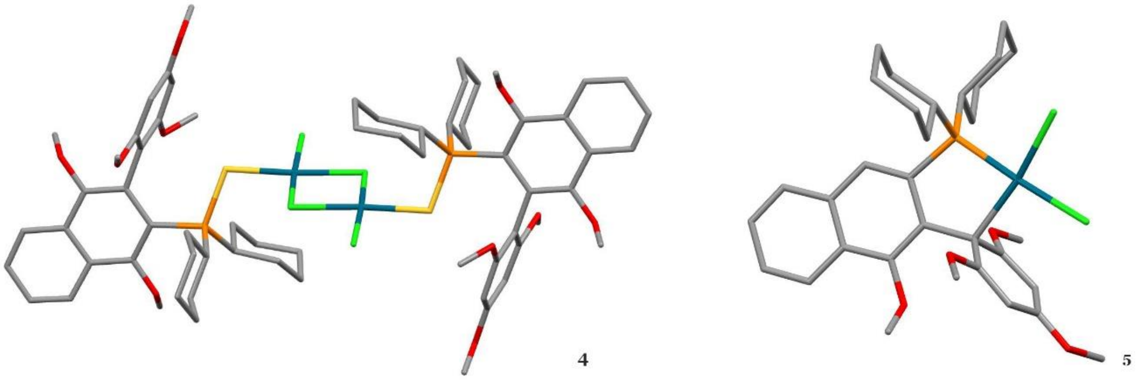

Figure 2. X-ray structures of the complexes **4-5**.

The presented results give insight into the diversity of coordination abilities of the studied phosphine ligand, which complexes are belong to the known class of the excellent catalysts of different types of cross-coupling reactions [1-5]. The syntheses of the complexes and their further application in cross-coupling reactions will be discussed in details [6].

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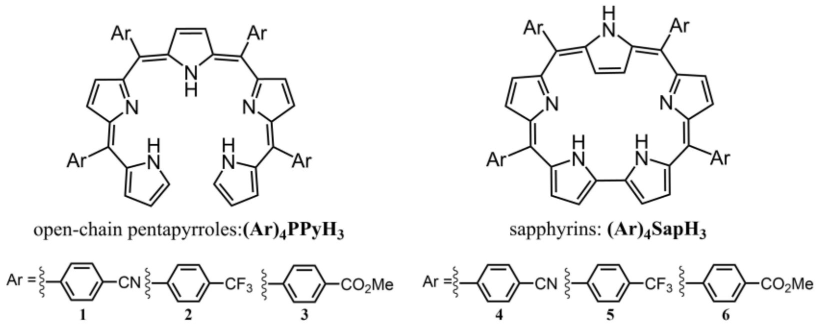
Preparation and characterization of open-chain pentapyrroles and sapphyrins with highly electron-withdrawing *meso*-tetraaryl substituents

Nicolas DESBOIS, [a] **Wenqian SHAN**, [b] **Mario L. NAITANA**, [a]
Valentin QUESNEAU, [a] **Claude P. GROS**, [a] **Yoann ROUSSELIN**, [a]
Wenhao HUANG, [c] **Zhongping OU**, [b,c] **Karl M. KADISH** [b]

[a] *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),*
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[b] *University of Houston, Department of Chemistry, HOUSTON, TX 77204-5003, USA*
[c] *Jiangsu University, School of Chemistry and Chemical Engineering,*
ZHENJIANG 212013, P.R. China.
nicolas.desbois@u-bourgogne.fr

Sapphyrin is a 22-π aromatic pentapyrrolic macrocycle containing one direct link and four bridging methine groups between five pyrrole subunits [1]. This macrocycle is an early member of the group of "expanded porphyrins" and was first discovered as a byproduct in the synthesis of corroles. A series of open-chain pentapyrroles and sapphyrins with highly electron-withdrawing *meso*-tetraaryl groups were synthesized (Figure 1) and characterized as to their electrochemistry and protonation reactions in nonaqueous media. An X-ray structure for one of the pentapyrroles will be presented [2]. The introduction of different metals in pentapyrroles and sapphyrins will be also discussed.



open-chain pentapyrroles:**$(Ar)_4PPyH_3$**   sapphyrins: **$(Ar)_4SapH_3$**

Figure 1. Structures of investigated compounds.

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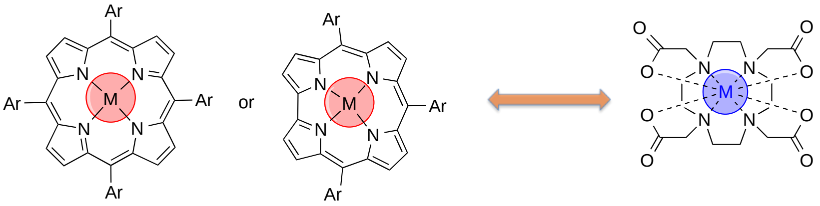
Synthesis and preliminary studies of heterobimetallic complexes: A porphyrin or a corrole-cyclen association for MRI/PET imaging

Nicolas DESBOIS, Sandrine PACQUELET, Claude P. GROS

Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
nicolas.desbois@u-bourgogne.fr

Magnetic resonance imaging (MRI), positron emission tomography (PET) or single photon emission computed tomography (SPECT) are actually the most commonly used imaging modalities. In the last decade, the concept of coupling different imaging modalities to exploit the complementarities between each technique has emerged. In this work, we have designed new multimodal porphyrinoids-DOTA-like agents incorporating different metals ions *e.g.* Mn, Ga, In and Gd of potential interest in medical imaging [1-4]. The preliminary relaxivity measurements show that the developed complexes are promising medical imaging agents for contrast enhancement in MRI techniques. These compounds can be also grafted onto folic acid derivative for biovectorization.



	Porphyrin/Corrole	DOTA
Bimodal contrast agents	Cu (PET)	Gd (MRI)
	Ga (PET)	Gd (MRI)
	In (SPECT)	Gd (MRI)
	Mn (MRI)	Ga (PET)

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Photopolymerization under visible light: Towards high efficiency photoinitiators with thermally activated delayed fluorescence (TADF) complexes

Frédéric DUMUR, [a] **Damien CAMPOLO**, [a] **Jacques LALEVEE**, [b] **Didier GIGMES** [a]

[a] *Aix Marseille Université, CNRS, Institut de Chimie Radicalaire, UMR 7273,*
13397 MARSEILLE, France
[b] *Institut de Science des Matériaux de Mulhouse IS2M – UMR CNRS 7361 – UHA,*
15, rue Jean Starcky, 68057 MULHOUSE Cedex, France
frederic.dumur@univ-amu.fr

Considering the serious environmental pollution and energy crisis resulted from human activities, light-activated chemical reactions are of critical importance for the sustainable development of mankind. In this regard, photocatalysis has attracted great interest and researchers from academia, industry, and government research laboratories have made remarkable progress in this field, including solar fuels (CO_2 capture, water splitting, etc.), pollutants degradation, and chemical synthesis. Recently, the concept of visible-light *photoredox catalysis* has been successfully adopted in polymer synthesis upon soft conditions [1,2]. Organometallic compounds with excellent photochemical properties (e.g. strong visible light absorption, long excited state lifetimes) have a great potential as photoinitiators for free-radical initiated [(meth)acrylates)] and cation initiated (epoxides or vinyl ethers) polymerizations. Over the years, a series of ruthenium-, iridium-, zinc-, or copper-based complexes have been successfully developed and applied as photoinitiators [1,2]. However, the search of photocatalysts based on low-cost and none-toxic metals and allowing efficient polymerization reactions at low concentrations in the photocurable formulation remains today highly interesting and challenging.

Since 2012 and the impressive works of Chihaya Adachi on Thermally Activated Delayed Fluorescence (TADF) materials, this new family of luminescent materials has been the focus of numerous research [3]. Herein, we present unprecedented works of TADF metal complexes used as photoinitiators of polymerization. These results pave the way towards the development of third generation visible-light photoinitiators operating under soft irradiation conditions.

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Optical sensors for monitoring of mercury and copper cations in aqueous solutions

Elizaveta ERMAKOVA, [a)] Michel MEYER, [b)] Alla BESSMERTNYKH-LEMEUNE, [b)]
Roger GUILARD, [b)] Oleg RAITMAN, [a)] Maria KALININA, [a)] Vladimir ARSLANOV [a)]

[a)] Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Pr. 31, 119071 MOSCOW, Russia
[b)] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302), Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870, 21078 DIJON Cedex, France
evermakova92@gmail.com

One of the most important research topics in chemistry and material sciences that covers various areas of human activity including health is the development of diagnostic systems. These systems should furnish efficient monitoring of various harmful ions and molecules in industrial processes, in clinical toxicology, environmental monitoring and household.

Various types of optical sensors with high selectivity and sensitivity for the determination of mercury and copper cations in aqueous solutions are considered in this work. Sensors are produced from 1,8-bis(amino)anthraquinone-based ligands endowed with hydrophilic diethoxyphosphoryl groups and two alkyl chains [1-2]. The colorimetric sensors with absolute selectivity allow one to carry out both visual and spectrophotometric determination of mercury ions in water without sample preparation.

Liquid and solid-state thin-film sensors, produced by Langmuir monolayers and Langmuir-Blodgett film techniques, are capable of selectively determining mercury cations in aqueous solutions up to 10^{-7} M. Highly sensitive SPR (surface plasmon resonance) sensors for the selective determination of $Hg^{2+}$and Cu^{2+} ions in an aqueous medium to 10^{-11} M and 10^{-15} M, respectively, as well as polymer films and test strips for the rapid analysis of these cations are developed. These sensors possess the necessary sensitivity and selectivity for the direct determination of mercury and copper ions at levels, as required for industrial-process, waste-disposal, or environmental monitoring or even for household applications.

Acknowledgments: this work was carried out in the frame of the International Associated French–Russian Laboratory of Macrocycle Systems and Related Materials (LAMREM) of CNRS-RAS. The authors thank Russian Foundation for Basic Research for financial support (project № 16-29-05272 and № 17-53-16018).

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Assembly and properties of 2D multichromophoric supramolecular arrays on surface of liquid and solid substrates

Elizaveta ERMAKOVA, [a)]**Yulia ENAKIEVA,** [a)]**Alexandra ZVYAGINA,** [a)]
Yulia GORBUNOVA, [a,b)]**Maria KALININA,** [a)]**Vladimir ARSLANOV** [a)]

[a)] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Pr. 31, 119071 MOSCOW, Russia*
[b)] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Pr. 31, 119991 MOSCOW, Russia*
evermakova92@gmail.com

Coordination polymers composed of porphyrins and metal ions provide an enlightening example of supramolecular synthesis for fabricating multichromophoric arrays for various applications. Herein, we report a new strategy of self-assembly of 2D coordination networks in Langmuir monolayers. Unlike common approach, our strategy uses metal-free tetrapyridyl porphyrin as a primary building unit instead of metal complex of this ligand. This approach relies on the interactions of metal ions both with peripheral groups and with a central cavity to achieve periodically ordered structure of 2D multiporphyrin arrays with face-on orientation of macrocycles. We found that the control of metalation-demetalation processes of porphyrin ring is a key factor for both formation of 2D multiporphyrin arrays and their further transformation into SURMOFs. For the monolayer at the air/water interface, the incorporation of zinc into the porphyrin ring requires a considerably longer time as well as higher concentration of salt in the subphase, when compared to similar reaction in bulk solution. Zinc ions boost the fluorescence of TPyP in organic solvent, whereas their presence in the subphase under the monolayer of TPyP results in fluorescence quenching. Uniformity of the networked films formed on Zn-containing subphase and deposited on solids was demonstrated by SEM and AFM techniques.

Acknowledgments: this work was supported by Russian Science Foundation, Grant 16-13-10512.

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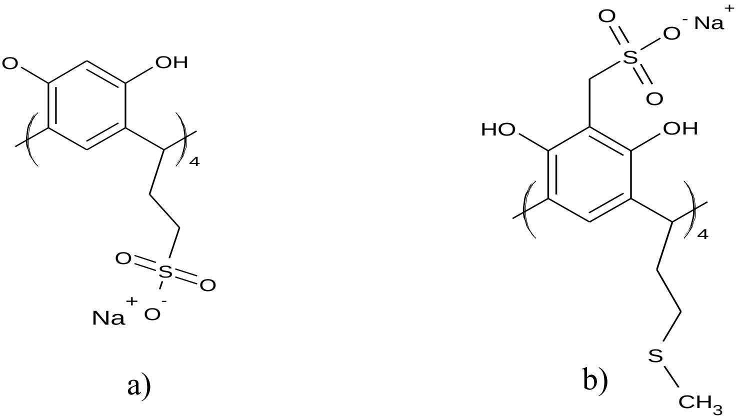
Effect of resorcin[4]arenes on the behaviour of bovine serum albumin in aqueous solutions

Valeria ESLAVA-RUIZ, **Andrea ORDÓÑEZ**, **Edgar F. VARGAS**

Universidad de los Andes, Cra 1 N° 18A - 12, 111711, BOGOTÁ, Colombia
v.eslava29@uniandes.edu.co

The physico-chemical study of macrocycles has received great attention in recent decades due to their property of forming supramolecular complexes of interest in chemical and biological systems [1]. The physicochemical study of the macrocycles in solution provides valuable information about the formation process of complex or aggregates. In this work two water-soluble resorcin[4]arenes (figure 1) were studied using two experimental techniques, surface tension (ST) and isothermal titration calorimetry (ITC), as a function of concentration at 298.15 K. The data obtained shows the presence of aggregation concentration, C_{agg}, for both sulfonated resorcin[4]arenes. In addition, the effect on the stability of Bovine Serum Albumin (BSA) at both regions (preaggregation and post aggregation) was studied by dynamic surface tension and ITC in aqueous solution. The results suggest the formation of a resorcin[4]arene – BSA supramolecular complex.



a) b)

Figure 1. Molecular structure of the two sulfonated resorcin[4]arenes studied.
a) Na_4CSRA and b) Na_4BRA.

Acknowledgements: the authors wish to thank the Faculty of Science of Universidad de los Andes for financial support.

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Influence of oxygen-by-sulfur substitution on the complexation of environmental interest metals by model compounds of organic matter

Cécilia FALANTIN, Annaïg LE PERSON, Aurélien MONCOMBLE,
Jean-Paul CORNARD

Univ. Lille, CNRS, UMR 8516 - LASIR - Laboratoire de Spectrochimie Infrarouge et Raman,
59655 VILLENEUVE D'ASCQ, France
cecilia.falantin@ed.univ-lille1.fr

Dissolved organic matter (DOM) is the result of degradation and condensation of molecules from biomass. DOM in water consists of a complex mixture of low molecular weight organic substances and macromolecules containing a variety of different organic functional groups. Oxygen-containing groups like carboxyl (R-COOH) and phenol (R-OH) are most abundant, but less abundant functional groups like thiols (R-SH) form stronger complexes with metal ions in the environment [1]. Despite a better understanding of the metal-DOM interaction, the impact of the functional group on the complexing properties remains barely elucidated. It seemed interesting to study similar model compounds with only one complexation site, oxygenated or sulfur-containing, to observe and compare speciation changes and complexing power between both ligands. Benzene compounds and flavonoids are at the origin of DOM formation and there is evidence that in some cases the chemical activity of interest with this kind of components involves metal-based [2]. Therefore, we chose to study 3-hydroxyflavone (3-OHF), 3-hydroxyflavothione (3-OHFT), benzenediol (BDD) and benzenedithiol (BDT). The two types of envisaged structures involve very different complexing sites (hydroxyl-keto or catechol).

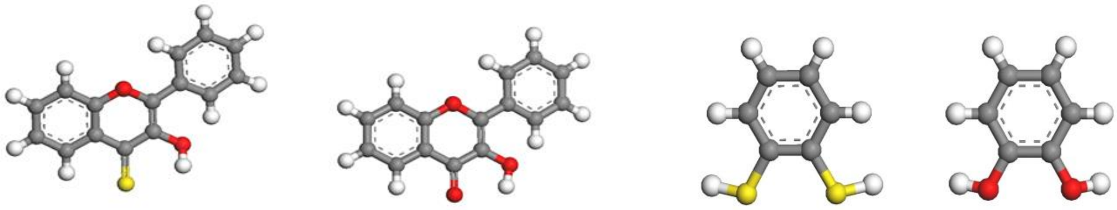

Figure 1. Structure of 3-OHFT, 3-OHF, BDT and BDD.

The main objectives of this study are, first to identify the nature of the complexes formed between several metal cations (Zn^{2+}, Co^{+}, Cd^{2+}, Pb^{2+}, Ni^{2+}) usually found in the environment and the four model compounds and secondly to compare the complexing properties of the various functions. The complexation reaction was followed, in the same conditions, by UV-visible absorption and fluorescence spectroscopies. The molar ratio method was used to estimate the stoichiometry of the complexes formed. Then, chemometric methods were used for a more extensive treatment of the results and notably for the calculation of the conditional stability constants.

From a spectroscopic point of view, substitution of oxygen by sulfur leads to a bathochromic shift of the absorption bands of the ligand and an absence of fluorescence emission. All complexes formed with Ni^{II} and Co^{II} are not fluorescent whatever the ligand. Sulfured ligands form strong complexes with different stoichiometries (1:1, 1:2), whereas oxygenated ligands show lower or non-existent complex in some cases. Although it is difficult to make a direct link between the complexing power ranking of a given ligand with chemical properties of metal cations, in all cases, sulfur functions appear more complexing than the oxygen functional groups.

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Emerging technologies based on ionic liquids for the removal of boron in seawater

**Olivia GÓMEZ-LASERNA, [a)] Leire KORTAZAR, [a)] Alvaro MORALES, [a)]
Saioa ZORITA, [b)] Yolanda BELAUSTEGI, [b)] María Angeles OLAZABAL, [a)]
Luis Ángel FERNÁNDEZ [a)]**

[a)] *Department of Analytical Chemistry, University of the Basque Country (EHU/UPV),
P.O. Box 644, 48080 BILBAO, Spain.*
[b)] *Tecnalia Research & Innovation, Materials for Energy and Environment Area,
48160 DERIO-BIZKAIA, Spain
luis-angel.fernandez@ehu.eus*

Seawater desalination is considered one of the most important sources for potable water supply in the world. In fact, many countries have developed different desalination technologies to ensure the domestic supply of water to their populations. In the last years, the desalinated seawater market has been expanding, in parallel with the moderation of the desalination costs, achieving a global desalination capacity of 100×10^6 m^3/day, which is expected to double by 2025. Nowadays, the technique of reverse osmosis (RO) has been generalized as a reference technology for the desalination of seawater, since it has lower energy consumptions, smaller production costs and can be applied on a large scale. However, despite the competitive advantages of RO over other desalination techniques, it still does not get an efficient boron removal. In fact, osmotized seawater shows concentrations of boron that are toxic to the crops assuming significant economic losses. Thereupon, the adequacy of the boron concentration to the requirements of *The World Health Organization* (WHO) requires specific post-treatments or a second stage of RO to reduce its concentrations to 0.5 mg/l of boron in drinking water, and 0.3 mg/l in irrigated water.

According to this, the goal of this work has been to develop a technology based on ionic liquids (ILs) which can reduce the boron content in water below the WHO specifications. For that purpose, UPV/EHU and TECNALIA have investigated the capability of different ionic liquids (ILs) to extract boron from seawater, studying the liquid-liquid extraction technique as first step. In this way, a characterization of seawater has been carried out in order to study the chemistry of the Boron by chemical and thermodynamic modeling, using Chemical Equilibrium Diagrams and information on stability constants, included in the software programs HYDRA (Hydrochemical Equilibrium Constant) and Medusa (Make Equilibrium Diagrams Using Sophisticated Algorithms).

The study has showed that the concentration of boron in seawater is around 4.75 mg/L and therefore, the polynuclear species can be neglected. Thus, boric acid, $B(OH)_3$, behaves as a Lewis acid according to the following dissociation equation.

$$B(OH)_3 + H_2O \leftrightarrow B(OH)^{-}{}_4 + H^+ \qquad pK_a = 9.24$$

As the pH of seawater varies between 7.95 and 8.2, in real saline conditions only about 80% of boron is found as boric acid and 20% as borate. Then, the presence of boron in different molecular species has a great effect on the efficiency of its elimination of aqueous solutions (See Figure 1).

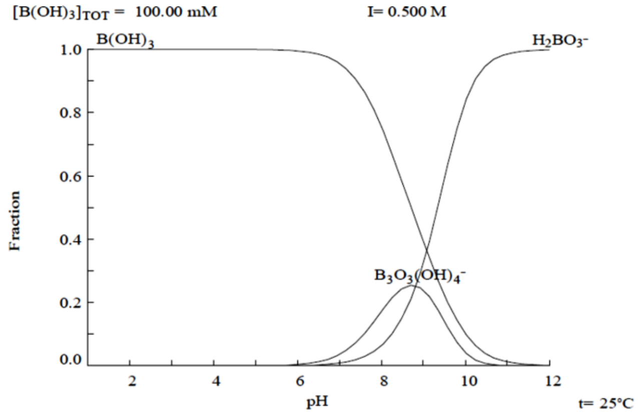

Figure 1. Distribution of boron species in aqueous phase at different.

Therefore, taking into account the effect of the chemical structure of the extracting ILs on the ability to selectively extract boron, and the effect of several variables (temperature, boron concentration, presence of impurities and pH), the ILs studied have been mixtures of (a) Cyanex 272 and Cyphos 101, (b) Aliquat 336 and Cyanex 272, as well all the pure compounds Cyphos 104, Cyphos 109 and 1-(2,3-dihyroxylpropyl)-3-methylimidazolium bis(trifluorosulfonyl)imide in different organic solvents.

The results have pointed out extraction capacities greater than 67% using Cyphos 104 dissolved in hexane at pH = 7.6. The next step will be its implementation in supported liquid membranes due to their advantages such us small organic phase requirement, minimum contamination risk, extraction and re-extraction are in a single stage, highly selectivity, easy automation and low cost.

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Cur(e)cumin: New perspectives in early diagnosis of Alzheimer's disease

Giulia ORTECA, [a] **Mattia ASTI,** [b] **Sara RUBAGOTTI,** [b] **Michele IORI,** [b]
Pier Cesare CAPPONI, [b] **Stafania CROCI,** [b] **Zuzana BEDNARIKOVA,** [c]
Zuzana GAZOVA, [c] **Maria Cristina MENZIANI,** [a] **Francesco TAVANTI,** [a]
Erika FERRARI [a]

[a] Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via Campi 103, 41125 MODENA, Italy
[b] Nuclear Medicine Unit, Advanced Technology Department, Santa Maria Nuova Hospital – IRCCS, via Risorgimento 80, 42100 RE, Italy
[c] Department of Biophysics, Institute of Experimental Physics, Slovak Academy of Sciences, 041 67 KOSICE, Slovakia
erika.ferrari@unimore.it

The accumulation of amyloid-beta (Aβ) aggregates as soluble oligomers and senile plaques in brain are key landmarks for Alzheimer's disease (AD) and their presence can be exploited as a selective target for diagnostic and therapeutic drugs [1]. Recently, several studies revealed that curcumin has high affinity for Aβ-amyloid plaques *in vitro* and *in vivo* and anti-AD properties due to its ability to bind and subsequently disrupt the aggregation of amyloid peptide and fibrils. Therefore, radio-labelled curcumin derivatives could be potential biomarkers for imaging of Alzheimer's disease by means of nuclear medicine imaging techniques. In this study, new curcuminoids are used as chelating agents to bind radiometals suitable for nuclear medicine applications. If compared with fluorine-18 and technectium-99m, gallium-68 exhibits advantageous features, being a generator produced positron emitter radionuclide with characteristics suitable for diagnostic nuclear medicine and direct labelling of biomolecules (89% β^+, maximum energy = 1.92 MeV; $T_{1/2}$ = 67.7 min), hence it was selected to label curcumin derivatives. Our aim is to investigate the biological properties *in vitro* of $^{nat/68}$Ga-curcuminoids complexes exploiting both the intrinsic fluorescence of these derivatives and the radioactive properties of gallium-68. The results will give insight into the possibility to employ these compounds as radiotracer for monitoring the presence of Aβ-amyloid plaques *in vivo* by positron emission tomography.

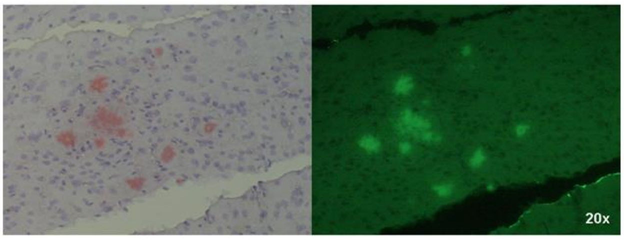

Figure 1. Micrographs of hippocampal sections showing Aβ-amyloid plaques stained with Ga-curcuminoids complexes (right panel) and Congo-Red (left panel).

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Macrocyclic thallium(III) complexes as potential diagnostic radioisotope carriers

Tamás FODOR, **Gyula TIRCSÓ**, **Imre TÓTH**

University of Debrecen, Department of Inorganic and Analytical Chemistry, Egyetem tér 1.,
4032 DEBRECEN, Hungary
tamas.fodor@u-bourgogne.fr

Metal complexes of macrocyclic polyamino-polycarboxylate-based ligands, with the ability to bind additional anions as ternary complexes have the potential to serve as diagnostic in vivo radio-isotope carriers: Al(III)–organic ligand–$^{18}F^{-}$compounds were introduced recently and promising results were reported [1]. Analogously to the interaction between the hard Al(III) and F^{-} ions, similar ternary complexes of the soft Tl(III) may be used to bind I^{-} ions [2]. The $[Tl(dota)]^{-}$ complex (dota=1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) was initially thought to be a good candidate as it has shown to be quite robust in solution. The Tl(III) in this complex does not possess a free coordination site however, only forming a labile ternary complex with cyanide ions [3]. Tl(III) complexes of ligands with fewer donor groups, such as do3a, pcta, aazta, *t*do2a, *c*do2a were screened but only [Tl(*c*do2a)]$^{+}$ was found to form ternary complexes with I^{-} ions as evidenced by ^{205}Tl-NMR. Solution equilibrium properties and iodide-binding ability of [Tl(*c*do2a)]$^{+}$ were studied with multinuclear NMR, UV-vis spectroscopy and potentiometry, stability and kinetic data on the two complexes will be presented.

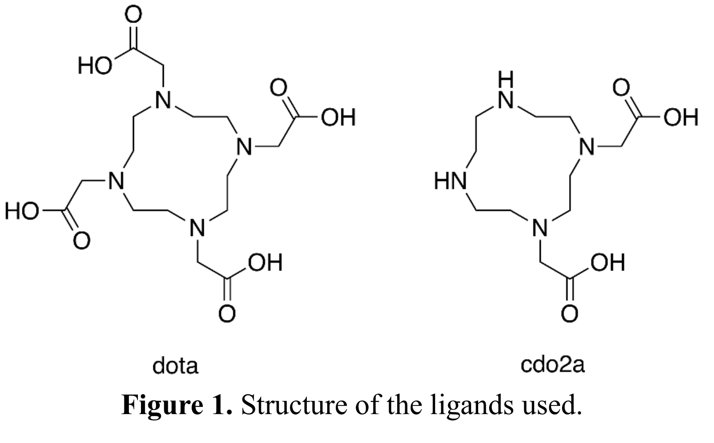

Figure 1. Structure of the ligands used.

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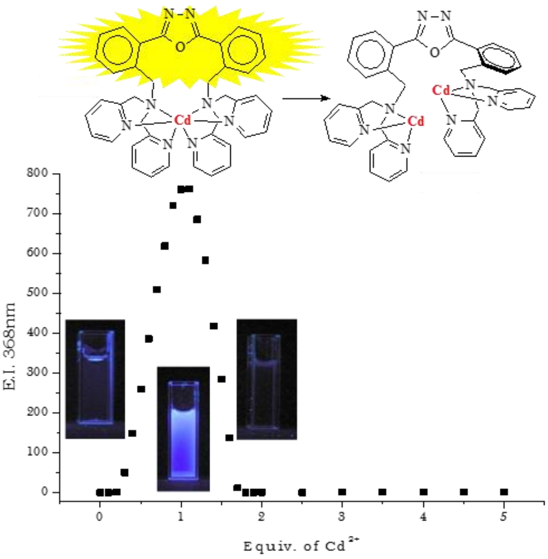
PPD-based chemosensors to selective sensing of cadmium

Gianluca AMBROSI, a) Mauro FORMICA, a) Vieri FUSI, a) Luca GIORGI, a)
Alessandra GARAU, b) Vito LIPPOLIS b)

a) [a]Department of Pure and Applied Sciences, University of Urbino, via della Stazione, 4
61029 URBINO, Italy
b) Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, S.S. 554
Bivio per Sestu, 09042 MONSERRATO, Italy
mauro.formica@uniurb.it

Cadmium is a toxic metal for animals and man as it does not have a biological role in these species. The toxicity of cadmium continues to be a significant public health; in this context, the determination of Cd(II) ion in all systems is a challenge as well as the design and synthesis of non-invasive sensors suitable to easy detect its level. In particular, the development of selective fluorescent chemosensors for Cd(II) is attractive because the fluorescence is a fast, simple and non-invasive analytical method particularly suitable for *in vivo* applications. Recently we reported the synthesis and spectroscopic properties of a class of macrocyclic ligands incorporating the 2,5-diphenyl[1,3,4]oxadiazole (PPD) fluorophore in their macrocyclic skeleton, in which the donor atoms of the coordinating part was nitrogen and/or sulfur [1,2]. The insertion of PPD allowed a drastic improvement in the fluorescence quantum yield of these ligands over most of those already known. The coordination of suitable metal ions at the macrocycle unit changed the UV-vis and the emission properties of the PPD. Here, we describe three new open structured symmetrical ligands based on PPD, in which two coordinating polyamine side arms are spaced by the PPD fluorophore. The flexible topology allows to recognize Cd(II) ion in aqueous solution at physiological pH = 7.4 switching ON the fluorescence which is further modulated by the stoichiometry of the complex formed.



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Competition between luminescence of a lanthanide complex and singlet oxygen generation: Careful choice of the lanthanide atom

Margaux GALLAND, [a] **Jeanne CRASSOUS**, [b] **Cyrille MONNEREAU**, [a]
François RIOBÉ, [a] **Fabrice POINTILLART**, [b] **Boris LE GUENNIC**, [b]
Olivier MAURY, [a] **Chantal ANDRAUD** [a]

a) *Laboratoire de Chimie de l'ENS de Lyon (UMR CNRS 5182),*
46 allée d'Italie, 69007 LYON, France
b) *Institut des Sciences Chimiques de Rennes (ISCR, UMR CNRS 6226),*
Avenue Général Leclerc, 35700 RENNES, France
margaux.galland@ens-lyon.fr

Lanthanide complexes are well known for their use in luminescence for bioimaging purposes and the emission of light can be achieved thanks to an energy transfer from an antenna to the lanthanide ion [1]. It has already been observed that the intensity of the lanthanide luminescence can be dependent of the concentration in oxygen dissolved in the media [2-3]. Indeed, the triplet state of the antenna can either transfer its energy to the emissive level of the lanthanide ion, emit light through phosphorescence or react with oxygen to generate singlet oxygen or. All these processes are competitive and therefore an optimization of the system can be achieved thanks to a careful choice of the lanthanide ion depending on which of those properties (luminescence or singlet oxygen generation) is desired.

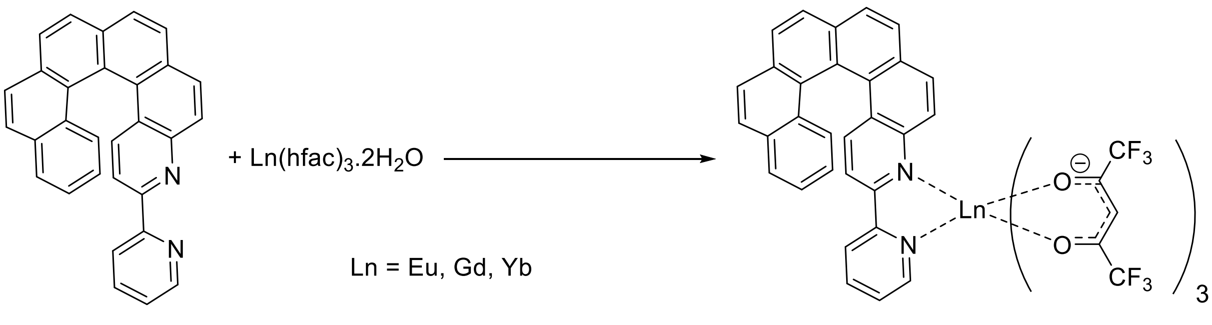

Figure 1. Synthesis of the family of lanthanide complexes studied [4].

We present a study based on a family of complexes composed of a helicen ligand and two hexafluoroacetylacetone (hfac) ligands which are coordinated to a lanthanide ion as shown in Figure 1 [4]. Those complexes are able to emit light through the emissive lanthanide but also helicen ligand by fluorescence or phosphorescence. They can also act as a photosensitizer and generate singlet oxygen. The question we aim to answer now is: "can we favor one of these deactivation pathways with a careful choice of the lanthanide metal?" To that aim, the complete photophysical study of this series of complexes has been achieved and will be presented.

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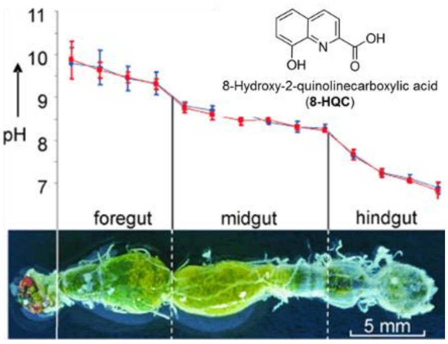
8-Hydroxyquinoline-2-carboxylic acid and the iron metabolism on the gut of *Spodoptera littoralis*: A thermodynamic approach

Sofia GAMA, [a] **Mariachiara FRONTAURIA**, [a] **Jan Frieder MOHR**, [a]
Thomas WICHARD, [a] **Demetrio MILEA**, [b] **Wilhelm BOLAND**, [c] **Winfried PLASS** [a]

[a] *Institute für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, JENA, Germany*
[b] *Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, MESSINA, Italy*
[c] *Max-Planck-Institut für Chemische Ökologie, JENA, Germany*
sofia.gama@uni-jena.de

The absorption of fundamental micronutrients as iron, occurs mainly in the digestive tract (gut), being done by a rich and complex community of microorganisms (microbiota). This community is highly influenced by the composition and the nutritional value of the ingested food. In particular, the amount of iron in the diet directly influences the population of microbiota. Moreover, the microbiota itself may also alter host iron metabolism [1,2].

For a better understanding of the iron metabolism regulation, special attention has been given to the study of microbiota of *Spodoptera littoralis*. Recent studies show that the gut of *S. littoralis* and some other lepidopterans contains large amounts of the iron chelator 8-hydroxyquinoline-2-carboxylic acid (8-HQC), mainly biosynthesized during the larval stage. Since 8-HQC is a strong siderophore, it may act as a natural metal-binding chelator that affects the iron-availability thereby controlling microbial growth [3].



The pH profile in the gut of *Spodoptera littoralis* [3]

In order to gain new insight on how 8-HQC influences, affects, changes and/or tunes iron availability of iron in the gut, we investigated the thermodynamic parameters of the $Fe^{2+/3+}$-8-HQC system and we evaluated the species distribution considering the already known pH profile and the 8-HQC concentration in the gut of *S. littoralis.*

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Interaction of DNA with the 1,10-phenanthroline-5,6-dione (phendione) ligand of the Ir(III) [Ir(ppy)$_2$(phendione)]Cl complex

**Carolina MONZÓN, Begoña GARCIA, José M. LEAL, Gustavo ESPINO,
Jairo FIDALGO, Natalia BUSTO**

University of Burgos, Plaza Misael Bañuelos, 09001 BURGOS, Spain
begar@ubu.es

Phenanthroline derivatives have attracted growing interest due to their potential activity against cancer, and viral, bacterial, and fungal infections [1]. In contrast to cisplatin, intercalating ligands, such as phenanthrolines and their metal complex derivatives, interact with DNA by aromatic π stacking between base pairs [2]. This interaction results in lengthening, stiffening, and unwinding of the helix [3]. Cytotoxic activity of phendione (1,10-phenanthroline-5-6-dione) and its Ir(III) complex([Ir(ppy)$_2$(phendione)]Cl) (Figure 1) over a cancerous colon cell line (SW480) was evaluated by means of the MTT assay. The values obtained for IC$_{50}$ (drug concentration yielding 50% survival cells) reveal that these compounds have a better antitumour effect than that observed for the well-known metal based anti-cancer agent, cisplatin. Therefore, the DNA binding ability of these compounds was studied in depth by firstly assessing their behaviour under the working conditions to avoid misinterpretations. To a second place, the interaction of these phenanthroline derivatives with calf thymus DNA (ct-DNA) has been studied by circular dichroism and absorbance spectrophotometry, differential scanning and isothermal titration calorimetry, agarose gel electrophoresis and viscosity measurements. The sets of results gathered allows one to discard groove binding and intercalation as the DNA modes of binding. The external binding is the most plausible mode of interaction with binding constants of $(1.066 \pm 0.1543)\cdot 10^7\ M^{-1}$ for phendione/ctDNA and $(6.05 \pm 0.71)\cdot 10^5\ M^{-1}$ for the Ir(III)complex/ctDNA. Thus, the metal complex displays less affinity than the ligand even if the conformational changes induced are more pronounced.

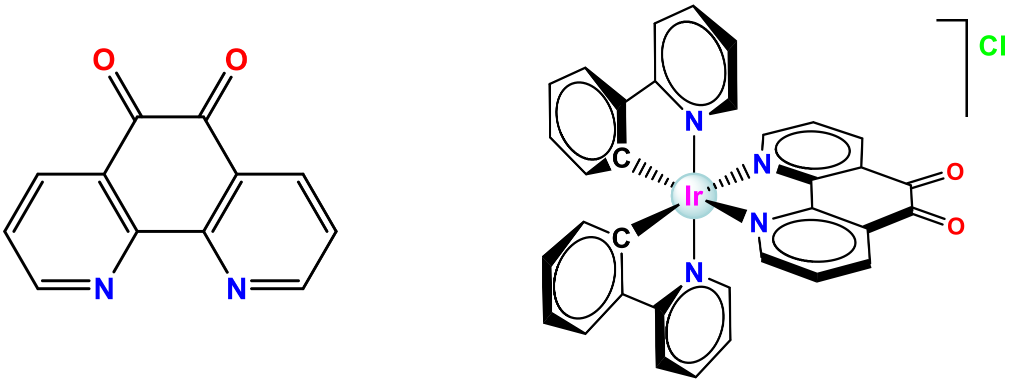

Figure 1. (Left) 1,10-phenantrolin-5,6-dione. (Right) [Ir(ppy)2(phendione)]Cl.

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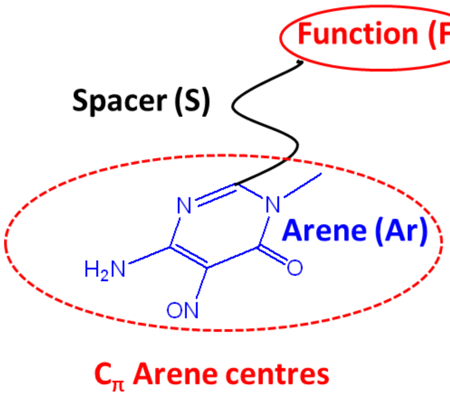
Anchored Pd(II)-complexes on MWCNTs: Preparation, characterization, and catalytic properties

Maria Luz GODINO-SALIDO, [a] **Maria Dolores GUTIÉRREZ-VALERO**, [a]
Maria Dolores LÓPEZ DE LA TORRE, **Manuel J. PÉREZ-MENDOZA**, [b]
Paloma ARRANZ-MASCARÓS [a]

[a] *Department of Inorganic and Organic Chemistry, Faculty of Experimental Sciences, University of Jaén, 23071 JAÉN, Spain*
[b] *Department of Inorganic Chemistry, Faculty of Sciences, University of Granada, 18071 GRANADA, Spain*
mlgodino@ujaen.es

Since their discovery by Iijima and Ichihashi [1] there has been a considerable interest in exploring the applications of the astonishing structural, electrical and mechanical properties of carbon nanotubes (CNTs) in different fields such as nanobiotechnology, material science and technological processes. In this context, it is noteworthy the growing interest of the usage of CNTs as either catalysts or catalyst supports in a great number of technological processes [2], due to their chemical stabilities, surface features and high adsorptivities. The suitable control of the surface chemistry of CNTs is a crucial issue to be considered in the preparation of new CNTs-based catalysts. Thus, the aim is to have catalysts with suitable amounts of surface-active sites homogeneously distributed.

Here we present the preparation and characterization of novel Pd(II)-based catalysts obtained by the anchorage of designed Pd(II)-complexes on commercial multiwalled carbon nanotubes (MWCNTs, Ref. NC3100^{TM}) provided by the company Nanocyl S.A. Molecules of Ar-S-F type (Scheme 1) were grafted on the MWCNTs by π–π stacking interactions between their Ar moiety and the graphene centers of the MWCNTs, thus favoring the retaining of the metal-complexing ability of F. Adsorption of Pd(II) by the MWCNTs/Ar-S-F hybrids occurs *vía* Pd(II)-complexation by F, resulting in materials with a homogeneous distribution of Pd(II) catalytic centres. It has been proved that the obtained materials can act as efficient catalysts on the hydrogenation of 1-octene. After being recovered by filtration, the catalysts have been reused in three additional reaction cycles without significant loss of activity. Formation of Pd(0) nanoparticles after the use of the catalysts has been observed.



Scheme 1

Acknowledgements: the support of the MINECO (Projects MAT2014-601404-C2-1-R and MAT2014-60104-C2-2-R), the Autonomous Regional Government (Junta de Andalucía, Groups PAIDI FQM273 and RNM342) and the University of Jaén (EI-FQM6_2017) is acknowledged.

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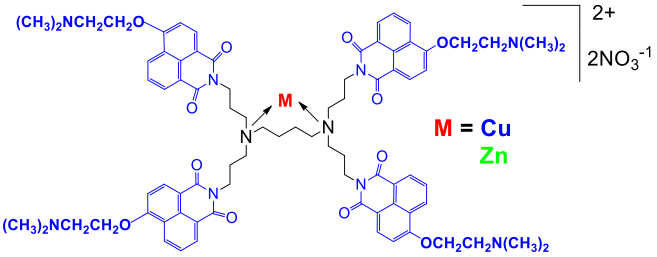
Synthesis, characterization and antimicrobial activity of blue fluorescent metallodendrimers

Desislava GRABCHEVA, [a] **Evgenia VASILEVA-TONKOVA**, [b] **Ivo GRABCHEV** [c]

[a] *University of Chemical Technology and Metallurgy, 1756 SOFIA, Bulgaria*
[b] *Institute of Microbiology, Bulgarian Academy of Sciences, 1113 SOFIA, Bulgaria*
[c] *Sofia University "St. Kliment Ohridski", Faculty of Medicine, 1407 SOFIA, Bulgaria*

In contemporary society, bacterial infections pose great challenges to human health, especially those caused by strains resistant to the antibiotics used in the classical medical practice. Therefore, there is a significant need for new more effective antimicrobial agents with different chemical structure and mechanisms of action against existing bacterial and fungal strains. In this direction, many investigations have focused on the synthesis of new metal complexes with various organic ligands as potential antimicrobial agents. On the other hand, the design and synthesis of specific ligands, which can coordinate with metal ions, is a major goal of many research groups because the biological activity of the metal complexes depends on the nature of the metal ions, the chemical structure of the ligands and the type of the relationship between them.

Two novel metal complexes of Cu(II) and Zn(II) ions with PPA dendrimer from first generation previously modified with four 4-(*N,N*-dimetylaminoethoxy)-1,8-naphtalimide units in the dendrimer periphery were synthesized and analyzed with different spectral and analytical methods.



One metal ion was determinated that coordinate with one dendrimer. Metal ions Cu(II) and Zn(II) didn't influence strongly the photophysical characteristics of dendrimer.

The results from microbiological investigations indicated that the new PPA dendrimer and its Cu(II) and Zn(II) complexes possess good antimicrobial activity, particularly against Gram-positive bacteria and yeasts thus expanding the potential biological application of the dendrimers. Significant activity of the samples comparable to that of the control drug was observed against *S. lutea*, with MICs of 3.82 ÷ 510 μM for dendrimer D and $[Cu(D)(NO_3)_2]$, and 6.40 ÷ 9.55 μM for $[Zn(D)(NO_3)_2]$ complex. Preliminary tests demonstrated antibacterial activity of the studied compounds released from the polymer polylactic acid matrix.

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Energy transfers in donor-acceptor dyads built upon a truxene core

Claude P. GROS, [a)] **Nicolas DESBOIS,** [a)] **Hai-Jun XU,** [a,b)] **Adam LANGLOIS,**[c)]
Paul-Ludovic KARSENTI, [c)] **Pierre D. HARVEY** [c)]

[a)] *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),*
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[b)] *College of Chemical Engineering, Nanjing Forestry University, NANJING, P.R. China*
[c)] *Université de Sherbrooke, Département de Chimie, 2500 boulevard de l'Université,*
J1K 2R1 SHERBROOKE, Canada
claude.gros@u-bourgogne.fr

Several donor-acceptor dyads built upon a central truxene core are assembled and studied from a photophysical standpoint in order to examine their photo-induced energy transfer properties. These dyads are composed first of a Zn(II)-porphyrin donor and free-base porphyrin acceptor [Zn-Fb$_2$] (Figure 1). Second a BODIPY donor and Zn(II)-porphyrin acceptor [BOD-Zn2]. Third a Pd(II)-porphyrin donor and Zn(II)-porphyrin acceptor [Pd-Zn$_2$]; and finally a Zn(II)-porphyrin donor and free-base corrole acceptor [Zn-COR$_2$]. The findings of the photophysical analysis show that the Dexter double electron transfer plays an important role in the energy transfer process despite the long distance between chromophores. This conclusion indicated that the truxene core serves as a conjugated "wire" between chromophores providing a significant orbital overlap between the donor and acceptors. This overlap then allows for a double electron exchange to occur through the truxene bonds allowing us to conclude that truxene can in fact be used as a small scale, soluble model for graphene which is notoriously well known for its excellent conductivity properties.

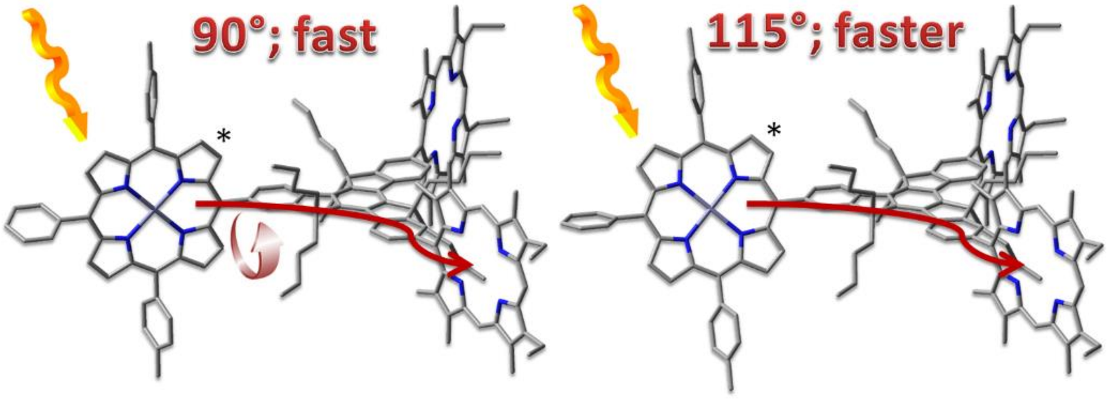

Figure 1

Acknowledgments: the "Consulat Général de France à Québec" and "Programme de Samuel de Champlain 2015/2016" are acknowledged for funding.

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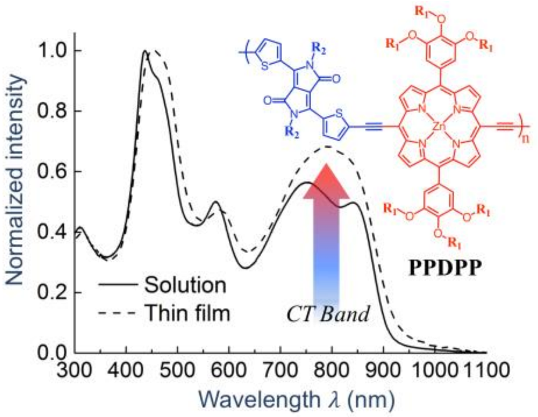
A very low bandgap (diketopyrrolopyrrole-zinc porphyrin) conjugated polymer

Claude P. GROS, [a] Léo BUCHER, [a,b] Loïc TANGUY, [b] Daniel FORTIN, [b]
Nicolas DESBOIS, [a] Pierre D. HARVEY, [b] Ganesh D. SHARMA [c]

[a] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[b] Université de Sherbrooke, Département de Chimie, 2500 boulevard de l'Université,
J1K 2R1 SHERBROOKE, Canada
[c] Department of Physics, LNM Institute of Information technology, JAIPUR, India
claude.gros@u-bourgogne.fr

A zinc porphyrin-diketopyrrolopyrrole-containing polymer (PPDPP) was synthesized. It shows impressive molar absorption coefficients from 300 to 1000 nm. Its photophysical and structural properties have been studied. When the PPDPP is used as electron donor along with PC71BM as electron acceptor, the bulk heterojunction polymer solar cell showed overall power conversion efficiency of 4.18% and 6.44% for as cast and two step annealing processed PPDPP:PC71BM (1:2) active layers respectively. These results are quite impressive for porphyrin-containing polymers, especially when those are directly included in the π-conjugated backbone, and offer interesting perspectives for the design of new materials based on this chromophore.



Acknowledments: the "Consulat Général de France à Québec" and "Programme de Samuel de Champlain 2015/2016" are acknowledged for funding.

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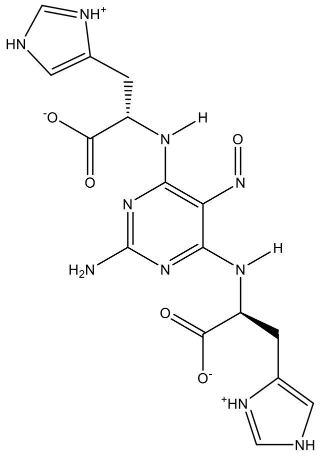
Non covalent functionalization of graphitized CNT surface with Cu(II) and Pd(II) complexes of L-histidine

Maria Dolores GUTIÉRREZ-VALERO, [a] **Celeste GARCIA-GALLARÍN**, [a]
F. Javier LÓPEZ-GARZÓN, [b] **Maria CAMARA-MORAL**, [a]
Rafael LÓPEZ-GARZÓN [a]

[a] Department of Inorganic and Organic Chemistry, Faculty of Experimental Sciences,
University of Jaen, Campus Las Lagunillas, s/n, 23071 JAÉN, Spain
[b] Department of Inorganic Chemistry, Faculty of Sciences, University of Granada,
Avda. de Fuente Nueva, s/n, 18071 GRANADA, Spain
mdgutie@ujaen.es

The special structure of graphene provides some unique properties to this material. The non-covalent functionalization of the graphene surface has the advantage that it does not affect the π-electron system of the former which is responsible of most of such properties. In this way, the possible synergy of the electronic properties of the added function and the π-electron system of the graphene moiety, represent a suitable way to control the properties of the functionalized graphene. E.g., the phototransference of electrons from the surface added-function to the conduction band of the graphene surface (or vice versa) makes these hybrids potential photocatalysts, including water splitting [1]. On the other hand, Cu(II) and Pd(II) complexes with suitable ligands act as active centers in various catalytic processes.

Having the above in mind, as a probe we have functionalized the graphene (folded) surface of graphitized carbon nanotubes (CNTs) by adsorbing Cu(II) and Pd(II) complexes of L-Histidine. For this, a two- step procedure implying non-covalent interaction of the metal-complex function with the graphene surface of the CNTs was used, as follows: *i*) firstly, a complexing water-soluble function, H_2L, bearing two histidine moieties (Scheme 1) was adsorbed on the CNT surface *via* π-π interaction of the pyrimidine moiety of the former with the folded graphene surface of the CNTs. The optimum conditions for this process were fit by studying the influence of pH on the adsorptivity and the stability of the CNTs/H_2L hybrids in water and this was determined by carrying out adsorption and desorption experiments. *ii*) By using the obtained CNT/H_2L hybrid as adsorbent for Cu(II) and Pd(II) metal ions in water solution, in (previously determined) suitable experimental conditions, they were achieved CNT/H_2L-Metal ion materials. Full characterization of these materials demonstrated that the adsorption of metal ions of CNTs/H_2L hybrids in selected conditions takes place by complexation with the histidine residues. Electrical conductivities and the absorption spectra of both pristine and functionalized CNTs have been also measured.



Scheme 1. Structure of H_2L.

Acknowledgements: the support of the MINECO (Projects MAT2014-601404-C2-1-R and MAT2014-60104-C2-2-R), the Autonomous Regional Government (Junta de Andalucía, Groups PAIDI FQM273 and RNM342) and the University of Jaén (EI-FQM6_2017) is acknowledged.

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Ampicillin-intercalated layered zinc hydroxide as a novel antibacterial nanocomposite

Moayad HOSSAINI SADR, **Hafezeh NABIPOUR**

Chemistry Department, Faculty of Science, Azarbaijan Shahid Madani University, TABRIZ, Iran hosainis@yahoo.com

LHSs are layered crystalline materials with unique properties because of their easily exchangeable interlayer anionic species [1]. Layered zinc hydroxide (LZH) is a layered hydroxide salt with the formula of $Zn_5(OH)_8(NO_3)_2.2H_2O$, and 1/4 of the octahedrally coordinated zinc atom sites are vacant and on either side of the empty octahedral. Meanwhile, there are Zn atoms tetrahedrally coordinated by OH groups, forming the base of a tetrahedron. Besides, the coordinated water molecules occupy the apex of the tetrahedrons, and the uncoordinated nitrate groups are located between the sheets of LZH [2]. Various methods have been reported for synthesis of LZH, such as urea hydrolysis [3], precipitation with alkaline solutions [4], and solid state reaction [5]. LZHs can act as host matrices for the intercalation of organic drugs to form nanocomposites. These layered nanocomposite materials usually show higher biocompatibility, better half-lives and improved drug solubility with controlled-release capability, and lower systemic side effects than the organic drugs. Ampicillin was intercalated in LZH by ion-exchange method. The resulted PXRD studies indicate that the drug was successfully intercalated into the interlay space of LZH as a mono layers and the basal spacing of LZH increased from 9.72 Å to 19.40 Å (Figure 1). The FTIR analyses confirmed the formation of the host–guest nanohybrid. The DTG studies revealed that the thermal stability of anion was increased after the intercalation into LZH. Antibacterial activity of the amoxicillin-LZH was also studied by an *in-vitro* test, such as the minimal inhibitory concentration (MIC) by agar dilution method. The results showed that the drug-LZH nanohybride has good inhibition against Gram-positive and Gram-negative bacteria.

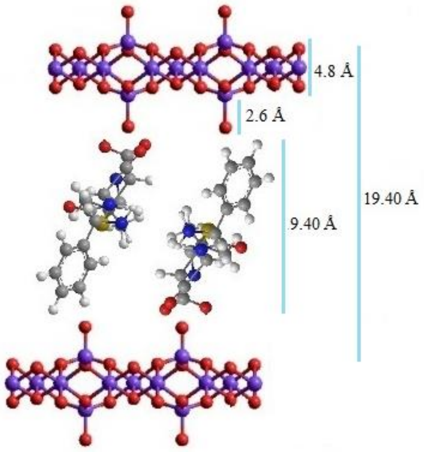

Figure 1. Spatial orientation of amoxicillin after intercalation.

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Bis-3-hydroxy-4-pyridinones: From the synthesis to the complexation with Al^{3+} and Fe^{3+} and the biological assays

Anna IRTO, [a] **Karam CHAND**, [b] **Rosalia Maria CIGALA**, [a] **Francesco CREA**, [a]
Lurdes GANO, [c] **Concetta DE STEFANO**, [a] **Silvio SAMMARTANO**, [a]
Maria Amélia SANTOS [b]

[a] *Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università di Messina, Viale F. Stagno d'Alcontres 31, 98166 MESSINA, Italy*
[b] *Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovísco Pais 1, 1049-001 LISBOA, Portugal*
[c] *Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 BOBADELA LRS, Portugal*
airto@unime.it

This contribution is the result of a work of synthesis of two new bis-3-hydroxy-4-pyridinones (called *DTPAPr(3,4-HP)₂* and *NTAPr(3,4-HP)₂*), derivatives of *DTPA* and *NTA,* and of the results of an investigation on their acid-base properties and binding ability towards trivalent metal cations namely Al^{3+} and Fe^{3+} in aqueous solution. Also some biological *in vivo* assays were carried out on mice. The 3-hydroxy-4-pyridinones (3,4-HPs) are derivatives of Deferiprone and represent a good alternative to the use of Deferoxamine in the chelating therapy for the detoxification of the human body from hard metal cations (*e.g.* Al^{3+}, Fe^{3+}), because they are effective at physiological conditions and do not involve significant undesired effects [1,2]. The 3,4-HPs can be synthesized from maltol for a reaction of protection of the –OH group with a benzyl group, followed by a double Michael-type addition. The compounds can be further derivatized with the formation of amide bonds. A deprotection of the hydroxyl group with a reaction of hydrogenation, catalyzed by 10% Pd/C concluded the synthetic procedure [3].

The synthetic work was performed during a period of research at the Centro de Química Estrutural of Instituto Superior Técnico of the Universidade de Lisboa. The study of their acid-base properties was carried out by UV-Vis spectrophotometry and spectrofluorimetry, at different experimental conditions. The protonation constants determined showed a good agreement between the two analytical techniques and with the data already reported in the literature for similar ligands [4,5].

The binding ability of *DTPAPr(3,4-HP)₂* and *NTAPr(3,4-HP)₂* towards Al^{3+} and Fe^{3+} was investigated by UV-Vis spectrophotometric and potentiometric measurements at $I = 0.15$ mol L^{-1} in $NaCl_{(aq)}$ and $T = 298.15$ K. The speciation models obtained consists of $M_pL_qH_r$ complexes with different stoichiometry, such as protonated, simple metal-ligand, hydrolytic mixed and polynuclear species.

Furthermore, the sequestering ability of the ligands towards the metal cations was studied by the determination of an empirical parameter, the $pL_{0.5}$, previously proposed by the research group [6], which represents the total concentration of ligand necessary to sequester the 50% of the metal cation present in trace in solution.

Finally, *in vivo* assays were performed to verify the absence of toxicity of *DTPAPr(3,4-HP)$_2$* and *NTAPr(3,4-HP)$_2$* and their ability for metal sequestration, if administered to mice preloaded with the radiotracer ^{67}Ga–citrate. Biodistribution studies indicate that these ligands have high *in vivo* chelating ability promoting the rapid elimination of the radiometal from the animal body.

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Polyoxopalladate / tungstate hybrids: Targets for molecular spintronics

Natalya V. IZAROVA, [a)] **Paul KÖGERLER** [a,b)]

[a)] *Peter Grünberg Institute, Electronic Properties (PGI-6), Forschungszentrum Jülich, 52425 JÜLICH, Germany*
[b)] *Institute of Inorganic Chemistry, RWTH Aachen University, 52074 AACHEN, Germany*
n.izarova@fz-juelich.de

Chemistry of palladium-containing polyoxometalates (POMs, discrete polynuclear oxo complexes of transition metals) has experienced an impressive development over the past ten years [1]. In particularly, a novel subclass of POMs built by square-planar Pd^{II} addenda ions has been discovered [1-2]. Here we report on a first series of hybrid polyanions composed by both tungsten(VI) and palladium(II) addenda. These species possess various nuclearity and structures and represent a logical link between "classical" complexes of Pd^{II} ions coordinated to polyoxotungstates and novel subclass of POMs, polyoxopalladates [4]. Solution behavior and potential application of new compounds as precursors for electrical contacts in molecular electronic / spintronic devices will be also discussed.

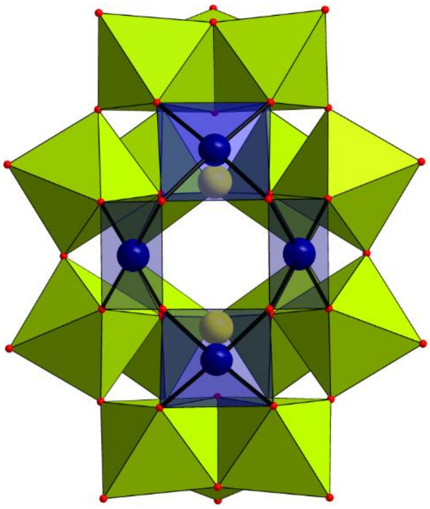

Figure 1. Structure of $[\gamma\text{-}Pd^{II}_4Se_2W_{14}O_{56}]^{12-}$. Color legend: WO_6 lime green octahedra, PdO_4 blue square; Se yellow, O red spheres.

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Conformation determination of the vanadium complexes of human serum transferrin by SAXS

Tamás JAKUSCH, [a] **Dániel SEBŐK**, [b] **Imre DÉKÁNY**, [b] **Tamás KISS** [a,c]

[a] Analytical and Inorganic Chemistry Department, University of Szeged, Dóm tér 7, 6720 SZEGED, Hungary
[b] Department of Physical Chemistry and Materials Science, University of Szeged, Tisza Lajos krt. 84-86, 6720 SZEGED, Hungary
[c] HAS-USZ Bioinorganic Chemistry Research Group, Analytical and Inorganic Chemistry Department, University of Szeged, Dóm tér 7, 6720 SZEGED, Hungary
jakusch@chem.u-szeged.hu

Vanadium compounds were considered as potential oral drugs for patients with diabetes mellitus, mostly neutral bis complexes of $V^{IV}O$ with bidentate organic ligands ("carrier ligands" e.g. maltol / picolinate) have been studied [1]. The Phase I clinical trial [2] of bis(ethylmaltolato) oxovanadium(IV) (BEOV) was completed in 2000, and the results of the Phase IIa clinical trial were first published in 2009 [3]. Among the many aspects of this field, focus was placed primarily on the possible biotransformation of the drug candidate vanadium compounds in the body, from the gastrointestinal tract to the target cells [4].

The oxidation states $V^{IV}O$ and V^{V} are both relevant as concerns the biochemistry of vanadium in the blood, but the reducing agent content (e.g. ascorbic acid and cysteine) is theoretically adequate to effective reduction of V^{V} to $V^{IV}O$ [1]. Under therapeutically relevant conditions ($c_V \leq 10$ μM), vanadium in oxidation state IV and V is bound to apoTf (or Tf in the blood) solely at the Fe^{III} free binding sites; all the original carrier ligands are displaced. The results of modeling calculations, together with the results of the separation measurements and complemented with the pharmacokinetic observation that BEOV dissociates soon after oral gavage administration [1,5].

Human serum transferrin are iron-binding blood plasma glycoproteins that control the level of free iron (Fe) in serum, it contains two specific high-affinity Fe(III) binding sites and bind iron tightly, but reversibly. The amino acids residues which bind the iron ion to the transferrin are identical for both lobes; two tyrosines, one histidine, and one aspartate. For the iron (or other) ion to bind, an anion is required, preferably carbonate (HCO_3^-). Upon uptake and release of iron major structural changes take place in both lobes of human serum transferrin: the iron loaded molecule has a closed conformation while the iron-free protein adopts and "open" conformation. The function of the conformation change is that the affinity of the transferrin receptor for the diferric transferrin is 25 times higher than for apotransferrin. Under physiological conditions, only some of the 30% of serum transferrin are occupied, besides iron a variety of "non-physiological" metal ions are capable of specifically to the transferrin [6].

Solution X-ray scattering is particularly well suited for the detailed characterization of the overall size and conformation of macromolecules in solution, it can be used to define the conformational differences between the apo- and iron-transferrins. This technique can be applied for other metal ions also: e.g. Cu(II), In(III) and Al(III) seems to be induce conformational change, however Hf(IV) does not [6].

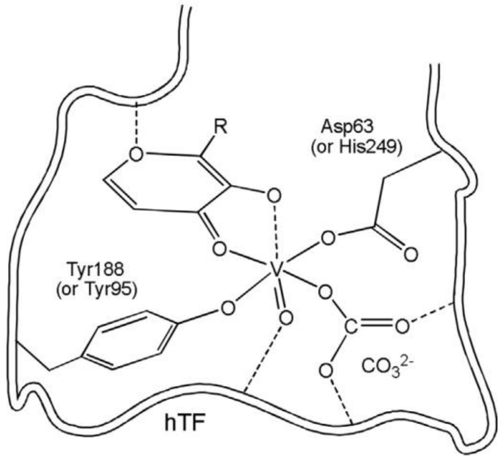

Figure 1. Theoretical binding mode of VO(IV) to apotransferrin.

It is a crucial question, whether the VO(IV)/V(V) ions is able to induce the conformation change or not, the human serum transferrin could be an effective transporter of the vanadium(IV)/(V) to the targeted cells or it behaves just a kind of “buffer”. Experimental facts, like no synergistic ion is need for the vanadium(V)-transferrin binding, the vanadium(IV)-transferrin complex is sensitive for oxygen, while the vanadium(III)-transferrin is not, suggested differences from the overall behavior. Our preliminary SAXS results seem to confirm that VO(IV)/V(V) do not induce conformational changes of the human serum transferrin upon binding; further experiments are still ongoing in our laboratory.

Acknowledgement: the research was supported by the National Research, Development and Innovation Office-NKFIH through project GINOP-2.3.2-15-2016-00038.

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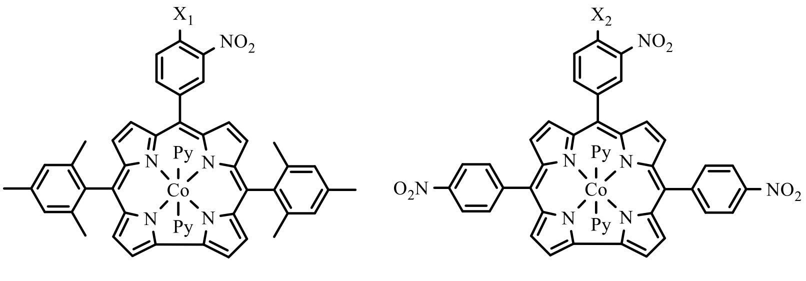
Electrochemistry of cobalt nitrophenylcorroles in nonaqueous media

**Xiaoqin JIANG, [a] Mario NAITANA, [b] Nicolas DESBOIS, [b] Claude P. GROS, [b]
Karl M. KADISH [a]**

*[a] Department of Chemistry, University of Houston, 4800 Calhoun Rd.,
HOUSTON TX 77204, USA*
*[b] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France*
jxiaoqin@uh.edu

Cobalt nitrophenyl corroles have been shown to undergo up to four oxidations and four reductions in nonaqueous media. Some occur at the conjugated macrocycle, some at the cobalt center which can exist in multiple oxidation states, and some at the *meso*-nitrophenyl groups of the compounds. As part of our continuing studies into elucidating the electrochemistry of corroles and related macrocycles, four newly synthesized cobalt corroles with 1-3 nitrophenyl groups on the *meso* positions of the macrocycle were characterized as to their electrochemical and spectroscopic properties in PhCN and pyridine. The structures of the investigated compounds are shown in Chart 1. The redox potentials for each electrode reaction were measured by cyclic voltammetry and spectra of the electroreduced and electroxidized forms of the corroles were obtained by thin-layer UV-vis spectroelectrochemistry. The effects of the solvent, macrocycle substituents and number of nitro groups on the *meso*-phenyl rings are discussed as they apply to reactions involving the **(i)** metal center, **(ii)** conjugated macrocycle and **(iii)** *meso* nitrophenyl groups.



1a **X_1 = F**
1b **X_1 = OMe**

2a **X_2 = F**
2b **X_2 = OMe**

Chart 1. Structures of investigated cobalt nitrophenyl corroles.

Structural study of novel coumarin-derived Schiff base complex with copper ions

Diana KALINOWSKA, [a] **Marcin KLEPKA**, [a] **Anna WOLSKA**, [a]
Aleksandra DRZEWIECKA-ANTONIK, [a] **Cristina Aparecida BARBOZA**, [a]
Elżbieta HEJCHMAN [b]

[a] *Institute of Physics Polish Academy of Sciences, Al. Lotników 32/46,*
02668 WARSAW, Poland
[b] *Medical University of Warsaw, Faculty of Pharmacy, Banacha 1, 02090 WARSAW, Poland*
diana.kalinowska@ifpan.edu.pl

Coumarin is a naturally occurring organic compound having a broad spectrum of biological activity. Thereby it can be used in the design of synthetic compounds that exhibit extensive pharmacological activity, i.e. anti-inflammatory, antioxidant, anticoagulants, antiviral, antibacterial, antihyperlipemic, hepatoprotective and anticarcinogenic or cytotoxic [1-4]. Schiff bases are the condensation products of carbonyl compounds and primary aromatic amines often used in the design of new therapeutic substances due to the formation of stable complexes with metal ions. Their complexes with transition metals are the subject of interest due to antimicrobial as well as anticancer activity. Restricting only to the connection with copper, Cu(II) complexes with coumarin derivatives show cytotoxic activity on tumor cells lines of human liver cancer (Hep62), human leukemia (HL60) and human prostate cancer (PC3). Cu(II) complexes with coumarin Schiff base derivatives were tested for antimicrobial activity on *Candida albicans* strains and showed activity comparable with popular antifungal drugs [5-9].

It is assumed that for bioactive compounds, the full structural characterization should be performed. The X-ray diffraction methods are commonly being applied for that purpose. However, quite often it is impossible to obtain a complex in a crystalline form. The use of aggressive solvents, in order to force crystallization, may cause structural changes. Therefore, to gather structural information about a complex X-ray absorption spectroscopy (XAS) is needed. This method is ideal to study compounds regardless of their crystal form or state. Extended X-ray absorption fine structure (EXAFS) analysis provides information about atom's local environment i.e. the number of atoms, their distance to absorbing atom as well as information about relative structural disorder. X-ray absorption near edge structure (XANES) is being called a fingerprint of chemical state of an element. It is sensitive to the spatial arrangements of the atoms around the absorbing atom and, as such, can provide information about coordination geometry around metal cation.

Our studies were focused on a novel bioactive copper complex synthesized from 7-hydroxy-8-[1-(4-methoxyphenylimino)ethyl]-4-methyl-2H-chromen-2-one. Both the ligand and its complex were tested for cytotoxic activity in vitro on tumor cell lines of human cervical cancer (HeLa), pancreatic cancer (CFPAC-1) and mouse melanoma cell *Mus musculus* (B16F10). For these compounds antitumor activity has been found.

EXAFS analysis revealed that the mononuclear complex is formed and the first coordination sphere of metal cation is composed of two oxygen and two nitrogen atoms. These information were used to construct structural models of studied complex. Next, the models were optimized with DFT algorithms and XANES spectra calculations.

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Mn^{2+} complexes of some 1,2-disubstituted-1,4,7,10-tetraazacyclododecanes: Thermodynamic, kinetic and relaxometric studies

Ferenc K. KÁLMÁN, [a] **Zoltán GARDA**, [a] **Szilvia LÓCZI**, [a] **Kristóf PÓTA**, [a]
Viktória NAGY, [a] **Tamás FODOR**, [a] **Do N. QUYEN**, [b] **Zoltán KOVÁCS**, [c]
Éva TÓTH, [d] **Imre TÓTH**, [a] **Gyula TIRCSÓ** [a]

[a] *University of Debrecen, Department of Inorganic and Analytical Chemistry, Egyetem tér 1,*
4010 DEBRECEN, Hungary
[b] *Department of Radiology,* [c] *Advanced Imaging Research Center, University of Texas*
Southwestern Medical Center, 5323 Harry Hines Blvd, DALLAS, TX 75390, USA
[d] *Centre de Biophysique Moléculaire, UPR CNRS 4301, rue Charles-Sadron,*
45071 ORLEANS Cedex 2, France
kalman.ferenc@science.unideb.hu

Over the past decades, research on novel Magnetic Resonance Imaging (MRI) Contrast Agents (CAs) has led to the development of structurally diverse ligands as well as the several metal ions as viable alternatives to Gd^{3+}. The Mn^{2+} ion with its half-filled electron shell and slow electron spin relaxation is an acceptable candidate for CA preparation. Mn^{2+} being an essential metal ion and biological systems have developed effective routes to control its homeostasis. However long exposure to large doses of Mn^{2+} salts results in its accumulation in the brain, leading to symptoms of dementia, resembling Parkinson's disease which is why the given metal ion can only be applied by using ligands capable of binding it in a stable, kinetically inert complex endowed with good relaxation properties. Macrocyclic ligands (e.g. NOTA and DOTA) were found to form stable and inert complexes with Mn^{2+}, but the absence of coordinated water molecule make these complexes poor relaxation agents (the denticity of these ligands is too high) [1]. By decreasing the number of donor atoms in DOTA it is possible to find monoaquated ($q = 1$) complexes (e.g. 1,4-DO2A or *cis*-DO2A), however "truncating" the DOTA ligand affects negatively the kinetic properties of the corresponding Mn^{2+} complexes [2]. With an aim to earn back some of the inertness lost on this avenue tricks known form the literature were applied to the given ligand platform. For instance, the replacement of negatively charged acetates in *cis*-DO2A for amide moieties (*cis*-DO2AM^{Me}) resulted in the formation of more inert complexes as evidenced by Prof. M. Botta and co-workers [3]. The *cis*-DO2AM^{Pyp} ligand was designed to improve further the kinetic properties as well as to get back at least partially the stability lost when the carboxylates in *cis*-DO2A were replaced by the amide pendant arms. While the results obtained for the *cis*-DO2AM^{Pyp} ligand are very promising the positive charge of its Mn^{2+} complex still needs to be addressed. Thus we have explored the use of steric hindrance applied at the side arms as a possible tool of improving the dissociation kinetic properties of the complexes. The *cis*-DO2MA ligand was found to form Mn^{2+} complex of similar stability (log K as well as pMn values) to that of [Mn(*cis*-DO2A)], whereas the acid catalyzed dissociation of [Mn(*cis*-DO2MA)] occurs considerably (nearly 6 times) more slowly than that of the [Mn(*cis*-DO2A)]. These findings make the given complex a very promising candidate for the development of safer alternatives to Gd-based MRI agents.

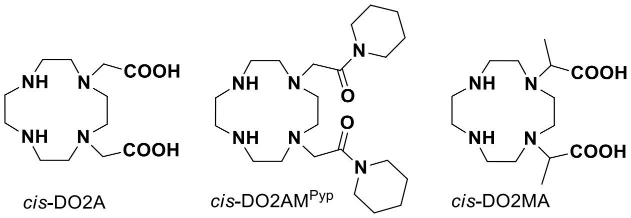

Figure 1. Formulae of the cis-DO2A, DO2MA and DO2AMPyp ligands studied.

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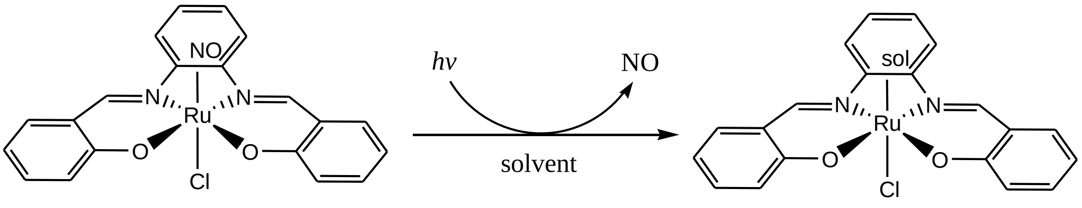
New series of photoactive NO-releasing ruthenium nitrosyl complexes

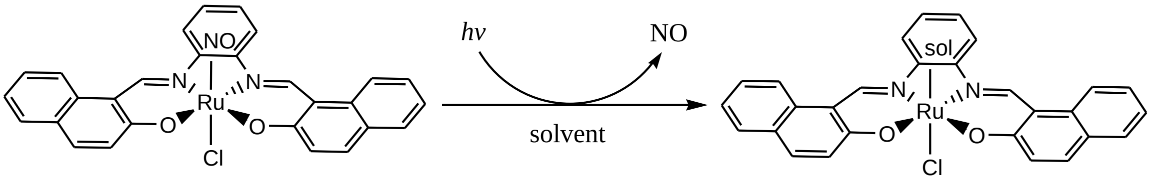
<u>Minyeong KIM</u>, Hong-In LEE

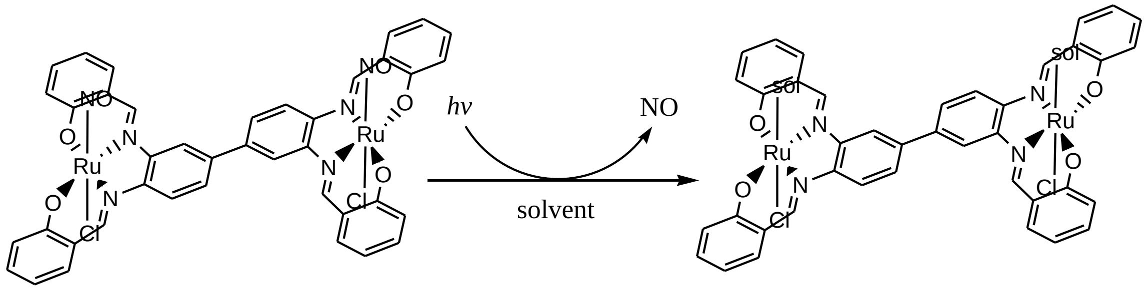
Department of Chemistry, Kyungpook National University, DAEGU 702-701, Korea
kmy2368@nate.com

Since the discovery of Nitric Oxide (NO) as one of the major signal-transduction molecules in cells, there have been many attempts to devise acute NO-delivering systems for the purpose of developing disease therapies as well as studying cell functions. Metal-nitrosyl complexes are often releasing NO by light activation. This ability can be adapted to killing cancer cells with high specificity because high concentration of NO in cells induces apoptosis. Among them, ruthenium nitrosyl complexes have been proposed as attractive photodynamic therapeutic agents in biomedicine and in tumor treatment.

This research aims at developing Ru-NO complexes which absorb long wavelength visible light to release NO with high quantum yield. Previously, we have developed a new Ru-NO bis-pyridyl/biscarboxamide compound, [Ru(III)(ebpp)(Cl)(NO)], where H_2ebpp = *N*,*N*'-(ethylene-di-*p*-phenylene)bis(pyridine-2-carboxamide), to be tested as a model NO-releasing agent. Here, we present the strategies to develop visible-light sensitive NO-releasing Ru complexes with higher quantum yield. We introduce new series of ligands, salophen and naphophen, to develop Ru-NO complexes. In this poster, we present UV-VIS and EPR data which can be interpreted as that the diamagnetic $[\text{Ru-NO}]^6$ electronic state of the complex becomes low-spin Ru(III) (d^5, S = 1/2) state upon losing NO by photoactivation.



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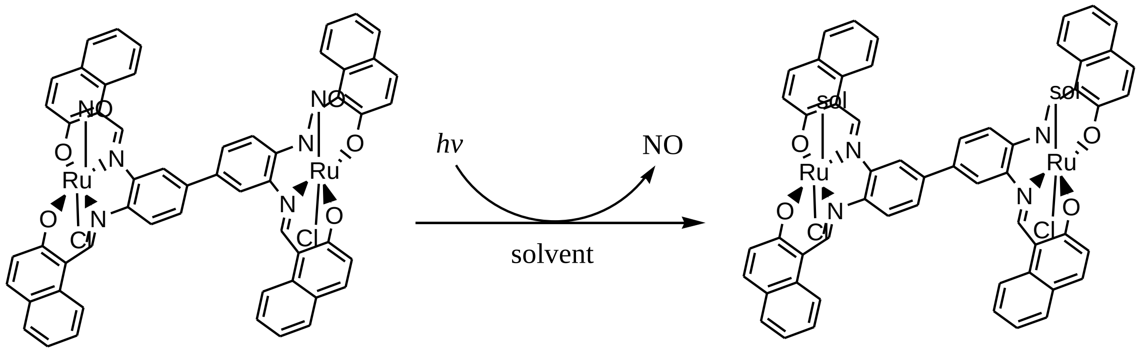
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Removal of heavy metals from aqueous solution using silica-supported biosorbents [exemplified for Ni(II)]

Moumin ADEN, [a,b] **Michael KNORR,** [b] **Jerome HUSSON,** [b] **Myriam EUVRARD** [b]

[a] Matériaux et Surfaces Fonctionnelles, Institut UTINAM UMR CNRS 6213, Université de Bourgogne-Franche Comté, 16 Route de Gray, 25030 BESANÇON, France
[b] Faculté des Sciences, Université de Djibouti, Avenue Djanaleh, DJIBOUTI 1904
michael.knorr@univ-fcomte.fr

Submicronic particles, functionalized by grafting or by encapsulation with bio-polyelectrolytes, open potential applications in applied sciences and diverse industrial sectors (use as composite coatings, as adsorbents, as water purification materials…). The preparation of these composites is based on the deposition of biomass-derived biopolymers such as chitosan (CS), carboxymethyl-chitosan (CM-CS) or alginate on SiO_2 [1-3]. Organo-mineral composites allow combining the properties of a mineral skeleton with the chemical reactivity of the organic functions present in these abundant and low-cost biopolymers. The aims of this research are (i) to functionalize and characterize submicronic composites by grafting, followed-up by encapsulating of colloidal silica or (ii) extrusion of alginate to study the capacities of these hybrid materials for the adsorption of toxic heavy metal ions from aqueous solutions.

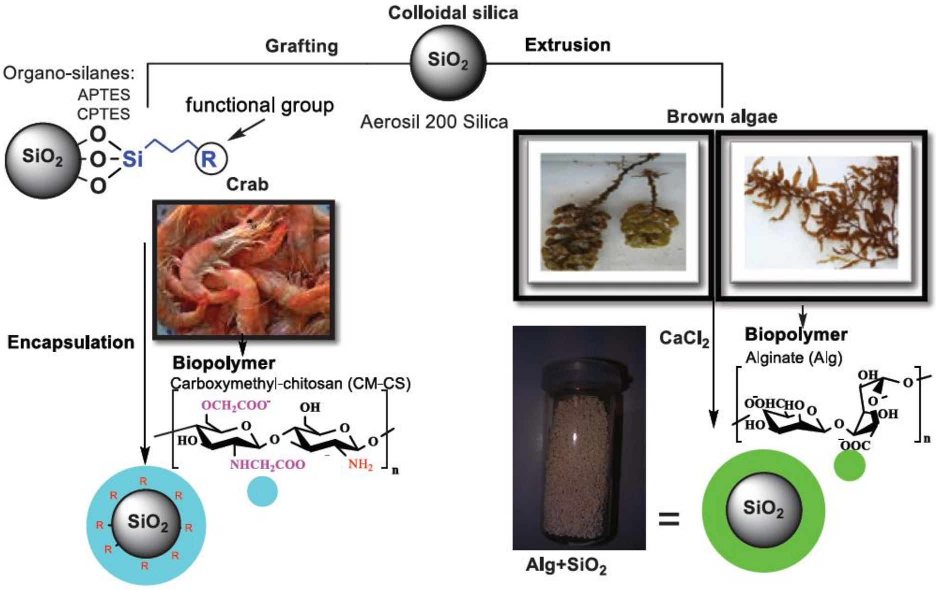

Figure 1. Strategies for the preparation of our biocomposites.

The composition and physicochemical properties of these materials were characterized by means of elemental analysis, nitrogen adsorption–desorption and FT-IR spectroscopy. The analytical data confirm the successful grafting of the biopolymers CM-CS and alginate on colloidal Aerosil 200 silica. The Ni^{2+} ion was chosen as model for divalent metal ions to evaluate the effectiveness of the new sorbents for wastewater treatment. The influence of hybrid particles doses, buffer pH, contact time and nature of the counter ion was assessed through batch experiments. The results point out a high adsorption capacity of the hybrid particles to complex Nickel (> 200 mg.g^{-1} of sorbent). The Sips and Redlich-Peterson isotherm models give the best interpretation for the equilibrium data. The adsorption kinetics follow the mechanism of the pseudo-second-order equation for the systems studied.

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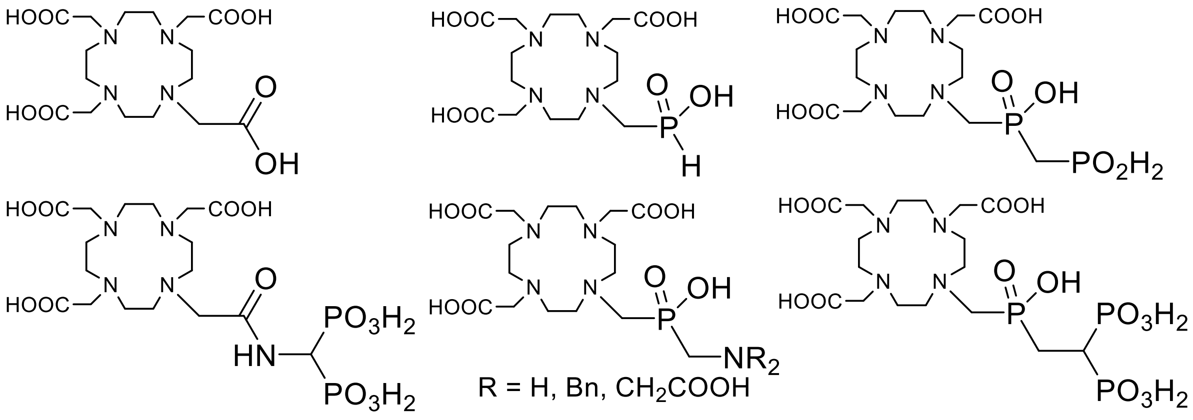
"Out-of-cage" complexes of DOTA-like ligands: What is optimal stability?

Soňa PROCHÁZKOVÁ, Vojtěch KUBÍČEK, Petr HERMANN

Charles University, Faculty of Science, Department of Inorganic Chemistry, Hlavova 8,
128 40 PRAGUE 2, Czech Republic
kubicek@natur.cuni.cz

Many lanthanide radioisotopes are used as contrast agents in medical imaging techniques. Prior to application, the metal ion must be bound in a complex to prevent nonspecific deposition in tissues. The ligands used for complexation of lanthanides mostly belong to DOTA family. Unfortunately, the ligands suffer from low complexation rate.

The complexation rate is modified by changing the pendant arms in the DOTA structure. Of particular interest are those pendant arms containing additional coordinating group. The coordinating group interacts with the metal ion in the initial phase of the complexation process and, so, it improves formation and stability of the "out-of-cage" intermediates in which the metal ion is coordinated by oxygen atoms of pendant arms. We have synthesized several DOTA-analogues with phosphorus based pendant arms additional chelating groups in the pendant arm. We have evaluated stability and formation of their lanthanide(III) complexes with respect to potential application as metal isotope carriers. The complexation rate of the studied ligands differs by several orders of magnitude. This is given by stability of the "out-of-cage" intermediate as well as by nature of the spacer between the macrocycle and the pendant chelating group. The results show that very high complexing ability of the pendant arm is not desirable as it leads to the decreased overall complexation rate due to excessive stabilization of the reaction intermediates.

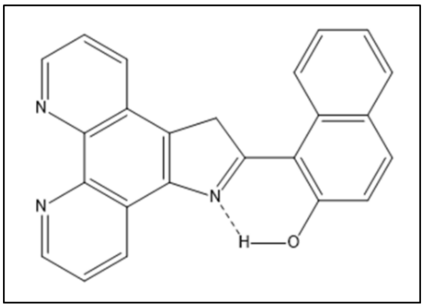


Study of the interaction of DNA with $[Ir(ppy)_2(HNAIP)]Cl$ and 2-(hydroxy-1-naphthyl)imidazo-[4,5-f][1,10]phenanthroline (HNAIP)

**Judit MARTÍN, José M. LEAL, Natalia BUSTO, Gustavo ESPINO,
Jairo FIDALGO, Begoña GARCÍA**

*University of Burgos, Chemistry Department, Plaza Misael Bañuelos s/n,
09001 BURGOS, Spain
jmleal@ubu.es*

Organometallic complexes are prone to bear a large variety of C-bound ligands and they can display a wide slate of potential applications in medicine, even though so far there are only relatively few examples of clinical use. In recent years, small molecules, especially organometallic complexes, have been studied as chemotherapeutic agents [1]. Many antitumour drugs can act either by regulating the gene expression or by interfering with the DNA transcription mechanisms, that is, DNA-drug direct interaction [2]. This interaction can proceed in many ways. 2-(Hydroxy-1-naphtyl)imidazo-[4,5-f][1,10]phenanthroline (HNAIP) can develop a remarkable coordinating ability [3]. To properly evaluate the potential antitumour activity of HNAIP and ([Ir(ppy)2(HNAIP)]Cl), namely, (2-(hydroxy-1-naphthyl)imidazo-[4,5-f][1,10]phenanthroline)bis(2-phenylpyridine)iridium chloride (Figure 1), their mode of binding with ctDNA has been addressed. To this aim, spectrophotometric, circular dichroism, differential scanning calorimetry, viscosity, cytotoxicity and electrophoretic essays were performed to characterize this mode of binding. Both drugs can interact weakly through external binding. Both HNAIP and the iridium complex present electrostatic binding with the DNA groove. The two compounds produce cellular apoptosis, but the organic ligand presents greater cytotoxicity.



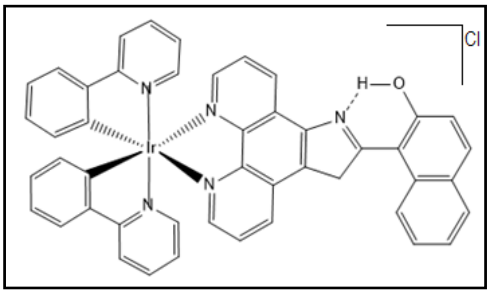


Figure 2. (Left): HNAIP Structure. (Right): [Ir(ppy)2(HNAIP)]Cl Structure.

Acknowledgements: the research leading to these results has received funding from “la Caixa” Foundation (project OSLC-2012-007), MINECO (CTQ2014-58812-C2-2-R, FEDER Funds) and Junta de Castilla y León (BU042U16, FEDER Funds), Spain.

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New chromo-fluorogenic probe containing a BODIPY unit for the detection of Hg(II) in water

Maria LO PRESTI, [a] **Maria Manuela MARQUES RAPOSO**, [b]
Ramón MARTÍNEZ-MAÑEZ, [a] **Félix SANCENÓN** [a]

[a] *IDM, Instituto Interuniversitario de reconocimiento Molecular y Desarrollo Tecnológico, Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022 VALENCIA, Spain*
[b] *Centro de Química, Departamento de Química, Universidade do Minho, Campus de Gualtar, 4710-057 BRAGA, Portugal*
malopre@upvnet.upv.es

Detection and quantification of transition metal cations in environmental chemistry and clinical toxicology has been extensively explored, in the last years, due to its high polluting power [1,2]. The design and synthesis of chemosensors with high selectivity and sensitivity for heavy metal cations has received noticeable attention because they have caused serious risks for the environment and human health. Among them, mercury is one of the most toxic metal ions, even at slow concentrations. Accumulation of mercury over time in the human body can lead to many cognitive and motion disorders and Minamata disease [3-5].

We present here a new chomo-fluorogenic probe able to detect in water Hg(II) with the "naked-eye" in the visible wavelength region (see Figure 1). The probe is composed by a BODIPY fluorophore, as signaling subunit, because of its high quantum yields, high solubility in water and organic solvents. This BOPIPY fluorophore was electronically connected with a crown ether (containing nitrogen, oxygen and sulfur atoms) that presented a high Hg^{2+} affinity.

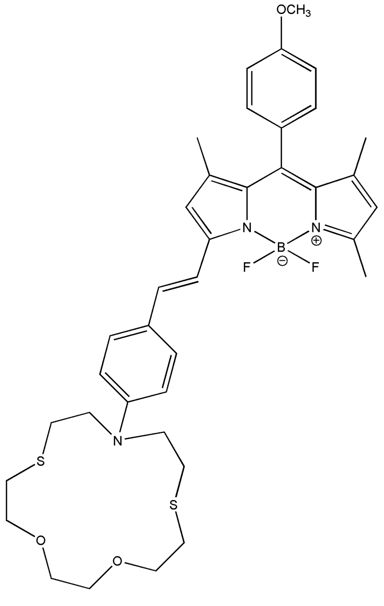

Figure 1

Solutions of receptor in water-acetonitrile 95:5 v/v at pH 7.0 present an absorption band centered at 614 nm, which gives an intense blue color. UV-visible and fluorescence spectra of probe were studied in the presence of 10 equivalents of several metal cations (Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Ba^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+}, Al^{3+}, In^{3+}, Cr^{3+}, Ga^{3+}, Fe^{3+}, As^{3+}). Of all the tested cations only Hg^{2+} is able to change the color of the solution (from blue to pink clearly discernible by the naked eye) (See Figure 2).

Figure 2

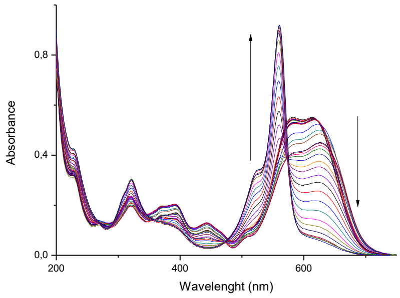

Figure 3

UV-visible spectra of probe **BP6** (5.0×10^{-5} $molL^{-1}$) in water-acetonitrile 95:5 v/v (pH 7.0) at increasing concentrations of Hg^{2+} (0-25 eq.)

These changes are reflected in the appearance of a new band in the visible region, centered at 561 nm. (See Figure 3). On the other hand, a significant increase in fluorescence upon addition of Hg(II) cation was also observed (See Figures 4 and 5).

Figure 4

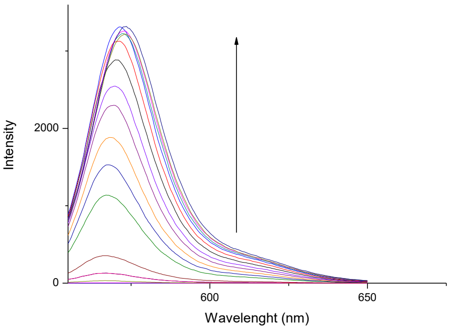

Figure 5

Fluorescence spectra of probe **BP6** (5.0×10^{-5} $molL^{-1}$) in water-acetonitrile 95:5 v/v (pH 7.0) at increasing

From the titration profiles, a limit of detection of 99 ppm of Hg^{2+} was measured. Besides, Job plot analysis indicated the formation of 1:1 stoichiometry probe-Hg^{2+} complex.

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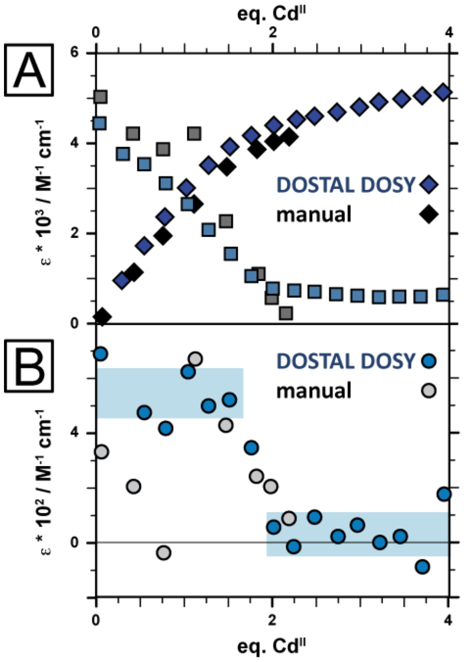
Deducing metal binding properties of proteins and nucleic acids by only one UV-vis experiment

Jens LOEBUS [a,b)]

[a)] Institute of Inorganic Chemistry, University of Zurich, Winterthurerstrasse 190,
8057 ZURICH, Switzerland
[b)] DOSTAL GmbH, Schillerstr. 59, 06114 HALLE/SAALE, Germany
jens.loebus@dostal-gmbh.com

Metallothioneins (MTs) are small (2-10 kDa), cysteine-rich (up to 33%) metallo-proteins coordinate preferentially d^{10} metals ions, forming metal–thiolate clusters. The plant MT E$_c$-1 from *Triticum aestivum* (bread wheat), is one of the most important Zn^{II} coordinating proteins in wheat grain. Upon binding of up to six Zn^{II} ions E$_c$-1 folds into two independent metal-thiolate clusters containing domains (β$_E$ and γ). The solution structures of Zn$_4$-β$_E$-E$_c$-1 along with Zn$_2$-γ-E$_c$-1 and Cd$_2$-γ-E$_c$-1 have been reported previously [1,2]. Here we investigate the metallation pathway of the smaller γ-domain and follow its metallation from apo to Cd$_2$-γ-E$_c$-1 and apo to Co$_2$-γ-E$_c$-1 by UV-vis spectroscopy. By only one titration experiment followed photo-spectroscopically between 200 and 800 nm, the metallation pathway is discernable. Moreover, the potential of automated „*in situ*“ titration inside the UV-vis spectro-photometer with mixing is demonstrated, observing the interaction between a metal-complex and a short strand of nucleic acid.



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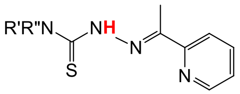
Oxidation of [Fe^{II}(thiosemicarbazone)$_2$] complexes in solution; hydrogen bonding established by activation volumes

Paul V. BERNHARDT, [a] **Miguel A. GONZÁLVEZ,** [b] **Manuel MARTÍNEZ** [b]

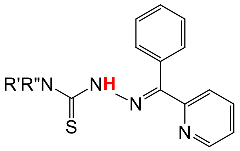
[a] *School of Chemistry and Molecular Biosciences, University of Queensland, BRISBANE 4072, Australia*
[b] *Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, 08028 BARCELONA, Spain*
manel.martinez@qi.ub.es

Thiosemicarbazones are iron chelating agents which have shown definite biological activity [1]. Recently they have been having special attention due to its pharmacological activity in a variety of rather serious medical conditions [2,3].

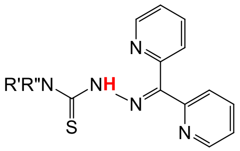
In this contribution we present a kinetico-mechanistic study on the oxidation by air in solution of a series of bis-thiosemicarbazone complexes of Fe(II) of the HApt, HBpT and HDpT series (see Scheme 1) with different degrees of substitution of the terminal amino group.



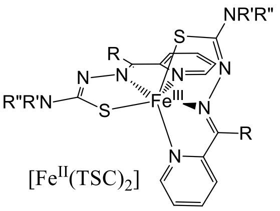
HApT



HBpT

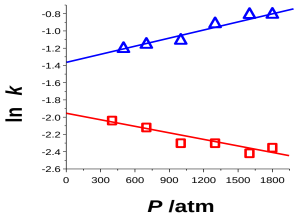


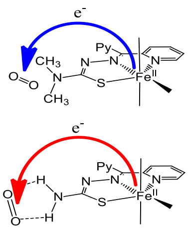
HDpT



[Fe^{II}(TSC)$_2$]

The experiments have been carried at varying oxygen concentrations, and in a margin of temperatures and pressures in order to determine the kinetic and thermal and pressure activation parameters for the process. Its interpretation thus allowing the interpretation of the reaction observed.





The process has been observed to be a single step producing hydrogen peroxide as the final ROS of the Fe(II) complex oxidation. Interestingly, while the values of ΔGP follow the trends expected for the known values of the redox potential of the complexes, the determined values for the activation volumes in methanol are clearly related to the presence of possible hydrogen bonding interactions between the terminal amino group of the thiosemicarbazone and the oxidizing oxygen molecule.

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Morphology-controlled thorium-based powders through wet chemical route

Jérôme MAYNADIE, [a] **Nicolas CLAVIER**, [a] **Adel MESBAH**, [a]
Nicolas DACHEUX, [a] **Daniel MEYER** [a]

[a] *Institut de Chimie Séparative de Marcoule, UMR 5257 CEA/CNRS/ENSCM/Univ. Montpellier, Site de Marcoule, BP 17171, 30207 BAGNOLS-SUR-CÈZE, France*
jerome.maynadie@cea.fr

The development of future generations of nuclear reactors led to consider wet chemistry routes for the fabrication of the fuel ceramics (e.g. UO_2 and $(U,Pu)O_2$ solid solutions) as they provide interesting powder properties (homogeneity, sintering capability) and enhance the resistance toward proliferation. Such processes are mainly based on the initial precipitation of low-temperature precursors (such as nitrates, carbonates or oxalates) which are further converted into the final compounds through a heat treatment step operated at high temperature. However, the resulting oxide powders can still incorporate some impurities [1] and frequently suffer from a poor flow ability inherited from the morphology of the parent precursor.

In this context, several wet chemistry routes were developed aiming to precipitate directly hydrated actinides oxides in solution, with a particular attention paid to the control of their morphology. The first method retained is based on the formation of hydroxides colloids which rapidly aged in solution to yield nano-crystalline $AnO_2.nH_2O$.[2] Preliminary tests indicated that such powders can be directly sintered (i.e. without any prior heating step). They led to a significant decrease of the temperature required for a complete densification and allowed the preparation of a wide range of microstructures, particularly in term of final grain size.

Currently, the hydrolysis of actinides under mild hydrothermal conditions in presence of aspartic acid as a shaping agent [3], was investigated to prepare morphology-controlled actinide powders (see Fig.1). In this case, different operating parameters were studied (such as temperature, duration and aspartic acid concentration) and can be used to tailor the nature, the size and the shape of the final grain, which can be of interest for future nuclear fuel cycles.

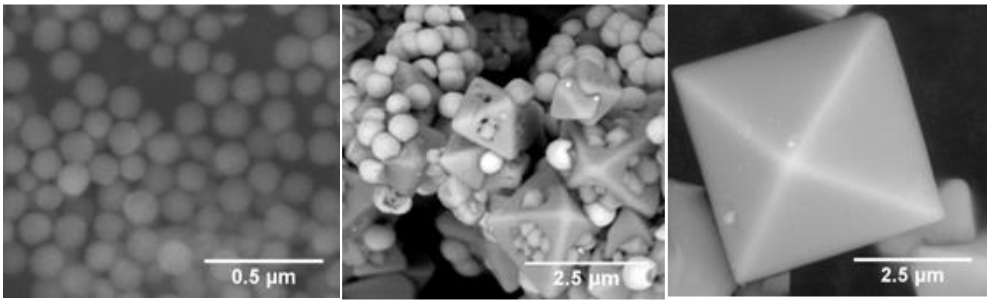

Figure 1. Shape evolution of thorium-based powders according to the synthesis conditions.

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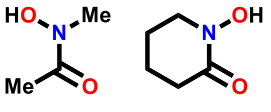
Coordination chemistry of uranium(VI) with hydroxamic siderochelates

Michel MEYER, [a] **Alejandra SORNOSA-TEN**, [a] **Shanthilal AMARASINGHE**, [a]
LéVi NGUYEN, [a] **Pawel JEWULA**, [a] **Mélanie BOURDILLON**, [a]
Stéphane BRANDES, [a] **Christine STERN**, [a] **Yoann ROUSSELIN**, [a]
Jean-Claude CHAMBRON, [a] **Vladimir SLADKOV** [b]

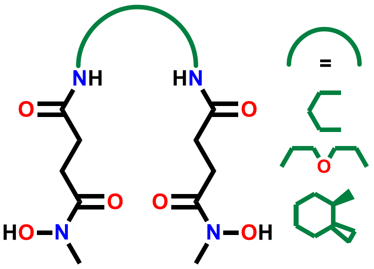
[a] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[b] Institut de Physique Nucléaire d'Orsay (IPNO), UMR CNRS 8608, 15 rue G. Clemenceau,
91406 Orsay Cedex, France
michel.meyer@u-bourgogne.fr

The management and remediation of uranium-contaminated fields and the disposal of nuclear wastes in deep geological repositories are societal issues of great concern. Predicting the behavior of actinides under environmental conditions is of paramount importance, but modeling their speciation in waters and soils requires an accurate knowledge of the thermodynamic and kinetic parameters related to their complex formation and dissociation equilibria. In particular, migration and bioavailability of actinides in the biosphere are highly dependent upon the presence of organic ligands [1]. Because such data are scarce and often unreliable in the case of the transuranium cations, considerable research efforts are still required [2,3].

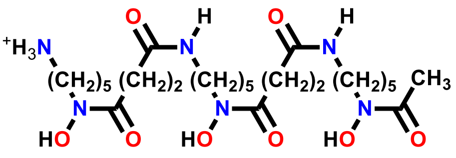
Our aim is to investigate the coordination chemistry in aqueous media of selected 4f and 5f elements with environmentally-relevant, widespread chelators, namely natural and abiotic hydroxamic acids. The former, also called siderophores, are excreted by most bacteria and some yeasts to supply them with iron(III). However, desferrioxamines, pyoverdines, and rhodotorulic acid have recently been shown to form stable complexes with various actinides and to efficiently mediate plutonium uptake by several bacterial strains [4].



Monohydroxamic acids



Dihydroxamic acids



Desferrioxamine B

By combining potentiometric and spectrophotometric titration techniques with capillary zone electrophoresis, the speciation of linear and cyclic monohydroxamates, abiotic dihydroxamates, and desferrioxamine B in the presence of uranyl could be unraveled. X-ray absorption and RAMAN spectroscopies enabled to probe the chemical environment around the uranium center in the different species prevailing in solution. Finally, the proton-assisted step-by-step dissociation mechanism of the $[UO_2(DFB)H_2]^+$ complex, as established by stopped-flow spectrophotometry, will be presented.

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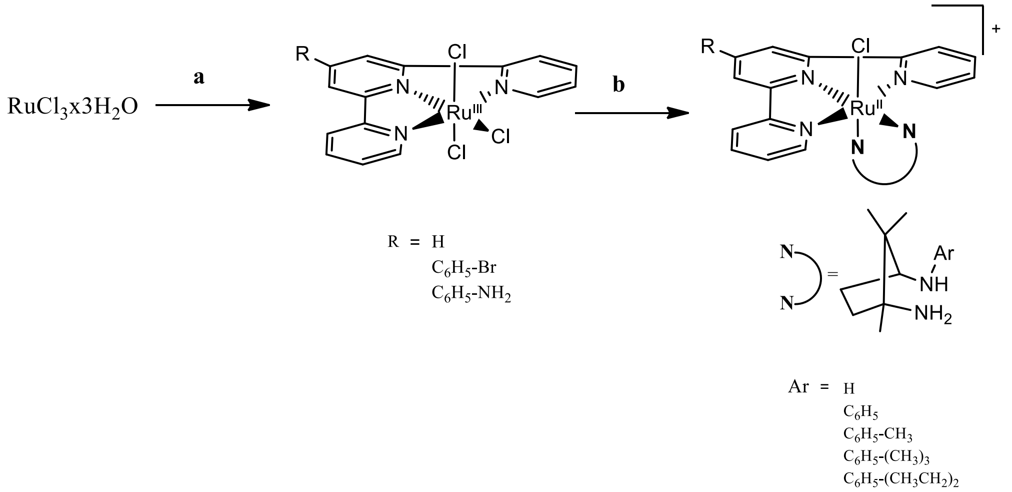
Synthesis and characterization of new Ru(II) terpyridine complexes with new camphor based diamine ligands: Kinetic investigation and DNA/BSA binding ability

Milan M. MILUTINOVIĆ, [a,b] **Živadin D. BUGARČIĆ**, [b] **René WILHELM** [a]

[a] Department of Organic Chemistry, University of Paderborn, Warburger Straße 100,
33098 PADERBORN, Germany
[b] Faculty of Science, University of Kragujevac, R. Domanovića 12,
34000 KRAGUJEVAC, Serbia
milanm@mail.uni-paderborn.de

With the aim of expanding the structure-activity relationship study of Ru(II) complexes and of investigating new bidentate chiral enantiopure diamine camphor based ligands, a series of Ru(II) terpyridine complexes of the type [Ru(Cl-Ph-tpy)(*N-N*)Cl]$^+$ previously described by us (where 4’-(4-chlorophenyl)-2,2’:6’,2”-terpyridine (Ph-Cl-tpy), *N-N* = 1,2-diaminoethane (en), 1,2-diaminocyclohexane (dach) or 2,2'-bipyridine (bpy)) [1,2] was extended to R-tpy (where R-tpy = 2,2':6',2''-terpyridine, 4'-bromo-2,2':6',2''-terpyridine, 4'-amino-2,2':6',2''-terpyridine, *N-N* = k^2(1S,3R)-ArNH∩NH$_2$) [3]. All new terpyridine complexes with camphor diamine based ligands were fully characterized by NMR and IR spectroscopy, ESI-MS spectrometry, UV-Vis spectrophotometry and elemental analysis. The chemical behavior of the new complexes in aqueous solution and their binding properties towards biomolecules as model DNA bases such as 5'-GMP, 9MeG etc., were investigated by UV-Vis and NMR spectroscopy. The kinetics of the aquation of selected complexes and of the subsequent interaction with guanine derivatives and amino acids were established quantitatively by UV-Vis and NMR spectroscopy. The DNA binding ability (CT-DNA or HT-DNA and oligonucleotides), BSA interactions and cytotoxic properties of these complexes are under investigation (Scheme 1).



Scheme 1. Synthetic pathways for the preparation of complexes. Reagents and conditions: (**a**) R-tpy (0.9 eq.), EtOH, reflux; (**b**) *N-N* (1.2 eq.; *N-N* = k^2(1S,3R)-ArNH/NH$_2$), EtOH/H$_2$O (3:1), Et$_3$N (3.0 eq.), LiCl (10.0 eq.).

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Functionalized chitosan and elaborating injectable nanoparticles for lymphatic system MRI

**J. MOREAU, [a] V. GHERAN, [b] C. HENOUMONT, [c] A. ROBERT, [a]
M. CALLEWAERT, [a] G. RIGAUX, [a] C. CADIOU, [a] L. Vander ELST, [c,d]
S. LAURENT, [c,d] R.N. MULLER, [c,d] A. DINISCHIOTU, [b] S. N. VOICU, [b,e]
F. CHUBURU [a]**

*[a] Institut de Chimie Moléculaire de Reims, CNRS UMR 7312, Université de Reims
Champagne-Ardenne URCA, 51685 REIMS Cedex 2, France*
[b] Biochem. & Mol. Biol. Department, BUCHAREST, Romania
[c] UMONS, NMR & Mol. Im. Lab., MONS, Belgium
[d] CMMI, CHARLEROI, Belgium
*[e] Faculty of pharmacy, Department of Pharmacy, Titu Maiorescu University,
BUCHAREST, Romania*

Drug encapsulation in biocompatible nanoparticles allows to reduce the unwanted toxic side effects of the active substances and to prolong their circulation time [1]. Hydrophilic bio-sourcing polymers, like chitosan or hyaluronic acid, are good candidates to elaborate this type of nanoparticles. Recently, we have shown that an important relaxivity enhancement of gadolinium chelates was obtained between 20 and 60 MHz, when these hydrophilic chelates were encapsulated within these nanoparticles [2-3]. The second generation of these nanoparticles consists on the elaboration of functionalized or targeted nanoparticles. The aim of targeting is to reduce nanoparticle uptake by the reticuloendothelial system (RES) and/or to foster their specific accumulation in tissues.

In the first part of the presentation, we will describe chitosan functionalization by PEG or fluorinated groups. These groups are be chosen because of their ability to enhance nanoparticle accumulation in lymph nodes [4-5]. The characterizations of Functionalized chitosan characterization by ^{1}H and ^{19}F NMR (for fluorinated-chitosan) will be presented and we will demonstrate that DOSY experiments are mandatory first to provide evidence of PEG or fluorinated synthons grafting and second to allow the estimation of chitosan degree of substitution. This latter information is necessary to select functionalized chitosans suitable to be involved in physical gelation for the synthesis of functionalized nanohydrogels.

In the second part of the presentation, we will describe the incorporation of gadolinium chelates (GdCAs) in functionalized nanohydrogels and analyze the ability of these new structures to boost GdCA relaxivity. Finally, the functionalized nanoparticles *in vitro* toxicity will be evaluated towards RAW 264.7 murine macrophages (which are a good model for the lymphatic system) and compared with the one of un-functionalized nanoparticles.

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Aurophilic and other supramolecular interactions in triphenylphosphine gold(I) fluorothiolates

Guillermo MORENO-ALCÁNTAR, [a] **Luis TURCIO-GARCÍA**, [a] **José Manuel GUEVARA-VELA**, [b] **Ángel MARTIN-PENDÁS**, [b] **Tomás ROCHA-RINZA**, [c] **Marcos FLORES-ALAMO**, [a] **Hugo TORRENS** [a]

[a] Faculty of Chemistry, Universidad Nacional Autónoma de México, Ciudad Universitaria,
04510 CIUDAD DE MÉXICO, México
[b] Department of Physical and Analytical Chemistry, Universidad de Oviedo,
Julián Clavería 8, 33006 OVIEDO, Spain
[c] Institute of Chemistry, Universidad Nacional Autónoma de México, Ciudad Universitaria,
04510 CIUDAD DE MÉXICO, México
lgma@comunidad.unam.mx

Molecular tectonics of gold(I) linear compounds is often directed by the prevalence of aurophilic interactions [1,2], sterical hindrance is one of the main features that could prevent those contacts to form, therefore, competing weaker interactions could act to avoid the formation of the expected stronger aurophilic contact [3]. In this work, we analyse the prevalence of aurophilic interaction over other possible supramolecular interactions promoted by the molecular changes in structure, that simultaneously modify the electronical environment of gold atoms. To that end, we have synthesized and characterized 11 new gold(I) compounds with the formula $[Au(SR_F)(Ph_3P)]$ were Ph_3P = Triphenylphosphine and SR_F = SC_6F_5 (**1**), SC_6HF_4-4 (**2**), $SC_6F_4(CF_3)$-4 (**3**), $SC_6H_3F_2$-2,4 (**4**), $SC_6H_3F_2$-3,4 (**5**) , $SC_6H_3F_2$-3,5 (**6**), $SC_6H_4(CF_3)$-2 (**7**), SC_6H_4F-2 (**8**), SC_6H_4F-3 (**9**), SC_6H_4F-4 (**10**), SCF_3 (**11**), SCH_2CF_3 (**12**). The changes in the fluorination of the thiolate group coordinated to the gold atom drastically influences the interactions directing the molecular tectonics in the crystal packing.

Per the kind of interactions driving the crystalline arrangement the eleven synthetized compounds could be classified into three groups depending on the prevalent interaction: π stacking [4], hydrogen bond [5,6] or aurophilic [7] (Figure 1).

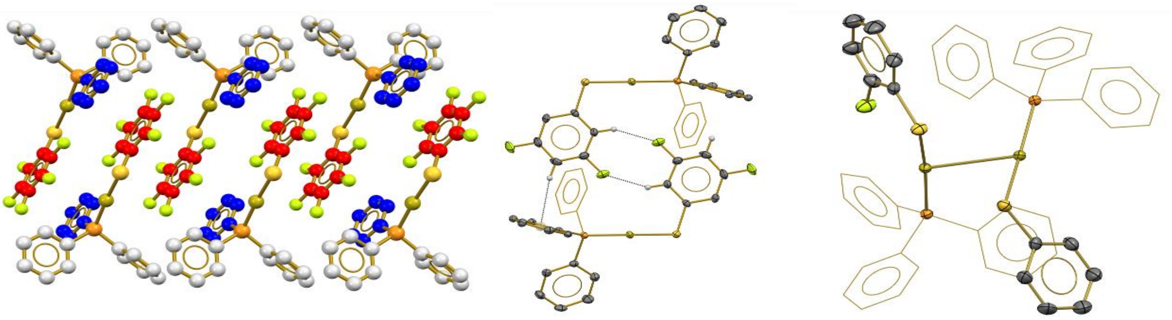

Figure 1. Examples showing π stacking (Compound **1**), C-H···F bond (Compound **6**) and aurophilic interaction (Compound **8**).

We further examined the supramolecular interactions through the NCI index [8], an indicator derived from the electron density and its reduced gradient. To carry out this analysis, we used the NCIPlot [9] program, whose results were visualized with the VMD software [10].

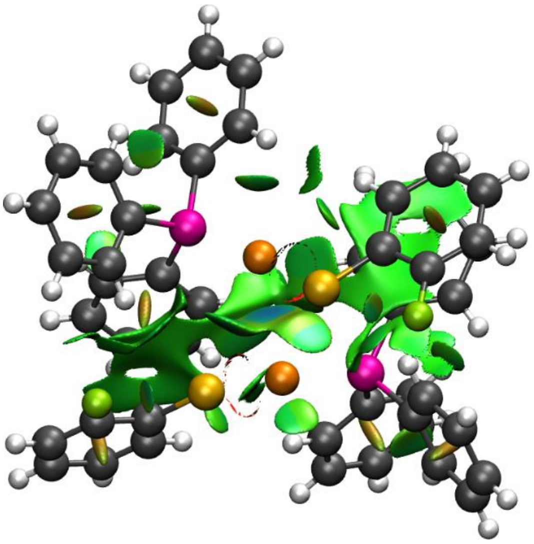

Figure 2. General view of the NCIplot interaction analysis in compound **8**. Aurophilic attractive interaction could be noted as blue colored surface. Code: Au: golden, F: green, S: yellow, P: orange, C: gray and H: white.

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Mixed-metal clusters based on $\{Re_3Mo_3Se_8\}$ core: Synthesis, crystal structure and properties

Viktoria K. MURAVEVA, [a,c] **Yakov M. GAYFULIN**, [a] **Pierric LEMOINE**, [c]
Dmitriy A. PIRYAZEV, [a,b] **Maxim R. RYZHIKOV**, [a,b] **Igor N. NOVOZHILOV**, [a]
Stéphane CORDIER, [c] **Nikolay G. NAUMOV** [a,b]

[a] *Nikolaev Institute of Inorganic Chemistry SB RAS. 3, Acad. Lavrentiev Ave.,*
NOVOSIBIRSK 630090, Russia
[b] *Novosibirsk State University, 2 Pirogova Str., NOVOSIBIRSK 630090, Russia*
[c] *Institut des Sciences Chimiques de Rennes, UMR 6226 UR1-CNRS, Université de Rennes 1,*
Campus de Beaulieu, 35042 RENNES Cedex, France
viktoria.muravyeva@univ-rennes1.fr

Chemistry of the octahedral chalcogenide clusters of a $\{M_6Q_8\}$ (M = Re, Mo; Q = S, Se, Te) type is in a stage of rapid development. An interest to these compounds is caused by a fascinate chemistry and a set of perspective physical properties including structural features, redox transformations of cluster core, magnetism and luminescence [1,2]. Recently, it was shown that nonisovalent partial substitution of metal atoms within the cluster core significantly changes the electronic structure of the resulting compounds in comparison with homometallic species [3,4].

Here we report on the synthesis and detailed experimental and theoretical study of mixed-metal octahedral clusters based on novel $\{Re_3Mo_3Se_8\}^n$ core ($n = -1 \div +2$). Mixed-metal cluster species were prepared by the reaction of $ReSe_2$ and $MoSe_2$ in molten KCN at high temperatures. It resulted in formation of polymeric compound having the composition $K_6[Re_3Mo_3Se_8(CN)_5]$ (**1**) (Figure 1). The $\{Re_3Mo_3Se_8\}^{1-}$ cluster core has 24 clusters valence electrons (CVE) as confirmed by composition and diamagnetic behavior of **1**. The cluster excision reaction allowed to obtain the water-soluble molecular complex with the composition of $K_5[Re_3Mo_3Se_8(CN)_6]\cdot 10H_2O$ (**2**) comprising $\{Re_3Mo_3Se_8\}^{1+}$ cluster core with 22 CVE. Metathesis reaction of **2** and Ph_4PBr resulted in the formation of paramagnetic compound $(Ph_4P)_4[Re_3Mo_3Se_8(CN)_6]\cdot DMF$ (**3**) containing $\{Re_3Mo_3Se_8\}^{2+}$ core with 21 CVE.

In the present work, practical aspects of synthesis, crystallographic studies, spectroscopic data and electronic structure calculations are discussed for mixed-metal octahedral clusters based on $\{Re_3Mo_3Se_8\}^n$ core. Redox properties of the $[Re_3Mo_3Se_8(CN)_6]^{n-}$ cluster anion were investigated using cyclic voltammetry in aqueous and DMF solutions. Novel 5^- charged cluster cyanide anion $[Re_3Mo_3Se_8(CN)_6]^{5-}$ was used as a building block for synthesis of inorganic coordination polymers with a number of transition metal cations. The compounds with crystal structures of different dimensionalities, including chain-like, layered and 3D-network assemblies, were structurally investigated.

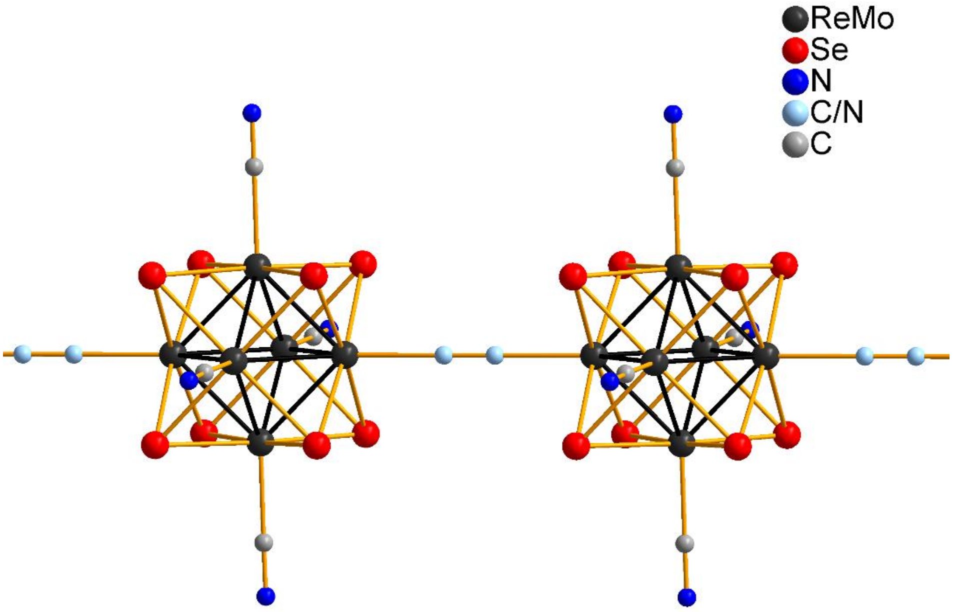

Figure 1. Fragment of polymeric chain $[Re_3Mo_3Se_8(CN)_4(CN)_{2/2}]^{6-}{}_{\infty}$ in compound **1**.

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Characterization of the interaction of Pd(II) or Pt(II) ions and peptide hydroxamic acids in solution

András OZSVÁTH, Róbert DIÓSZEGI, Péter BUGLYÓ

University of Debrecen, Department of Inorganic and Analytical Chemistry, Egyetem tér 1.,
4032 DEBRECEN, Hungary
ozsvath.andras@science.unideb.hu

Cisplatin (*cis*-[Pt(NH_3)$_2$$Cl_2$]) is the most commonly used metallodrug in cancer therapy, but it has several side-effects because of the low selectivity. The selectivity can be increased by targeting the physiological differences of healthy and cancer tissues. One of these differences is that cancer tissues have undeveloped vascular system because of the fast growing, therefore the poor blood supply causes hypoxic conditions. For this reason, development of hypoxia activated prodrug complexes could be advantageous. One group of these compounds are $[Co^{III}(4N)L]^{n+}$ (4N = a tripodal amine, L = bidentate ligand) type complexes. Reduction of these to labile Co^{II} species in the hypoxic tissues and release L with antitumor potential may provide with a high selectivity.

Some hydroxamic acids ($R_CC(O)N(R_N)OH$) are well-known antitumor agents for example SAHA is used in the cancer therapy. For this reason, incorporation of hydroxamic acids into a $[Co^{III}(4N)]$ complex we have chance to synthesize effective antitumor agents [1,2]. The effectiveness could be increased, if the hydroxamic acid also contains another donor atom set, where another metal ion can co-ordinate with anticancer potential. Peptide hydroxamic acids can be great candidates for this purpose as beside the hydroxamate group they also contain amino, amide and hydroximate nitrogens to co-ordinate another metal ion e.g. Pt(II) or Pd(II).

In this study we have synthesized primary and secondary di- and tripeptide hydroxamic acids (AlaAlaNHOH, AlaAlaN(Me)OH, AlaGlyGlyNHOH and AlaGlyGlyN(Me)OH) [3, 4], and we have investigated the interaction of these ligands with Pd(II) and Pt(II) ions in aqueous solution to explore the formation conditions of likely heterodinuclear Co(III)/Pt(II) complexes. This contribution will summarize the results obtained by the combined use of pH-potentiometry, ^{1}H-NMR, and ESI-TOF-MS spectrometry.

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Sequestering ability of landfill leachate towards toxic metal ions

Salvatore CATALDO, [a)]**Gabriele LANDO,** [b)]**Demetrio MILEA,** [b)]
Nicola MURATORE, [a)]**Santino ORECCHIO,** [c)]**Alberto PETTIGNANO,** [a)]
Silvio SAMMARTANO [b)]

[a)]Dipartimento di Fisica e Chimica,Università d Palermo, viale delle scienze,
90128 PALERMO, Italy
[b)]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli studi di Messina, Viale Ferdinando Stagno d'Alcontres 31, 98166 MESSINA, Italy
[c)]Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche, Università di Palermo, viale delle scienze, 90128 PALERMO, Italy
alberto.pettignano@unipa.it

The great part of municipal solid wastes is worldwide stored in sanitary landfills. The interaction of organic and inorganic wastes with rainwater produces in the landfill a leachate of extremely variable composition. It depends on several variables such as the type of wastes, the age of landfill, the pH, the redox potential, etc [1-2]. Four are the recognized categories of pollutants in landfill leachate: inorganic macrocomponents, dissolved organic matter (DOM), heavy metals and xenobiotic organic compounds [3]. In particular, heavy metals (arsenic, cadmium, copper, lead, mercury, etc.) are usually present at concentration of few ppb and up to some ppm.

A variable but consistent fraction of DOM is constituted by humic and fulvic-like compounds, formed through a series of biological and chemical processes that involve DOM, especially during the methanogenic phase of wastes decomposition [3]. The great number of binding sites in humic like substances, mainly carboxylic and phenolic groups, are responsible of the high sequestering ability of leachate towards metal ions. As consequence, the speciation scheme of all the toxic metal ions contained in the landfill is strictly influenced by the amount and composition of DOM fraction in leachate.

Due to the imperfections or the possible damages of landfill liners, the leachate can contaminate superficial and ground waters in proximity of the landfill causing serious environmental pollution and human health risks. In a previous study the presence and the amount of landfill leachate, also in trace, on some groundwater samples collected in proximity of Bellolampo landfill was evaluated [4]. The obtained results showed a leachate concentration of ~ 130 $\mu g\ L^{-1}$. Landfill of Bellolampo is a solid waste sanitary landfill near Palermo (Sicily). The landfill has been created in 1960s and become a controlled dump site in 1980s. Previous ICP-OES measurements on Bellolampo leachate have been shown a Pb, Cd and Cu concentrations in the ranges 0.05 - 2.3, 0.02 - 0.12 and 0.02 - 0.6 mg L^{-1} respectively.

The environmental and health risks related to the presence of toxic heavy metal ions in leachate depends on the species that metals form with the other components and at the conditions of the contaminated groundwater, with particular attention to the amount of free metal ions, the most dangerous among their possible species in aqueous solution.

For this reason, the study of the sequestering ability of landfill leachate towards toxic metal ions is of fundamental importance to establish the environmental impact of leachate contamination. Here we present a potentiometric and voltammetric (Differential Pulse Anodic Stripping Voltammetry, DP-ASV) study on the acid-base properties and on the sequestering ability of leachate samples collected in Bellolampo landfill towards Cd(II), Pb(II) and Cu(II) ions. The voltammetric and potentiometric titrations were carried out in NaCl aqueous solution, at $I = 0.1$ mol L^{-1} in order to simulate the mean experimental conditions typical of groundwaters. The acid – base properties of the filtered leachate were compared to those of the soluble fraction of humic substances, with carboxylic and phenolic groups as main binding sites of the macromolecules. Two units namely $leach_1$ and $leach_2$ containing COOH and phenol OH groups, respectively were considered and the Diprotic Like model has been used to process the ISE-H^+ potentiometric data [5].

The voltammetric titrations of toxic metal ions solutions with leachate (diluted or as it is) were carried out adjusting the pH of titrand solutions at 5. The results shown an appreciable sequestering ability of leachate towards the heavy metal ions considered and an estimation of the metal complexes stability has been done by calculating rough metal – leachate formation constants.

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High-pressure NMR spectroscopy: An *in situ* tool to study tin-catalyzed synthesis of organic carbonates from carbon dioxide and alcohols

Laurent PLASSERAUD, [a)]**Michel PICQUET**, [a)]**Gabor LAURENCZY** [b)]

[a)] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[b)] Institut des Sciences et Ingénierie Chimiques (ISIC), Ecole Polytechnique Fédérale de
Lausanne, 1015 LAUSANNE, Switzerland
Laurent.Plasseraud@u-bourgogne.fr

Organotin(IV) compounds are known to be efficient catalysts for the transformation of carbon dioxide into useful chemicals such as linear dialkyl carbonates, cyclic carbonates, and oxazolidone [1]. In the past, we showed in particular the positive role of diorganotin(IV) alkoxides, $R_2Sn(OR')_2$ (R = *n*-Bu, *tert*-Bu, Bz; R' = Me, Et, ^{i}Pr), as catalytic precursors for the direct carbonation of alcohols (Eq. 1) [2].

$$CO_2 + 2\,ROH \longrightarrow (RO)_2CO + H_2O \qquad (1)$$

Although several CO_2- and carbonate-adducts have been characterized by X-ray crystallography [3], the reaction mechanisms remain still unclear. In this aim, high pressure $^{119}Sn\{^1H\}$NMR spectroscopy experiments, under CO_2 pressure and in deuterated alcohols, were achieved [4].

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Technetium metal-metal bonds: Molecular and solid-state halides

Frederic POINEAU, [a] **Eric JOHNSTONE**, [a] **Tanya TODOROVA**, [b]
Laura GAGLIARDI, [c] **Paul FORSTER**, [a] **Ken CZERWINSKI**, [a]
Alfred SATTELBERGER [a]

[a] Department of Chemistry and Biochemistry, University of Nevada Las Vegas, 4505 Maryland Parkway, LAS VEGAS, NV 89154, USA
[b] Laboratoire de Chimie des Processus Biologiques, UMR 8229 CNRS, UPMC-Paris 6, Collège de France, 11 Place Marcelin Berthelot, 75231 PARIS, France
[c] Department of Chemistry and Supercomputing Institute, University of Minnesota, MINNEAPOLIS, MN 55455, USA
poineauf@unlv.nevada.edu

Transition metal compounds with metal-metal multiple bonds play an important role in inorganic, materials, bioinorganic and organometallic chemistry. Compounds with metal-metal multiple bonds can be found in various dimensionalities: molecular clusters and solids with extended structures (i.e., binary halides). More than 4000 dinuclear complexes and several binary halides with metal-metal multiple bonds have been characterized. Multiple bonds between metal atoms were first identified in $Re_3Cl_{12}^{3-}$ and $Re_2Cl_8^{2-}$. Rhenium trichloride and $(n\text{-}Bu_4N)_2Re_2Cl_8$ have been extensively used as precursors for the synthesis of polynuclear complexes and have contributed significantly to the development of rhenium metal-metal bond chemistry.

One element whose metal-metal bond chemistry is not well developed is technetium, the lighter rhenium congener. As of the year 2005, the number of complexes with multiple Tc-Tc bonds was limited: 25 dimers, 4 hexanuclear and 6 octanuclear halide clusters had been structurally characterized; no Tc binary halides with multiple Tc-Tc bonds and no complexes with a Tc_3^{9+} core were reported.

In this context, we have focused on expanding the chemistry of dinuclear complexes and identifying new binary halides of technetium. We have investigated the synthetic chemistry of technetium binary chlorides and reported four new phases which contain metal-metal bonds: α/β-$TcCl_3$ and α/β-$TcCl_2$. We also investigated the molecular chemistry of Tc complexes and studied the molecular and electronic structure of the octahaloditechnetate $Tc_2X_8^{n-}$ (X = Cl, Br; n = 2, 3) anions. In this contribution, the preparation, structure and properties of the new technetium binary chlorides as well as the $Tc_2X_8^{n-}$ (X = Cl, Br; n = 2, 3) anions are presented.

Complexation properties of new hydrosoluble polyvinyl alcohol (PVA)-based chelating polymers

Julien MULLER, Bénédicte PRELOT, Sophie MONGE, Jean-Jacques ROBIN, Jerzy ZAJAC

Institut Charles Gerhardt de Montpellier, UMR 5253 CNRS-UM-ENSCM, C.C. 1502,
Place Eugène Bataillon, 34095 MONTPELLIER Cedex 5, France
benedicte.prelot@umontpellier.fr

Hydrosoluble polymers are interesting species for metal cations retention thanks to their ability to interact easily with soluble ions. In such context, the chemical modification of biocompatible and non toxic polyvinyl alcohol (PVA) chains with ethylene diamine tetraacetic acid (EDTA) groups led to new hydrosoluble polymers of PVA(EDTA). Modification was carried out using Mitsunobu's reaction as original pathway to afford controlled functionalization rates of EDTA in the PVA polymers. Then, heavy metal sorption properties of such structures containing 15% of chelating agent have been assessed via ionic chromatography (HPLC), and polarography. Several metal cations have been used to evaluate the sorption properties of PVA(EDTA)15% including Co(II), Ni(II), Zn(II), Sr(II), Pb(II), Cd(II), Cu(II), Cs(I) and Eu(III). Additionally, the performances of the polymers were tested in an effluent simili made of Ca(II) and Mn(II) cations. Results obtained showed high sorption capacities for Pb(II), Ni(II), Zn(II) and good selectivity towards some cations consistent with EDTA-metal complex formation constants. Studies about the variation of several parameters including EDTA rate and chain length allowed the determination of the optimal polymeric structure. The influence of the adsorbed cation valence on sorption capacities of PVA(EDTA) has also been described. This study permitted to highlight the interest to modify basic commercial polymers in chelating agents compatible with the Polymer Enhanced Ultrafiltration (PEUF) process.

Cobalt corroles for selective detection of carbon monoxide

Valentin QUESNEAU, [a)] Mario L. NAITANA, [a)] Stéphane BRANDES, [a)]
Nicolas DESBOIS, [a)] Meddi VANOTTI, [b)] Virginie BLONDEAU-PATISSIER, [b)]
Claude P. GROS [a)]

[a)] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[b)] Institut FEMTO-ST Département Temps-Fréquence (FEMTO-ST, UMR CNRS 6174)
26 chemin de l'Epitaphe, 25030 BESANÇON Cedex, France
valentin.quesneau@u-bourgogne.fr

Carbon monoxide, a colorless, tasteless and odorless gas, is known as the « silent killer », causes around one hundred of deaths per year only in France, according to the INPES institute [1]. Detection of CO at levels lower than 10 ppm should avoid such poisoning. One another interest of a high sensitive carbon monoxide detector is for PEM (Proton Exchange Membrane) fuel cell application. Fuel cells needs pure dihydrogen to produce energy but due to its industrial synthesis, some traces (up to 1%) of carbon monoxide are present in dihydrogen and deactivate the catalyst based on palladium.

Corroles are molecules belonging to the porphyrinoïd family. This family has a great interest in coordination chemistry, medical imaging, fluorescence detection of ions or small molecules and catalysis [2,3]. Corroles stabilize cobalt at the +III oxidation state, that gives to the complex a high binding affinity for carbon monoxide even in the presence of nitrogen and dioxygen, the two major components of the atmosphere [4,5]. Interestingly, cobalt corroles can now be involved in the elaboration of selective and sensitive gas detectors.

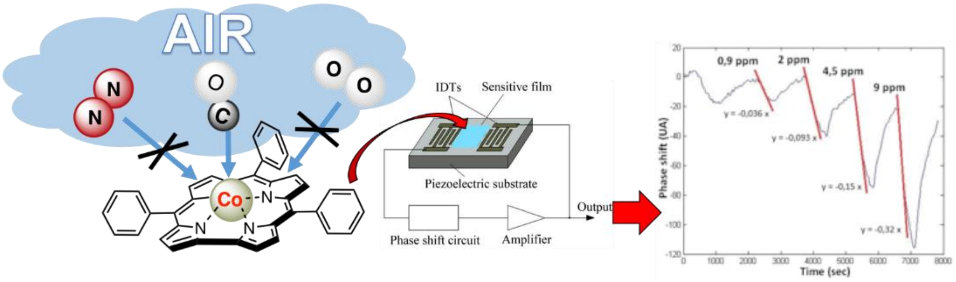

Figure 2. Carbon monoxide detection with a SAW type sensor.

Our work consists in the synthesis of different cobalt corroles and the study of their coordination properties of carbon monoxide. We have particularly studied the influence of steric hindrance and electronic effects of different substituents at the *meso*-position of the corrole macrocycle. Their deposition on a guiding surface of a SAW (Surface Acoustic Wave) has been done to develop selective CO sensors [6]. Preliminary results gave low level carbon monoxide detection and works are still ongoing to develop a procedure that yields a very sensitive and robust sensor.

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COT1 mediated zinc transport in *Candida albicans* – Searching for the metal binding site

Magdalena ROWIŃSKA-ŻYREK, [a] Denise BELLOTTI, [b] Maurizio REMELLI [b]

[a] Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie 14,
50-383 WROCŁAW, Poland
[b] Department of Chemical and Pharmaceutical Sciences, University of Ferrara,
via Fossato di Mortara 17, 44121 FERRARA, Italy
rmm@unife.it

In the last two decades, the incidence of drug resistant invasive fungi has increased dramatically, in both immunosuppressed and non- immunosuppressed patients [1]. New resistance mechanisms emerge, making common infectious diseases untreatable. Pathogens resistant to standard forms of treatment are becoming a serious threat and novel, effective treatments and ways to specifically deliver them to drug resistant invasive mycoses are being actively sought.

One of the biggest obstacles in finding effective, pathogen-specific therapeutics that will not cause severe side-effects in patients arises from the fact that fungi share essential metabolic pathways with humans, many more than with bacteria (both fungi and humans are eukaryotes). In order to design a highly specific antifungal drug, it is crucial to understand and aim at differences in the metabolism of humans and pathogens. Although fungus-selective targets are scarce, there is at least one significant difference between the fungal and mammalian cells: the transport system of zinc.

Zinc, the second most abundant transition metal in living organisms (after iron) [2], is also a crucial survival and virulence factor for pathogens. It is present in superoxide dismutases (SODs), central enzymes in bacteria and fungi associated with the detoxification of ROS generated by host cells during host-pathogen interactions [3]. Zinc-binding metalloproteases are involved in pathogen invasion; they are secreted by distinct species of pathogenic fungi such as the ADAM metalloproteinases or deuterolysin [4]. Both the uptake and safe storage of zinc in vacuoles must be strictly controlled.

COT1 is a transmembrane protein composed of 199 amino acid residues, located in the vacuolar, mitochondrial and cell membrane. Its main function is the transport of cobalt and zinc ions, and its structure remains unsolved [5]. We used Phyre2 [6] to simulate and analyze the predicted, highly probable structure. It occurs that the most probable Zn(II) binding sites of COT1 are located at the C-terminal region, in the extracellular/cytoplasmic part of the protein (Figure 1).

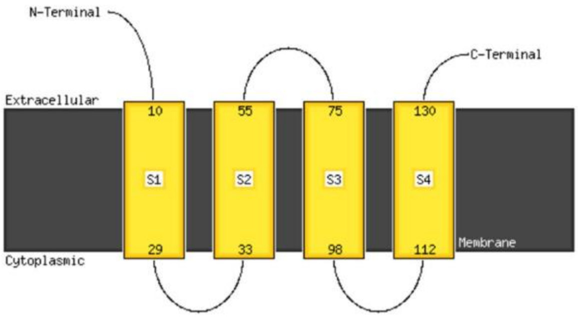

Figure 1. Probable secondary structure of COT1 predicted by Phyre2 [6]; transmembrane domains are highlighted in yellow.

In this work, we try to understand the thermodynamics of Zn(II) binding to COT1. We focus on the FHEHGHSHSHGSGGGGGGSDHSGDSKSHSHSHSHS sequence (residues 131-165) from the C-terminal region of COT1, since it is quite well conserved among zinc-binding proteins from fungal species (Fig. 2). We use mass spectrometry to understand the stoichiometry and potentiometric titrations to measure the affinity of binding. In order to establish which part of this sequence is a better Zn(II) binder, we work on three separate peptides: Ac-FHEHGHSHSHGSGGGGGG-NH_2, Ac-SHSHSHSHS-NH_2 and Ac-FHEHGHSHSHGSGGGGGGSDHSGDSKSHSHSHSHS -NH_2.

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C4YJH2      C4YJH2_CANAW      120    GLVSNGVGLVLFHEHGHSHSHGSGGGGGSDHSGDSKSHSHSHSHSHGE-ATTFSQGDEE    178
A0A1D8PGL8  A0A1D8PGL8_CANAL  120    GLVSNGVGLVLFHEHGHSHSHGGG-GGGGSDHSGDSKSHSHSHSHSHGE-ATTFSQGDEE   177
P20107      ZRC1_YEAST        121    GLISNVVGLFLFHDHGSDSLHSHSHGSVESGNNDLDIESNATHSHSHASLPNDNLAIDED   180
B9WAQ7      B9WAQ7_CANDC      120    GLISNGVGLVLFHEHGHSHSHGTNHSGDSN-----SNSNSTSHSHSHGEVATTFTQGDEE   174
                                     **:** ***.***:**  .   *. . .. .      . . . :*****.. .      **:
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Figure 2. The alignment of the transmembrane sequence of COT1 from *C. albicans* (C4YJH2) with a transmembrane Zn(II) transporter from *C. albicans* (A0A1D8PGL8), Zrc1, a zinc/cobalt resistance protein from *Saccharomyces cerevisiae* (P20107) and *Candida dubliniensis* (B9WAQ7).

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From 1D coordination polymers to 2D coordination layers. Different architectures of Co(II) complexes based on new derivatives of zoledronic acid

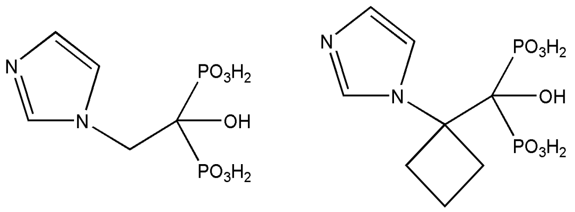
Tomasz ROJEK, [a] **Waldemar GOLDEMAN**, [a] **Katarzyna ŚLEPOKURA**, [b]
Ewa MATCZAK-JON [a]

[a] *Wrocław University of Science and Technology, Faculty of Chemistry, Wybrzeże Wyspiańskiego 27, 50-370 WROCŁAW, Poland*
[b] *University of Wrocław, Faculty of Chemistry, F. Joliot Curie 14, 50-383 WROCŁAW, Poland*
tomasz.rojek@pwr.edu.pl

Bisphosphonic acids, commonly known as bisphosphonates, are a class of compounds with a general formula $H_2O_3P–C(R_1)(R_2)–PO_3H_2$ which main application is associated with the treatment of bone disorders such as osteoporosis, Paget's disease and tumor-induced hypercalcemia of malignancy [1]. Among the commercially available compounds of this class, the highest activity is displayed by zoledronic acid (**1**).

Apart from interest of pharmaceutical industry and medical sciences bisphosphonates have been intensely studied in the field of supramolecular chemistry. Their ability to form highly complex hydrogen-bonded networks allow them to create coordination compounds of diverse supramolecular architectures and potentially wide range of applications with a variety of metal ions [2]. A specific architecture of final products is determined by various factors such as the degree of protonation of the phosphonate groups as well as geometrical preferences of the central atom. Additionally, the reaction conditions such as temperature, time of synthesis or metal/ligand stoichiometric ratio may be responsible for many possible variants of the reaction progress and topologies of final products.

As a part of our ongoing studies on new metal-bisphosphonate coordination compounds based on α,α-disubstituted derivatives of zoledronic acid [3] herein we present the crystal structures of Co(II) coordination compounds based on 1-hydroxy-2-[1-(1*H*-imidazol-1-yl)cyclobutyl]ethylidene-1,1-diphosphonic acid (**2**) comprising 1D coordination polymers and 2D coordination layer. Furthermore, we discuss the effect of reaction conditions on the architecture of the resulting product.



1 **2**

Figure 1. Zoledronic acid (**1**) and α,α-disubstituted analog (**2**).

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Effects of the stereoelectronic properties of organic anions on the stability of their anion-π complexes in aqueous solution

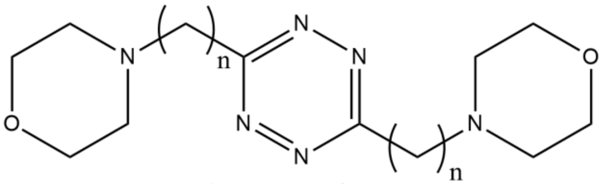
Matteo SAVASTANO, [a] **Carla BAZZICALUPI**, [a] **Antonio BIANCHI**, [a]
Celeste GARCÍA, [b] **Maria Dolores LÓPEZ DE LA TORRE**, [b] **Manuel MELGUIZO** [b]

[a] *Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 SESTO FIORENTINO, Italy.*
[b] *Department of Inorganic and Organic Chemistry, University of Jaén, 23071 JAÉN, Spain.*
msavastano@unifi.it

The binding of anions in solution generally revolves around a combination of weak forces, properly selected incorporating the required structural features in the receptor in its design stage: although individually weak, such interactions can collectively furnish enough stabilization to afford polyfunctional ligands capable of strong and selective anion binding [1].

Among the shortlist of supramolecular forces at our disposal, the most prominent were promptly recognized and investigated in detail (e.g. hydrogen bonding), while others, among which the anion-π interaction, required more time to be properly recognized by the scientific community. Alongside with the deeper appreciation of supramolecular forces, also the role of the solvent and its effects on complexation equilibria became more manifest: this is especially true for structured solvents like water, which on one hand compete strongly for charged species, while on the other are capable of promoting the association of poorly solvated species, mostly due to entropic effects, favoring, in some cases, otherwise limited associations.

We present our ongoing study on the interplay of different supramolecular forces in the binding in aqueous solution of different organic anions by our tetrazine-based receptors. Such molecules were devised as good model systems for the study of anion-π interactions in aqueous solution, conjugating a heterocycle with high positive Q_{zz} quadrupole moment with morpholine pendants to ensure water solubility without introducing very strong salt bridge donors. A primary study, concerning inorganic anions, demonstrated the correctness of such prediction, indicating a modest contribution of electrostatic forces, while the anion-π interaction, corroborated by important desolvation phenomena, was found to be a central feature of such complexes both in solution and in the solid state [2].



L1, n = 1; **L2**, n = 2

Potentiometric (pH-metric) titrations in water environment and in silico simulations were employed to evaluate L1 and L2 coordination properties towards a new set of anions presenting selected stereochemical features.

First, the effect of the basicity of the anion, or its tendency to accept a salt-bridge, was inspected comparing acetate with methanesulfonate. In second instance, their simplest aromatic analogues, benzoate and benzenesulfonate, were taken into consideration, as they added to the mix the possibility of π-π stacking interactions while enhancing the hydrophobic effect. Lastly, the effect of the insertion of a second charged group was examined studying phthalate and isophtalate anions, allowing to draw a parallel between the stability of the complexes of the two regioisomers. Influence of the mutual size of host and guest was indirectly taken into account due to the different length of the aliphatic spacers in the two ligands.

Needless to say, a complicated picture emerged, demanding further analyses and demonstrating, once again, how shedding light on the subtleties of the interplay of so many different effects, even within the framework of simplified model systems, still remains an ambitious task.

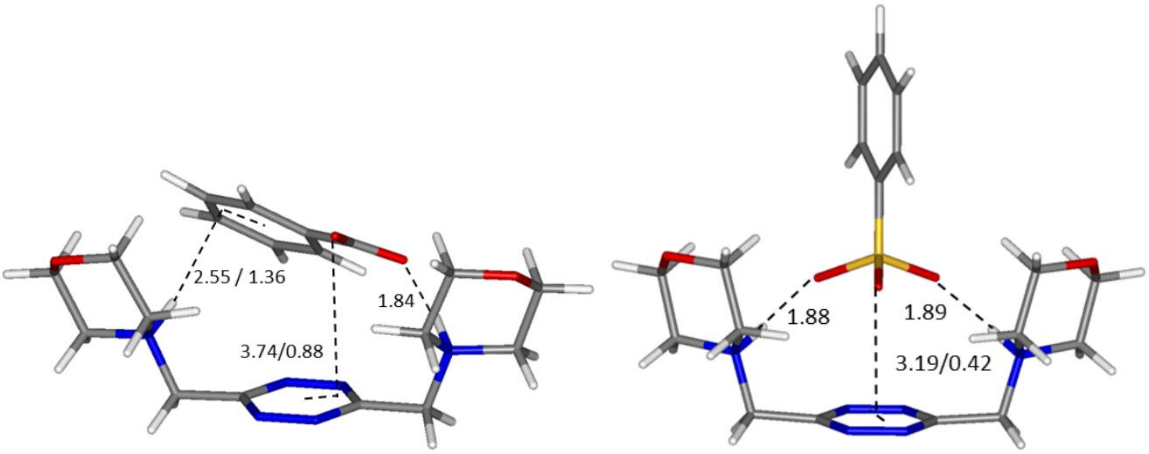


Figure 1. Calculated conformations for the adducts of H_2L1^{2+} with benzoate and benzenesulfonate anions.

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Design of catechol-derived rosamine ligands. Spectrophotometric behavior in the presence of biogenic amines

Filipe MONTEIRO-SILVA, a) Gerardo G. AGUILAR, a) Carla QUEIRÓS, b)
Andreia LEITE, b) Maria RANGEL, c) Tomás TORROBA, d) Ana M. G. SILVA b)

a) Centre for Applied Photonics, INESC TEC, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 4169-007 PORTO, Portugal
b) LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 4169-007 PORTO, Portugal
c) LAQV-REQUIMTE, Instituto de Ciências Biomédicas de Abel Salazar, Rua Jorge de Viterbo Ferreira 228, 4099-003 PORTO, Portugal
d) Departamento de Química, Facultad de Ciencias, Universidad de Burgos,
09001 BURGOS, Spain
ana.silva@fc.up.pt

Novel fluorescent ligands are currently a highly attractive research field with potential application in diversified areas such as environmental science, medicine, pharmacy and cellular biology. Possessing excellent photophysical properties, usually featuring good photostability, with long emission and absorption wavelengths in the visible spectra, rhodamine derivatives are of particular and useful interest and their myriad of applications has been demonstrated in fibre optic sensor devices [1], chemical dosimetry [2, 3], lysosomal pH probes [4, 5], among others.

Amines, on the other hand, are produced in ton scale worldwide and while being broadly used in pharmaceutical, agricultural and several industry-based applications (surfactants, hydrocarbon-related operations, coatings and corrosion inhibitors) might constitute a serious environmental and health issue [6].

Inspired by the protonation and redox behaviour of catechols and by the excellent photophysical properties of the xanthene scaffold, a series of novel rosamine ligands (**1-4**, Figure 1A) was successfully synthesized by adopting a microwave assisted protocol [7].

Ligands **3** and **4** containing a free catecholate unit have shown to be nearly non-fluorescent, due to the PET that occurs from the hydroxylate group to the xanthylium core. However, when ligand **4** is exposed to butylamine (Figure 1B), a remarkable increase and blue shift of fluorescence is observed due to the formation of the new 9-butylamine substituted xanthylium chromophore **5** (Figure 1C), with concomitant appearance of a radical signal (Figure 1D). The behaviour of ligand **4** was also explored in the presence of other amines including diethylamine, putrescine and cadaverine, affording the corresponding 9-alkylamine substituted xanthylium chromophores **6**, **7** and **8**. All 9-alkylamine substituted xanthylium chromophores (**5-8**) were characterized by NMR, UV-Vis, fluorescence spectroscopy and mass spectrometry.

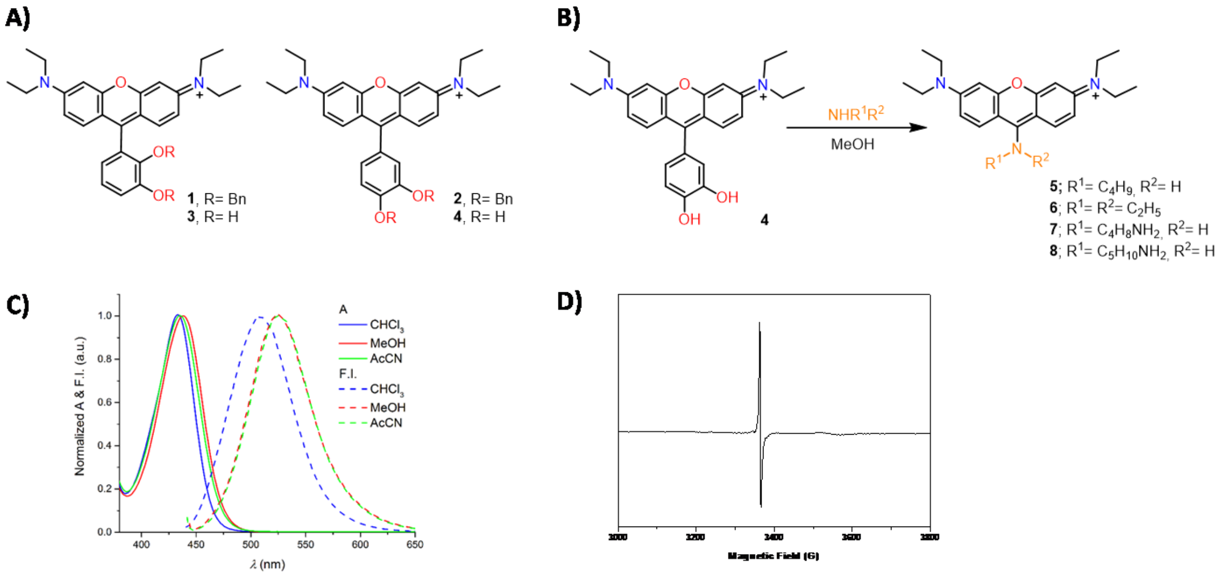

Figure 1. (A) Structures of catechol-derived rosamines **1-4**; (B) Structures of products **5-8** isolated from the reaction of ligand **4** with amines: butylamine, diethylamine, putrescine and cadaverine; (C) Absorption and fluorescence spectra of **5** in $CHCl_3$, MeOH and AcCN; (D) EPR spectrum of **4** after addition of butylamine measured at room temperature in $CHCl_3$.

Acknowledgments: this work was supported through UID/QUI/50006/2013 - POCI/01/0145/FEDER/007265 (LAQV/REQUIMTE) with financial support from FCT/MEC through national funds and co-financed by FEDER, under the Partnership Agreement PT2020 and also through the project M-ERA-NET/0005/2014, European Funds through project FP7-SEC-312411 (AE2013-0059), National Funds through project UID/EEA/50014/2013 and Spanish Funds through the project CTQ2012-31611. C.Q. and A.L. would also like to thank FCT for their grants SFRH/BD/79702/2011 and SFRH/BPD/85793/2012, respectively.

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Impact of the γ-irradiation on the palladium behavior in the PUREX process

Bénédicte SIMON, [a] **Christine BOUYER**, [a] **Stéphanie DE SIO**, [b]
Claude BERTHON, [a] **Frédéric MISERQUE**, [c] **Nathalie BOUBALS**, [a]
Alexandre CHAGNES, [d] **Laurence BERTHON** [a]

[a] CEA Marcoule, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes (DMRC/SPDS/LDPS), BP 17171,
30207 BAGNOLS-SUR-CÈZE Cedex, France
[b] AREVA NC, BUR/DT/DRDP, 92084 PARIS La DEFENSE
[c] CEA Saclay, Nuclear Energy Division, Physico-Chemical Department (DPC),
91190 GIF-SUR-YVETTE, France
[d] GéoRessources - UMR CNRS 7359-CREGU-Université de Lorraine, 2 rue du Doyen Roubault, 54518 VANDOEUVRE LES NANCY Cedex, France
benedicte.simon@cea.fr

The PUREX process uses 30%$_{\text{Vol}}$ tri-n-butylphosphate (TBP) diluted in tetrapropylen hydrogen (TPH, an hydrocarbon diluent) to selectively extract uranium(VI) and plutonium(IV) towards fission products such as ruthenium, molybdene, cesium, palladium, etc. In this process, the solvent is subject to radiolysis, which could result in a modification of the solution composition and the occurrence of cruds. The main consequence of these phenomena is a change in the extraction properties of the solvent, especially in terms of efficiency and selectivity. Many papers report detailed qualitative and quantitative investigations of TBP-TPH degradation due to radiolysis [1]. However, very few data report the influence of the radiolysis on the palladium behavior [2,3]. Indeed, some degraded products could interact with palladium to form either complexes or precipitates [4].

In this study, the impact of the radiolytic degradation of TBP-TPH on the palladium behavior will be thoroughly discussed. For that purpose, a fine characterization of the precipitates formed by γ-irradiation of the biphasic system TBP-TPH//Pd-HNO_3 will be detailed.

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About the prediction of speciation in binary aqueous solutions of multiply self-complexing electrolytes

Jean-Pierre SIMONIN

Laboratoire PHENIX, Université Pierre et Marie Curie, 4 place Jussieu,75005 PARIS, France
jpsimonin@gmail.com

Various publicly available and commercial software allow estimations of the speciation for many metal cations in aqueous solutions containing various types of anions. These software include MINEQL+, CHESS, SPECIES, MINTEQ, PHREEQC and CHEAQS. The determination of the speciation is based on a numerical solution to the chemical association equilibria. These software rely on previous determinations of the thermodynamic complex formation constants, β_n, which can be found in famous books, e.g., in the book by Sillen and Martell [1], or in the NIST or IUPAC databases. The solution to the chemical equilibria involves formulas for the computation of the activity coefficients of the species (free ions and complexes). These deviations from ideality (besides association) are computed using equations of the Debye-Hückel type with a correction, such as the Davies equation in CHESS, MINTEQ, PHREEQC or CHEAQS, or the specific interaction theory (SIT) which is available in MINTEQ for more concentrated solutions. Use of the Davies equation should be limited to concentrations below 0.1 M [2], but it has been proposed to extend its validity to 1 M in CHEAQS and MINTEQ.

To illustrate, in this work, we consider the case of aqueous solutions of zinc and cadmium halides. Of particular importance are chloride complexes in geochemical and environmental studies involving seawater, brines and hydrothermal solutions [3]. For a given salt concentration and a given set of β_n values for n going from 1 to 4, the speciation was solved by employing a Newton-Raphson method in 6 dimensions. The 6 equations to solve were the 4 equations for the complexation equilibria in which the activity coefficients were computed according to some model, and the 2 relations for the conservation of metal cation and halide anion. First, the equilibria were solved using the Davies equation for the deviations from ideality of the various species in solution (as done in the software mentioned above) together with the commonly admitted complexity constants values. Surprisingly, it was found that the mean salt activity coefficient values obtained from this procedure are *not* in agreement with the experimental data. Figure 1 shows the example of $ZnCl_2$ and $CdBr_2$.

This thermodynamic inconsistency was also examined using a simplified version of the mean spherical approximation (MSA) model [4], which is expected to be much more reliable than the Davies equation. Another advantage of this model is that it is a priori allows one to predict deviations from ideality up to higher concentrations, corresponding typically to ionic strengths of 3 M. In this model the only parameter characterizing an ion is its diameter. The diameters of the complexes were estimated on the basis of their structure. The Pauling size was utilized for the halide anions. Plots are shown in Figure 2 for the same salts as in Figure 1. Again, large discrepancies with respect to experimental data are observed. A significant discrepancy was similarly found in the case of $CdCl_2$ (results not shown). On the other hand, a satisfying agreement was obtained when using the MSA in the case of CdI_2.

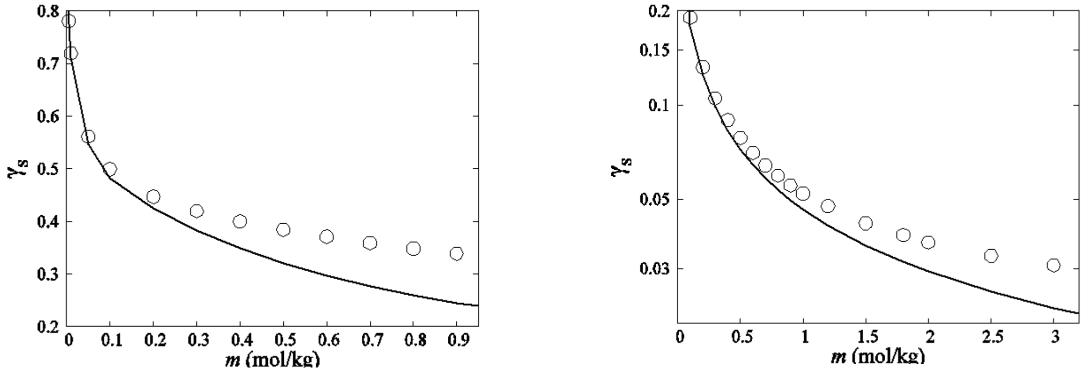

Figure 1. Mean salt activity coefficients for $ZnCl_2$ (left) and $CdBr_2$ (right). Symbols = experimental data; line = results using the Davies equation below 1 M ionic strength. Log-scale used for $CdBr_2$.

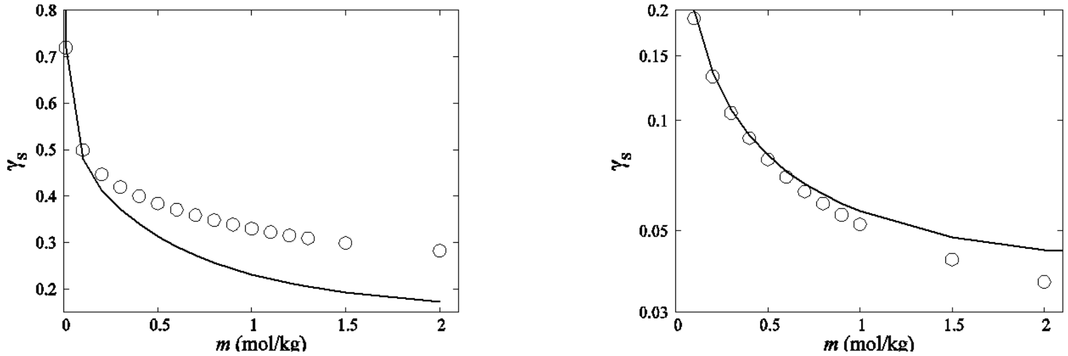

Figure 2. Same legend as for Figure 1, except that line = result from MSA.

These results suggest that the values for the complex formation constants might not be always accurate enough for the determination of speciation. In this first approach in which binary solutions are considered, revised values for the complexation constants of $ZnCl_2$, $ZnBr_2$, $CdCl_2$ and $CdBr_2$ have been optimized using the MSA. These values yield mean salt activity coefficients in keeping with the experimental data.

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Transfer hydrogenation of ketones catalyzed by novel arene ruthenium iminophosphonamides

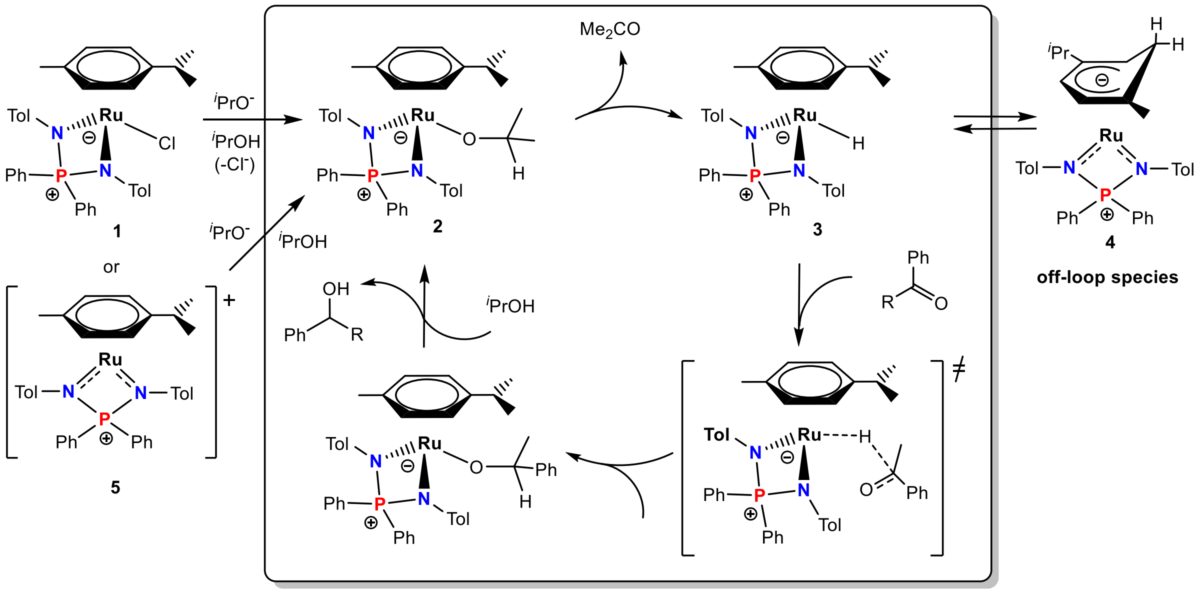
Iana S. SINOPALNIKOVA, [a,b] **Tat'yana A. PEGANOVA**, [a] **Alexander M. KALSIN**, [a] **Eric DEYDIER**, [b] **Rinaldo POLI** [b]

[a] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 Vavilov str., 119991 MOSCOW, Russia
[b] Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne,
31077 TOULOUSE Cedex, France
iana.sinopalnikova@lcc-toulouse.fr

Since the 1990's, after the discovery of the highly enantioselective catalysts [(arene)RuCl(Ts-DPEN)] [1] and [Cp*MCl(Ts-DPEN)] [2] (M = Rh, Ir) (DPEN = 1,2-diamino-1,2-diphenylethane), asymmetric transfer hydrogenation (ATH) of ketones has become a versatile and powerful method for the production of enantiomerically pure secondary alcohols. The quest for higher activities has provided extremely active [(Josiphos)RuCl{κ^3-C,N,N-1-(6-arylpyridin-2-yl)methanamines}] [3] and [(*p*-cymene)RuCl{1-(Pr_2P)-2-(NMe_2)-Indenyl}] [4], able to hydrogenate aromatic ketones in isopropanol with TOF up to $10^5 – 10^6$ h^{-1}. In spite of more than 20 years of further development, predicting the activity of such catalysts is however still a hard task, and the search for novel promising TH catalysts remains a topic of great current interest.

We have recently reported the synthesis and chemical properties of a series of 18ē and 16ē half-sandwich arene ruthenium iminophosphonamide (NPN) complexes of type [(arene)Ru{($R_2P(NR')_2$}(X)] (X = Cl^-, PF_6^-, BAr_4^-) [5], which are isoelectronic with and structural analogues of Noyori's catalysts. The zwitterionic NPN ligand is a strong σ,π-donor and can efficiently stabilize the coordinatively unsaturated 16ē NPN complexes.

We shall present here the first examples of catalytic transfer hydrogenation of acetophenone (Acp) with NPN-complexes [(arene)Ru{($Ph_2P(NTol)_2$}(X)] (arene: (**a**) *p*-cymene, (**b**) C_6Me_6) in isopropanol. In the absence of additional base, only the 18ē NPN-complexes (X = Cl) slowly catalyze the Acp reduction (TOF ~ 10 h^{-1}). However, the addition of 1 equiv. of a strong base makes both the 18ē and the 16ē complexes active (TOF ~ 200 h^{-1}). We have thoroughly scrutinized the catalytic mechanism for a *p*-cymene complex by experimental kinetics investigations as well as DFT calculations on a model system, resulting in the proposed catalytic cycle shown in the scheme. All numbered intermediates and off-loop species were either isolated or identified spectroscopically. The activity of the NPN-complexes with the C_6Me_6 ligand are significantly lower because of an increased stability of the isopropoxide complex **2** towards *β*-hydrogen elimination, which correlates with the higher measured dissociation enthalpy (ΔH_d) for the Ru–Cl bond in **1b** compared to **1a**. The *β*-hydrogen elimination of the alkoxide complex is therefore proposed to be the rate-limiting step of the catalytic cycle. Further investigations of the N- and P- substituent effects on catalysis are in progress.



Acknowledgements: the authors thank the Russian Science Foundation (grant no. 14-13-00801) for financial support. I.S. thanks the French Ministry of Foreign Affairs for a Ph.D. scholarship through the French Embassy in Moscow.

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Interaction of desferrioxamine B with lanthanide ions investigated by affinity capillary electrophoresis and liquid-liquid extraction

Mingjian HE, [a] Vladimir SLADKOV, [a] Claire LE NAOUR, [a] Michel MEYER [b]

[a] Institut de Physique Nucléaire, IN2P3-CNRS, Université Paris-Sud, Université Paris-Saclay, 91406 ORSAY Cedex, France
[b] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302), Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870, 21078 DIJON Cedex, France
sladkov@ipno.in2p3.fr

Siderophores are ubiquitous, high-affinity iron(III) chelators excreted by virtually all bacteria and yeasts under iron-stress conditions. Their primary biological role is to supply the microorganisms with iron, an essential nutrient and growth factor. As a mean to circumvent the extremely low bioavailability of this element at physiological pH, siderophores react with ferric (oxo)hydroxides and form thereby water-soluble complexes which are transported across the cell membranes according to an energy-driven mechanism involving specific outer-membrane uptake receptors. Hydroxamates are common bidentate chelating groups found in many siderophores, including desferrioxamine B (DFO, Figure 1) produced by the bacterium *Streptomyces pilosus*.

Figure 1. Chemical formula of desferrioxamine B.

As the concentration of siderophores in soils is typically in the µg/kg range, these compounds might significantly increase the solubility, migration rate, and bioavailability of highly toxic actinides in case of environmental contamination. Thus, in relation to the management and remediation of contaminated fields or the disposal of nuclear wastes in geological repositories, it is of outmost importance to gain a deeper understanding of the coordination chemistry of f-element by siderophores and related chelators. In this work, we are focusing on the complexation properties of DFO with respect to lanthanide ions (Ln^{3+}), often considered as "cold" surrogates of trivalent minor actinides (An^{3+}), such as Am^{3+} and Cm^{3+}. Our aim was to investigate by means of affinity capillary electrophoresis (ACE) and liquid-liquid extraction (LLE) the speciation of DFO in the presence of several lanthanides.

ACE measurements have been performed in aqueous perchloric acid solutions at a fixed pH value of 2.5 and ionic strength (I= 0.5 M $NaClO_4/HClO_4$). The electrophoretic mobility increase of DFO (positively charged in these conditions) induced upon addition of increasing amounts of lanthanide cations in the background electrolyte solution (up to 0.01 M) was monitored by UV absorption spectrophotometry. Since mobilities at given pH values reflect the chemical equilibria occurring in solution [2], the ACE data enabled us to propose a speciation model and to refine the corresponding stability constants.

LLE with γ-detection has also been used to study the interaction of DFO with $^{152}\text{Eu}^{3+}$ at the ultra-trace level (*ca.* 10^{-10} M). The distribution coefficients of $^{152}\text{Eu}^{3+}$ between the organic and aqueous phases have been determined as a function of the DFO content of the aqueous phase (10^{-5}–0.05 M) at a constant ionic strength and at fixed pH. The analysis of the distribution coefficient as a function of ligand concentration allows one to obtain information on the composition of the predominant species and to determine the stability constants of the formed complexes [3]. The LLE data enabled us not only to confirm, but also to complete, the speciation model deduced from ACE experiments. Both approaches are complementary, as each technique works in different total concentration ranges as well as metal/ligand concentration ratios.

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Complexation of U(VI) and Pu(VI) with succinic acid in aqueous acid solutions: Experimental data and DFT calculations

Vladimir SLADKOV, [a] **Alexei A. BESSONOV**, [b] **Jérôme ROQUES**, [a]
Alexandre M. FEDOSSEEV, [b] **Iraida A. CHARUSHNIKOVA** [b]

[a] *Institut de Physique Nucléaire, IN2P3-CNRS, Université Paris-Sud, Université Paris-Saclay, 91406 ORSAY Cedex, France*
[b] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences (IPCE RAS), 199071 MOSCOW, Russia*
sladkov@ipno.in2p3.fr

Uranium and plutonium migration in environmental systems is an important concern. Knowledge of their transport in the environment is crucial, not only for fundamental geochemistry, but for assessing the risk posed by long-term storage of nuclear waste [1]. The environmental impact strongly depends on the mobility of a given radionuclide in environmental aquatic systems [2]. The majority of uranium contaminated waters contain the uranium ions in degree oxidation VI. Natural oxidative conditions frequently occur in many environmental systems. Pu(VI) is stable in highly oxidized waters with high ionic strength [1,3]. The transuranium elements (Pu in particular) in their highest oxidized forms, +5 and +6, are rather mobile in environment. Among a variety of possible geochemical processes, complex formation with natural organic matter (NOM) present in the aqueous phase plays an important role in the eventual dispersion of radionuclides [4]. The formation of such complexes typically causes significant changes in their migration properties in the environment. Here we study the interaction of U(VI) and Pu(VI) with succinic acid. Succinic acid is chosen as a simple model of the structurally more complicated NOM. From literature data we have contradictory information about the formation of protonated complex species of U(VI) with succinic acid. To the best of our knowledge only two articles are devoted to the complexation of Pu(VI) with succinic acid.

The interaction of U(VI) with succinic acid has been studied in perchloric acid aqueous solutions (pH 2.0-2.5, 0.1 M ionic strength). The observed U(VI) mobility is found to decrease with increasing ligand concentration added to the background electrolyte solution (up to 0.1 M). Since metal-ion mobilities at different pH values reflect the chemical equilibria occurring in solution, the ACE data are employed to deduce the speciation model for uranyl in the presence of succinic acid [5]. The UV-vis spectrophotometry has been used to study the interaction of Pu(VI) with succinic acid in acid solutions. The different speciation models are proposed. The formation of protonated complex species is discussed. Moreover, the values of the stability constants at 0.1 M ionic strength are deduced by numerical data processing.

The U(VI) and Pu(VI) systems with succinic acid are also investigated by quantum chemical modeling (DFT method) in aqueous solutions. The obtained theoretical data are compared with the experimental ones.

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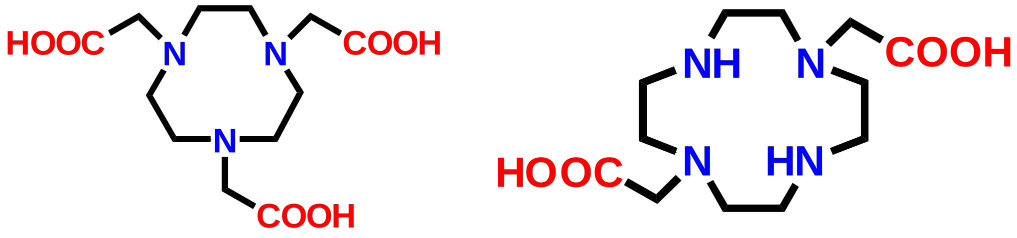
Kinetic study of Ln(III) complexes with hexadentate macrocyclic ligands

Filip SMRČKA, [a)] **Jakub VANĚK**, [a,b)] **Přemysl LUBAL**, [a,b)] **Petr HERMANN** [c)]

[a)] *Masaryk University, Faculty of Science, Department of Chemistry, Kotlářská 2,*
61137 BRNO, Czech Republic
[b)] *Central European Institute of Technology (CEITEC), Masaryk University, Kamenice 5,*
62500 BRNO, Czech Republic
[c)] *Charles University, Faculty of Science, Department of Inorganic Chemistry, Hlavova 2030,*
12840 PRAGUE, Czech Republic
filip.smrcka@gmail.com

Lanthanide(III) complexes of polyaza-macrocyclic ligands (mostly DOTA-like ligands) are utilized in many areas of medicine (*e.g.* complexes of metal radioisotopes as ^{90}Y, ^{153}Sm, ^{166}Ho, ^{177}Lu in nuclear medicine, Gd(III) complexes as MRI contrast agents, Eu(III) or Tb(III) complexes as luminescent probes). For any biomedical applications, such metal complexes should exhibit a high thermodynamic stability as well as kinetic inertness under physiological conditions and, therefore, knowledge of these properties is important.



NOTA ***trans*-DO2A**

Figure 1. Structural formulas of studied macrocyclic ligands.

The thermodynamic and kinetic data on Ln(III) complexes of some hexadentate azamacrocyclic ligands (see Figure 1: *trans*-DO2A = 1,4,7,10-tetraazacyclododecane-1,7-diacetic acid or NOTA = 1,4,7-triazacyclononane-1,4,7-triacetic acid) are rare [1,2] and some published experimental data are not in agreement [3-5]. Kinetic properties of several Ln(III) complexes of *trans*-DO2A and NOTA were studied by molecular absorption and luminescence spectroscopies in UV/VIS region. Reaction mechanisms of formation and acid-assisted dissociation of the Ln(III) complexes were proposed from time-resolved luminescence spectroscopy. The results obtained for the Ln(III) complexes of hexadentate tetraaza- and triazamacrocyclic ligands (*trans*-DO2A and NOTA, respectively) are compared. The NOTA ligand forms metal complexes with Ln(III) ions faster than DO2A ligand and those complexes are also more kinetically inert. In addition, the comparison is extended to experimental data found for similar Ln(III) complexes of tetraazamacrocyclic ligands of higher denticity [6-12].

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X-ray absorption studies on radioactive metal complexes at the MARS beamline of Synchrotron SOLEIL

Pier Lorenzo SOLARI

Synchrotron Soleil, L'Orme des Merisiers, Saint-Aubin BP 48,
91192 GIF-SUR-YVETTE Cedex, France
pier-lorenzo.solari@synchrotron-soleil.fr

The MARS beamline of the Synchrotron SOLEIL [1,2] is dedicated to advanced structural and chemical characterizations of radioactive matter (solid or liquid), coupling analytical tools such as X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD) and X-ray fluorescence (XRF).

Since September 2013, analyses on radioactive samples at ambient temperature and pressure with activities up to 20 000 times above the French exemption limit are now allowed (thus for actinides up to activities of 200 MBq). Yet, the final aim is to get an extension of the possibilities of analyses onto a larger variety of experiments and to activities up to 18.5 GBq. In this contribution we will give an overview of the design and capabilities of the beamline, followed by a selection of results related to XAS studies on radioactive metal complexes.

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Chiral bipyridine and bipyrimidine ligands and complexation studies

Atena B. SOLEA, [a,b] **Liangru YANG**, [c] **Katharina FROMM**, [b]
Christophe ALLEMANN, [a] **Olimpia MAMULA-STEINER** [a]

[a] *University of Applied Sciences of Western Switzerland, HEIA-FR, Pérolles 80,*
1705 FRIBOURG, Switzerland
[b] *University of Fribourg, Department of Chemistry, Chemin du Musée 9,*
1700 FRIBOURG, Switzerland
[c] *Henan University of Technology, School of Chemistry and Chemical Engineering,*
450001 ZHENGZHOU, P. R. China
atena-bianca.solea@hefr.ch

Ligands with two pyridine units fused to a pinene-type bicycle were first introduced in 1992 [1], and since then, they have been used extensively to predetermine the configuration in complexes of transition metals [2]. Moreover, by functionalizing these ligands with a carboxylic unit, several interesting lanthanide(III) complexes have been obtained [3].

We will present a series of novel, enantiomerically pure ligands based on pinene-bipyridine (**L1**, **L2**) and pinene-pyrimidine (**L3**-**L5**). These ligands were employed in complexation reactions with lanthanide(III) ions and the preliminary results of these studies will be presented. The existence of two binding sites in ligands **L3**-**L6** opens the way for obtaining d-f MOFs with interesting magnetic, luminescent and chiral proprieties.

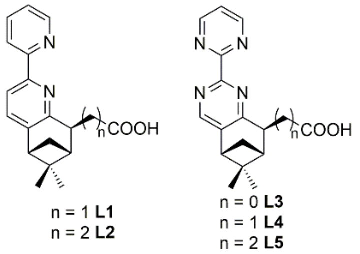

Figure 1. Structure of ligands **L1-L5**.

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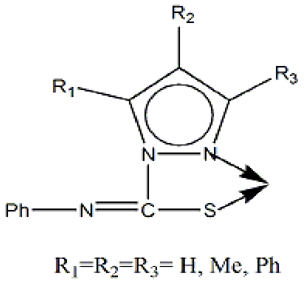
Nickel(II) complexes with a series of phenylisothiocyanate-pyrazole ligands: Antimicrobial, spectroscopic and fluorescence studies

Behzad SOLTANI, [a] **Christopher ZIEGLER**, [b] **Mina VALIPOUR** [a]

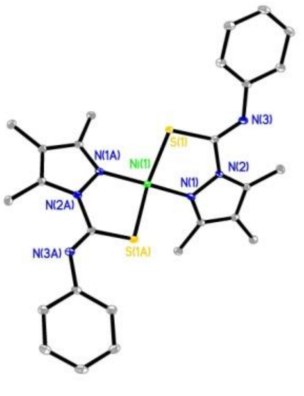
[a] *Chemistry Department, Science Faculty, Azarbaijan Shahid Madani University,*
TABRIZ, Iran
[b] *University of Akron, Department of Chemistry, AKRON, OH 44325, USA*
soltani@azaruniv.edu

Multidonor ligands containing nitrogen and sulphur atoms, and their versatile chelating ability with transition metal ions, have attracted considerable interest in biological systems [1-2]. Among these ligands, we have focused on pyrazole derivatives because of their rich coordination chemistry with transition metal ions and their broad pharmacological activity [3-4]. N,S-donor bidentate ligands show antimicrobial activity [1,5]. Keeping in view biological properties of N,S-donor pyrazole derived ligands and the potential chemistry of transition metals [6], a series of Ni(II) complexes of general formula [Ni(N^S)$_2$] were synthesized, where (N^S) is a bidentate anionic ligand: [PhNCSPz]$^-$, [PhNCSPz^{Me2}]$^-$, [PhNCSPz^{Me3}]$^-$, [PhNCSPz^{PhMe}]$^-$ (Pz = Pyrazole, Pz^{Me2} = 3,5-dimethylpyrazole, Pz^{Me3} = 3,4,5-trimethylpyrazole and Pz^{PhMe} = 3(5)phenyl-5(3)methylepyrazole) (Scheme 1).

The synthesized complexes were characterized by elemental analyses, spectral (UV-vis, IR, ^{1}H NMR, fluorescence) studies. Determination by X-ray diffraction analysis of [Ni(PhNCDPz^{Me3})$_2$] (**1**) showing a trans-square planar geometry with [Ni-S(1) = Ni-S(1A) = 2.177(5) Å] and [Ni-N(1) = Ni-N(1A) = 1.874(15) Å]. The ORTEP drawings of **1** with the atom numbering and a view of the molecular packing are shown in Figure 1. In order to evaluate the biological activity of N,S-donor ligands and to assess the role of metal ion on biological activity, the antibacterial properties of pyrazole-plenylisothisyanate ligands and their metal complexes have been studied in vitro against gram positive (*S. aureus*) and gram negative (*E. coli*) bacteria. Results evidenced that the N,S-donor ligands are biologically active and their metal complexes show that antibacterial activity against bacterial strains has increased in comparison with the free ligands.



Scheme 1. Pyrazole-based ligands [PhNCSPz^R]$^-$.



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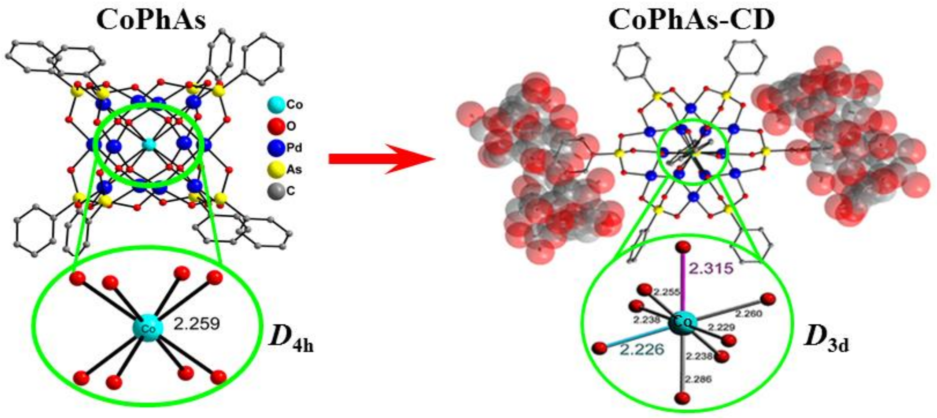
Host-guest interaction for magnetic anisotropy tuning of transition metal- and lanthanide-containing palladium(II)-oxo complexes

Maria STUCKART, [a,b] Natalya V. IZAROVA, [b] Jan van LEUSEN, [a]
Carolin SCHMITZ-ANTONIAK, [b] Paul KÖGERLER [a,b]

[a] *Institute of Inorganic Chemistry, RWTH Aachen University, 52074 AACHEN, Germany*
[b] *Peter Grünberg Institute (PGI-6), Forschungszentrum Jülich, 52425 JÜLICH, Germany*
m.stuckart@fz-juelich.de

Polyoxometalates (POMs) represent a huge class of discrete, structurally well-defined polynuclear metal oxide-based anions possessing valuable properties for prospective applications in catalysis, medicine and electronics [1]. The modification of POMs with organic moieties is actively explored as step towards the development of functional POM-containing hybrid materials [2]. One of the recently identified approaches for POM hybridization is a supramolecular host-guest interaction with macrocycles, namely, cyclodextrins (CDs) [3].

Here we present the results of functionalization of phenylarsonate-capped palladium-based POMs (polyoxopalladates) by α-CDs [4]. As an outcome of our work, a series of complexes of phenylarsonate-containing polyoxopalladates encapsulating either transition metal- or lanthanide ion and α-CD in 1:2 and 1:3 ratios, possessing the general formula $Na_aK_b{\cdot}x(C_{36}H_{60}O_{30}){\supset}[MO_8Pd^{II}_{12}(C_6H_5As^{V}O_3)_8]{\cdot}yH_2O{\cdot}zKCl$, was obtained ($M = Fe^{III}$ (**FePhAs-CD**), Co^{II} (**CoPhAs-CD**), Ni^{II} (**NiPhAs-CD**), Zn^{II} (**ZnPhAs-CD**), Gd^{III} (**GdPhAs-CD**), Dy^{III} (**DyPhAs-CD**), Ho^{III} (**HoPhAs-CD**); $a = 0 – 1$; $b = 4 – 6$; $x = 2 – 3$; $y = 28 – 45$; $z = 0 – 1$). All compounds were characterized in the solid state (elemental analysis, XRD, FT-IR, TGA) while the diamagnetic Zn(II)-based derivative **ZnPhAs-CD** was also studied in solution via ^{1}H and ^{13}C NMR spectroscopy.



Scheme 1. Compression of a POM by CD encapsulation.

According to the single-crystal XRD data, formation of POM-CD hybrids led to notable geometrical distortions in the coordination environment of the 3d or 4f heterometal ion in the centre of polyoxo-12-palladate shell compared to their perfect cubic coordination environment that is present in non-functionalized $\{Pd_{12}\}$-type polyoxopalladate structures (Scheme 1). This effect is apparently caused by the compression of the POM species between cyclodextrin moieties. The effect of this "chemical pressure"-induced geometric change was studied on **CoPhAs-CD** by SQUID, EPR, XMCD, XMLD and XANES spectroscopies.

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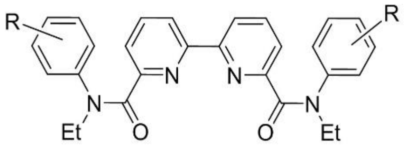
Complexes of diamides of 2,2’-bipyridyl-6,6’-dicarboxylic acid with lanthanides: The influence of ligand on the stability

Tsagana SUMYANOVA, **Natalya BORISOVA**, **Alexey IVANOV**

Radiochemistry Division, Chemistry Department, M.V. Lomonosov Moscow State University,
1/10, Leninskiye Gory st., 119234 MOSCOW, Russia
ts.sumyanova90@gmail.com

Diamides of N-donor heterocyclic carboxylic acids are promising extractants for the separation of f-elements ions; moreover, their complexes possess specific photophysical properties allowing their use in electronics and medicine.



R = *o*-F (**1**); *m*-F (**2**); *o,p*-diMe (**3**); *o,m*-diMe (**4**); H (**5**[1])

The aim of our work is to determine the influence of substituents in the amidic parts of diamides (**1-4**) on the stability constants of their complexes as well as changes in the stability in the lanthanides series. We investigated two groups of ligands: containing the electron-withdrawing fluorine atoms *o-* (**1**) and the *m*-fluorine-substituted diamides (**2**) and the electron-rich methyl groups of *o,p-* (**3**) and *o,m*-dimethyl-substituted (**4**) anilides, an unsubstituted amide (**5**) was used as a reference. The stability constants of a series of complexes of lanthanide ions with ligands **1-4** (Figure 1) were determined in dry acetonitrile by UV/VIS titration. All diamides form one complex with 1:1 metal-to-ligand stoichiometry. The log β_1 values for the investigated anilides complexes with lanthanides ions fall into 5.5-6.2 region. The ligands demonstrate different behavior according to the electronic properties of the substituents. The electron-rich dimethyl-substituted ligands insignificantly increase the stability of complexes except the complex of diamide **3** with thulium, and complexes of ligand **4** with holmium and lutetium. Whereas the electron-withdrawing groups act differently in dependence with the position of the substituent: the *o*-fluoro-substituted ligand **1** enhances the stability of the complexes comparing with unsubstituted diamide **5**, and the *m*-fluoro-substituted ligand **2** reduces, but the stability of complexes cerium and praseodymium with ligands **1** and **2** are equal within the error limits. The position of methyl substituents is of great importance: complexes of *o,m*-disubstituted anilide **4** are less stable than for *o,p*-isomer **3**.

The stability of lanthanide complexes depends slightly on the atomic number. As well as for unsubstituted anilide **5**, some diminution in the stability of complexes from the beginning of the series to europium ion is observed for its substituted analogs. Unlike unsubstituted anilide **5**, for fluorine-substituted diamides, the stability of complexes from gadolinium to lutetium strongly depends on the position of the substituent: the stability of complexes with *o*-fluoro-substituted anilide **1** increases while the constants with *m*-fluoro-substituted ones firstly increases for the gadolinium and terbium ions, and then drops down. The stability of the gadolinium complex with the electron-rich *o,m*-dimethyl-substituted ligand **4** is lower than the stability of europium complex, and then the stability of complexes increases with increasing the atomic number of the lanthanide to erbium complex.

Thus, halogen in the *o*-position of the anilide stabilizes the complex due to conjugation of halogen long pairs with the aromatic ring, which does not occur in the case of the *m*-isomer, which demonstrate mostly the electron-withdrawing properties. The electron-rich substituents have a less effect on the stability of complexes; this might be so because of the examination only *o*-substituted diamides, which may cause a decrease in the stability of complexes due to steric effects.

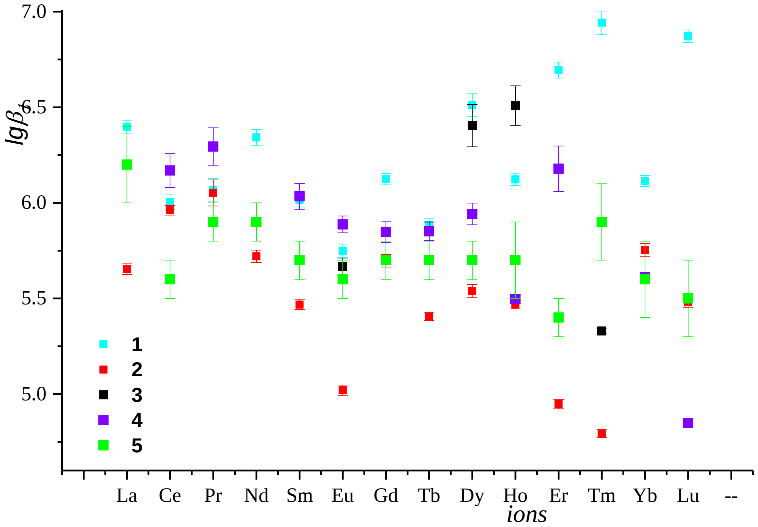


Figure 1. The lanthanide ion dependence of the stability constants values for anilides **1-5**.

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Gold(I) BODIPY-imidazole bimetallic complexes as new potential anti-inflammatory and anticancer trackable agents

Audrey TROMMENSCHLAGER, Florian CHOTARD, Benoît BERTRAND, Souheila AMOR, Lucile DONDAINE, Pierre LE GENDRE, Catherine PAUL, Christine GOZE, Ewen BODIO

Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
audrey.trommenschlager@u-bourgogne.fr

Metal-based drugs have been widely studied for the treatment of cancers. Especially, platinum derivatives are used in more than 70% of chemotherapeutic cocktails [1,2]. However, most of current treatments induce severe side effects. Among them, cardiotoxicity [3], which is reported as be caused by inflammation phenomena, strongly limits their use.

Thus, we decided to develop anticancer agents, which display anti-inflammatory properties. We draw our inspiration from auranofin – a gold(I) complex used to treat inflammation disorders and which recently enters Phase II clinical trial as a potential anticancer agent – and focus our attention on gold based complexes.

Moreover, our expertise in the conception of trackable therapeutic agents led us to integrate an imaging probe - a BODIPY – in the core of the complexes, in order to give crucial information on the behaviour and the localization some compounds in the cellular environment (cf. Figure 1). Among the gold(I) homobimetallic complexes synthesized, one of them displays both promising anticancer and anti-inflammatory properties and can be tracked *in vitro* at submicromolar range by optical imaging.

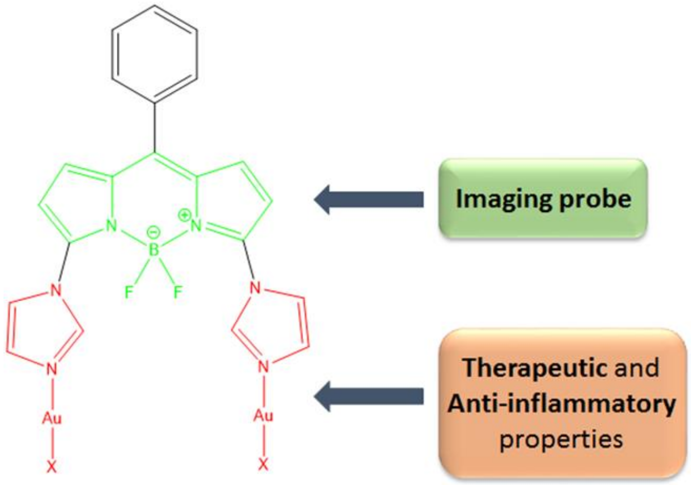

Figure 1. Stucture of gold(I) homobimetallic complexes.

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Lead complexes of cysteine containing peptides

Katalin VÁRNAGY, Györgyi SZUNYOG

University of Debrecen, Egyetem tér 1., 4032 DEBRECEN, Hungary
varnagy.katalin@science.unideb.hu

The lead is a serious environmental toxin, because it has accumulated in the environment much above the natural level due to the human activity during thousands of years. Based on the soft character of the metal ion, it can bind to the proteins and first of all the side chain thiol groups provide effective binding site for them. As a consequence, this metal ion is able to substitute the essential metal ions (e.g. zinc(II), nickel(II), calcium(II)) in the metalloenzymes and metalloproteins resulting drastic change in their biochemical functions [1]. The accumulation of toxic metal ions can cause carcinogenic effect or physiological change in the bones, kidneys or indirectly might take part in the development of neurodegenerative disorders.

The goal of our research was the designing and synthesis of peptides with high lead(II) binding affinity. We synthesized a series of peptides containing one or two cysteine residues. One group of the ligands have free N-terminal amino group and amide group on the C-termini: Ser-Ser-Cys-Ser-Ser-Ala-Cys-Ser-NH_2 (SSCSSACS-NH_2), Ala-Cys-Ser-Ser-Ala-Cys-Ser-NH_2 (ACSSACS-NH_2) and Cys-Ser-Ser-Ala-Cys-Ser-NH_2 (CSSACS-NH_2), while the other group of them are terminally protected peptides: Ac-Ser-Cys-Cys-Ser-NH_2 (Ac-SCCS-NH_2), Ac-Cys-Ser-Ser-Cys-NH_2 (Ac-CSSC-NH_2) and Ac-Cys-Ser-Ser-Ala-Cys-Ser-NH_2 (Ac-CSSACS-NH_2).

We studied the complex formation processes of these molecules in the presence of toxic lead(II) ions and compared to those of toxic cadmium(II) and essential zinc(II) ions [2]. The stoichiometry and stability constants of the metal complexes were determined by potentiometry, while their structures were supported by means of UV-, MS- and NMR-spectroscopy.

In the case of three peptides containing free terminal amino group the thiolate groups are the main binding site, but the coordination of terminal amino group can contribute to the formation of stable complexes.

For the terminally protected tri-, tetra- and hexapeptides the thiolate group is the primary binding site. The di-cysteine containing peptides bind metal ions through both thiolate groups resulting in mono- and/or bis(ligand) complexes with high stability. This coordination mode are able to prevent the hydrolysis of lead(II) ions and stable mixed hydroxido complexes are formed in equimolar solutions at high pH range.

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Synthesis of Mn polyporphine by electrochemical method

Olga I. ISTAKOVA, [a,b)]**Dmitry V. KONEV,** [a,b)] **Charles H. DEVILLERS,** [c)]
Mikhail A. VOROTYNTSEV [a,b,c,d)]

[a)] Institute for Problems of Chemical Physics of the Russian Academy of Sciences,
Academician Semenov avenue 1, 142432 CHERNOGOLOVKA, Russia
[b)] D. I. Mendeleev University of Chemical Technology of Russia, Miusskaya square 9,
125047 MOSCOW, Russia
[c)] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[d)] M. V. Lomonosov Moscow State University, Department of FPCE, Leninskiye Gory 1,
GSP-1, 119991 MOSCOW, Russia
mivo2010@yandex.com

Our team has recently proposed synthetic approaches towards novel representatives of a family of electroactive polymeric materials, polyporphines, via substitution of the central ion [1-3]. At the first stage Mg(II) cations have been removed from the polymer units of the Mg(II) polyporphine of type I [1], pMgP-I, thus providing the corresponding free-base polyporphine, pH_2P-I, which represents the starting substance for the further syntheses. At the second stage this polymer, pH_2P-I, was metallated with Zn(II) and Co(II) cations [1-3]. Their insertion was carried out either by preparative treatment of pH_2P-I with the salt of the corresponding metal [1,2] or via electrochemically induced ion exchange [3]. The latter procedure has allowed us to avoid long-term treatment of the polymer surface by concentrated solution of the salt, by replacing it with electrochemical polarization of the pH_2P-I film in contact with dilute solution of the salt within a certain potential range.

This electrochemical method has been applied in this study for incorporation of Mn(II) cations into porphine units of the metal-free polymer, pH_2P-I. Figure 1 demonstrates how the redox response of the film changes in the course of electrochemical cycling in contact with Mn(II) perchlorate solution. After this treatment the redox response of n-doping of pH_2P-I have disappeared completely. The final CV response is retained after the film transfer into background electrolyte.

An interesting feature of thus obtained film is the absence of redox peaks near –0.5 V having observed for monomeric porphyrins and related to the Mn(II)/Mn(III) transition [4]. Such inactivity in this potential range should be a consequence of poor electronic conductivity of the polymer film within this potential range. In conformity with this interpretation this Mn(II)/Mn(III) wave appears (Figure 1b) after electrochemical oxidation of this film of type I since the latter transforms the polymer into polyporphine of type II which possesses a condensed-tape structure and is electronically conducting within the whole potential range [5].

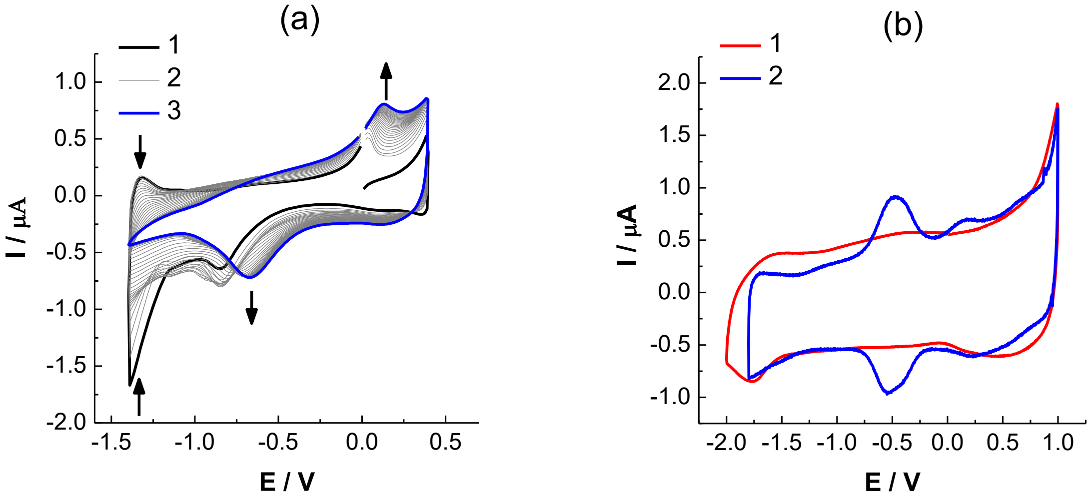

Figure 1. (a) Multi-cycle (30 scans) voltammetry of pH_2P-I coated Pt disk electrode (S = 0.78 mm^2) in contact with 0.5 mM $Mn(ClO_4)_2$ + 0.1 M $TBAPF_6$ in AN, scan rate 100 mV/s: cycle 1 (line 1), cycles from 2 to 29 (line 2), cycle 30 (line 3); (b) Cyclic voltammetry of the metallated film after its transformation into type II, pMnP-II (line 2), in comparison with its free-base analog, pH_2P-II (line 1), scan rate 100 mV/s.

Thus obtained films have been characterized by the UV-visible, IR and XPS spectroscopies which have confirmed the presence of Mn cation inside the film as well as its localization as central ion inside porphine monomer units. XPS data have allowed us to estimate also the content of Mn cations inside the polymer which has turned out to be close to those for previously obtained Co(II) polyporphines.

Acknowledgements: the study was supported by the Russian Science Foundation (grant 15-13-20038).

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Copper complexes with coumarin acid derivatives investigated with X-ray absorption fine structure techniques

Marcin T. KLEPKA, Anna WOLSKA, Aleksandra DRZEWIECKA-ANTONIK, Paweł REJMAK

Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46,
02668 WARSAW, Poland
wolska@ifpan.edu.pl

Coumarin and its derivatives represent an important type of O-donor heterocycles with typical benzopyrone framework. Their metal complex structures have been investigated and discussed due to interesting coordination properties and in some cases also biological activity [1, 2]. Three Cu(II) complexes with coumarin carboxylic acids were synthesized using direct and electrochemical methods. They were not obtained in a crystalline form, and as a result conventional diffraction studies couldn't be performed. Therefore, we had to find a technique suitable for powdered samples. We had decided to use X-ray absorption fine structure (XAFS) techniques which can be applied for crystal as well as amorphous materials.

The X-ray absorption spectroscopy measurements were performed at Cu K-edge at XAFS beamline at Elettra (Trieste, Italy). Both regions near edge (XANES) and extended (EXAFS) were being analyzed. EXAFS provided information on the quantity, type of neighbors and bond lengths. These data were used as a guideline to find and construct 3D models. For such models the XANES spectra were calculated. Then the models were modified and adjusted in order to obtain best agreement between calculated and experimental XANES spectra [3,4].

XAFS analysis combined with DFT calculations allowed to resolve 3D arrangement of studied complexes. Analysis revealed that coumarin-based ligands have different coordination modes in analyzed Cu(II) complexes. Among the mononuclear complexes the octahedral and tetragonal pyramid is observed around the metal cation, whereas for dinuclear complex the tetragonal pyramid geometry is found. We also found out that the two chemical method used for obtaining complexes did not introduced additional structural changes.

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Synthesis of CTV-porphyrin molecular wheels and their metal complexes

Jian YANG, [a,b] **Kin Shing CHAN,** [c] **Hai-Jun XU,** [b] **Mario NAITANA,** [a]
Léo BUCHER, [a] **Nicolas DESBOIS,** [a] **Claude P. GROS** [a]

[a] *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR CNRS 6302),*
Université de Bourgogne-Franche Comté, 9 avenue Alain Savary, BP 47870,
21078 DIJON Cedex, France
[b] *College of Chemical Engineering, Nanjing Forestry University, NANJING, P.R. China*
[c] *Department of Chemistry, The Chinese University of Hong Kong, SHATIN NT, Hong Kong*
jian.yang@u-bourgogne.fr

In Nature, the purple photosynthetic bacteria and the sulfur green bacteria comprise cyclic antenna assemblies that exhibit extremely well organized structures. Indeed, the light harvesting systems (I and II) and the chlorosomes, respectively, show well organized bacteriochlorophylls *via* supramolecular cofacial slipped dimers interactions in a circular manner. Cyclic systems where π-contacts between porphyrin units are present are rather rare and need further developments.

We will report the synthesis and spectroscopic characterization of porphyrin-CTV wheels and their metal complexes. Two CTV including three and six porphyrin units have been prepared and fully characterized [1]. Zinc complexes have been prepared and fully characterized. Electroreduction of dioxygen to water and carbon-carbon bond activation tests are under progress.

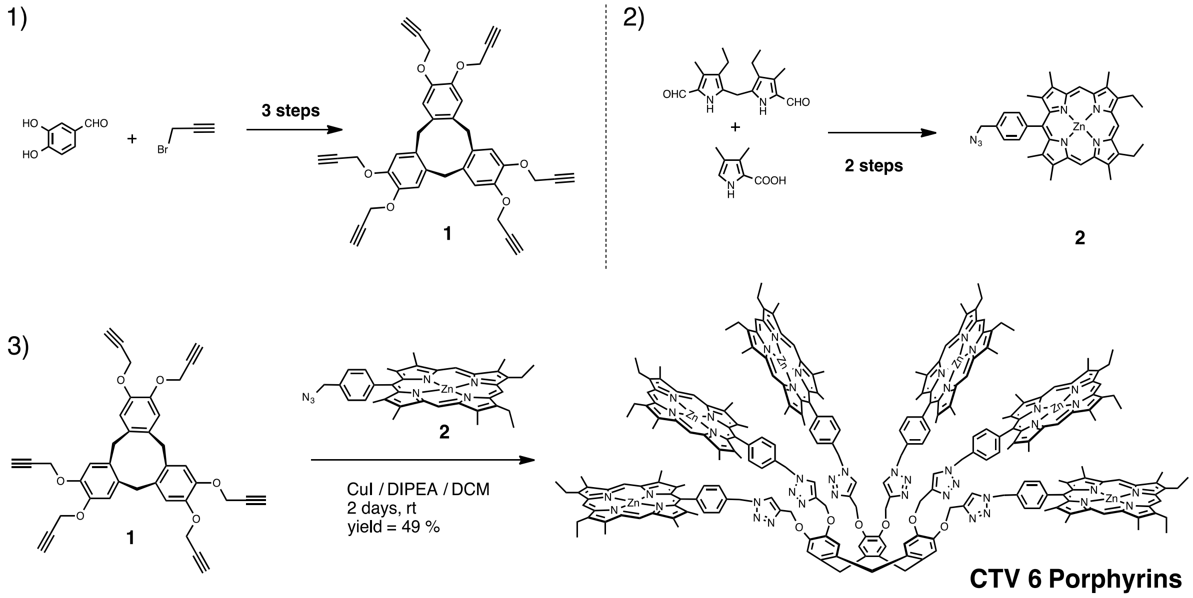

Figure 3. Few steps synthesis of CTV 6 porphyrins.

Acknowledments: we are thankful to the *Consulat Général de France* in Hong Kong and Campus France for a PHC PROCORE grant (2017 PROJET N° 37452YH).

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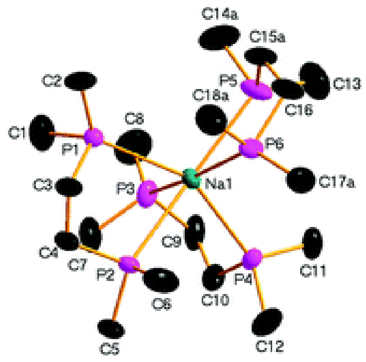
Electropositive group 1 and group 3 metal phosphine chemistry

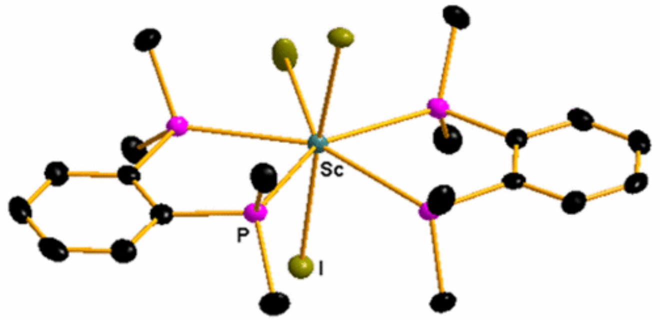
Marina CARRAVETTA, Maria CONCISTRE, William LEVASON, Gillian REID, Wenjian ZHANG

School of Chemistry, University of Southampton, SO17 1BJ SOUTHAMPTON, UK
wenjian.zhang@soton.ac.uk

Phosphine ligands are ubiquitous in mid- and late-transition metal chemistry, owing to their capacity to tune the electronic and steric properties, and hence the reactivity, of the complexes. This has led to wide utilisation of phosphine co-ligands in many transition metal catalysts and reagents [1]. Phosphine complexes containing p-block acceptors have also been developed substantially in recent years. However, examples of soft (neutral) phosphine coordination towards the hard oxophilic metal ions of Groups 1-3 are rare and have remained extremely elusive.

Here we report the unusual ScI_3 and YI_3 complexes with neutral diphosphine co-ligands and the first series of homoleptic phosphine complexes with Group 1 cations [2,3]. The solution speciation of these complexes was studied by comparing the solution and solid NMR spectra.





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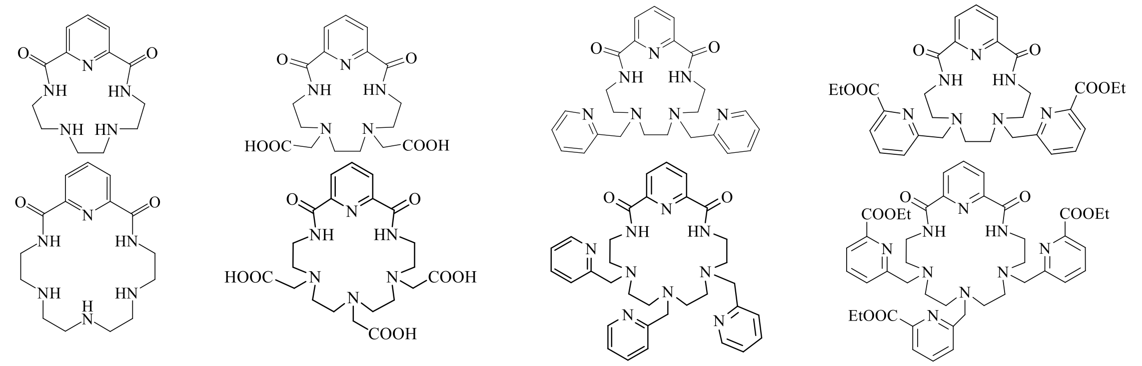
New chelators based on aryl containing azacrown compounds for transition and radioactive metal ions

Anastasia ZUBENKO, [a] **Bayirta EGOROVA**, [b] **Yuriy FEDOROV**, [a]
Stepan KALMYKOV, [b] **Olga FEDOROVA**[a,b]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), Vavilova St. 28, MOSCOW, Russia*
[b] *Lomonosov Moscow State University, Leninskie Gory, MOSCOW, Russia*
nastya.mutasova@yandex.ru

Recent biomedical applications of metal complexes have a growing interest in the synthesis and study of new chelators that form highly stable and kinetically inert complexes with various ions. Today, only complexes based upon DOTA (1,4,7,10-tetraazacyclododecane-tetraacetate) and DTPA (diethylenetriaminepentaacetic acid) have been used as clinical radiopharmaceuticals for many years. Unfortunately, complexes of DTPA are kinetically labile, and DOTA has low complex formation rate with metal ions. Thereby development of novel chelators for radioactive metal ions that have more favorable formation kinetics and remain inert toward dissociation is highly desirable.

In the present research a series of pyridine-containing 15- and 18-membered azacrown macrocycles with two or three pendant arms (carboxylate and pyridine) have been synthesized [1]. The coordination properties of their complexes with heavy and rare earth metal ions (Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Y^{3+}, Eu^{3+}, Lu^{3+}, Bi^{3+}) in aqueous solutions, as well as cytotoxicity and radiolysis resistance were investigated [2]. In order to provide binding the chelators with biomolecule additional functional groups were introduced in molecular structure.



It was demonstrated that both the size of the cavity and its heteroatom composition were important factors influencing on complex formation with the metal ions. The introducing of additional coordination groups improves the binding properties of pyridine-azacrown macrocycles. The greatest impact on the stability of the complexes provides the presence and amount of carboxyl substituents in macrocycles. Along with an increase in stability of complexes the reduction of selectivity of complex formation is observed. Also it was shown that pyridine-crown macrocycle with three carboxylic pendant arms is attractive ligand for binding of Cu^{2+} and Bi^{3+} ions applicable for synthesis of radiopharmaceuticals due to fast complex formation. X-ray diffraction analysis and potentiometric data showed that in ligands N-amide atoms do not participate in coordination with protons or metal cations. Nevertheless the rigid structure of pyridine-2,6-dicarbamide fragment and an open macrocyclic cavity provide a possibility to fast kinetics of complex formation. Thereby developed chelators based on azacrown compounds are promising for use in radiomedicine.

Acknowledgments: we thank the RSF grant № 16-13-10226 for financial support.

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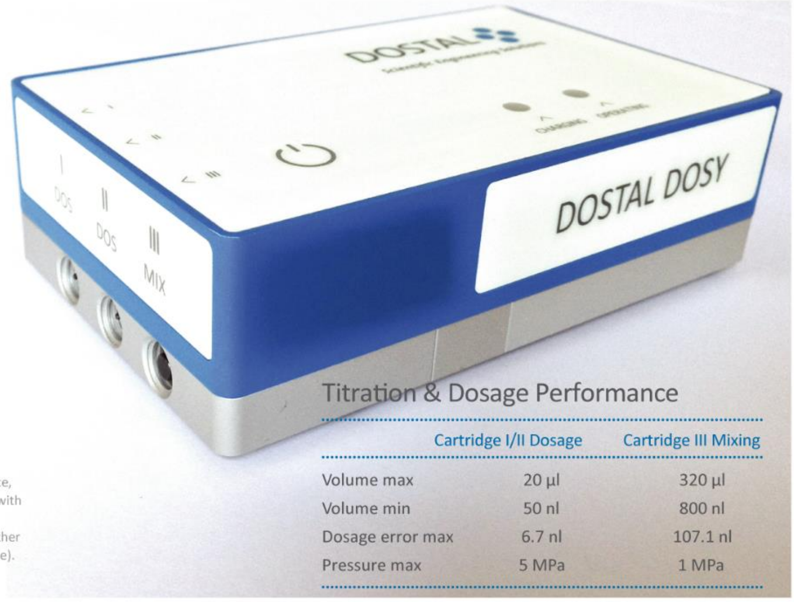
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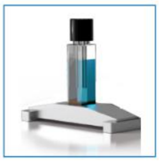



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PTFE (“Teflon”) Sealing Ring for greaseless conical Glass Joint and for All-Glass-Syringe

Dietmar Glindemann,* Uwe Glindemann
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There is a prejudice that PTFE (“Teflon”) is too inelastic to be a hermetic sealant for greaseless conical joints. Therefore, teaching books [1,2] recommend threaded or flanged “O-ring joints” for hermetic manipulation of air- and moisture sensitive chemicals if joint grease is no option.

Here we show that the common ground conical glass joint can be sealed relatively hermetic and at low cost with a narrow flat PTFE sealing ring (less than 1 mm wide and 0.1 mm thick, weight only 5 mg PTFE) [3]. The sealing ring is high-vacuum tight (air leakage rate 10^{-8}… 10^{-6} mBar*Liter/sec), solvent tight (loss of ethyl acetate out of containers < 0.1 mg/day) and resistant to fluctuation of temperature (freezing-thawing-heating cycles). The reusable PTFE sealing ring prevents stuck joints, is thin enough to be used with all joint clamps and is fixed elastically (without groove) on the glass joint. We demonstrate also that the common all-glass-syringe (1-100 mL) becomes gastight by a similar exchangeable sealing ring (PTFE) in a groove of the glass piston [4].

Figure 1. Left: PTFE-sealing ring fixed elastic (no groove necessary). Middle: Sealing ring intransparent without pressure. Right: Sealing ring transparent under sealing pressure. Far right: A similar PTFE ring and a piston groove make an allglass-syringe gastight.

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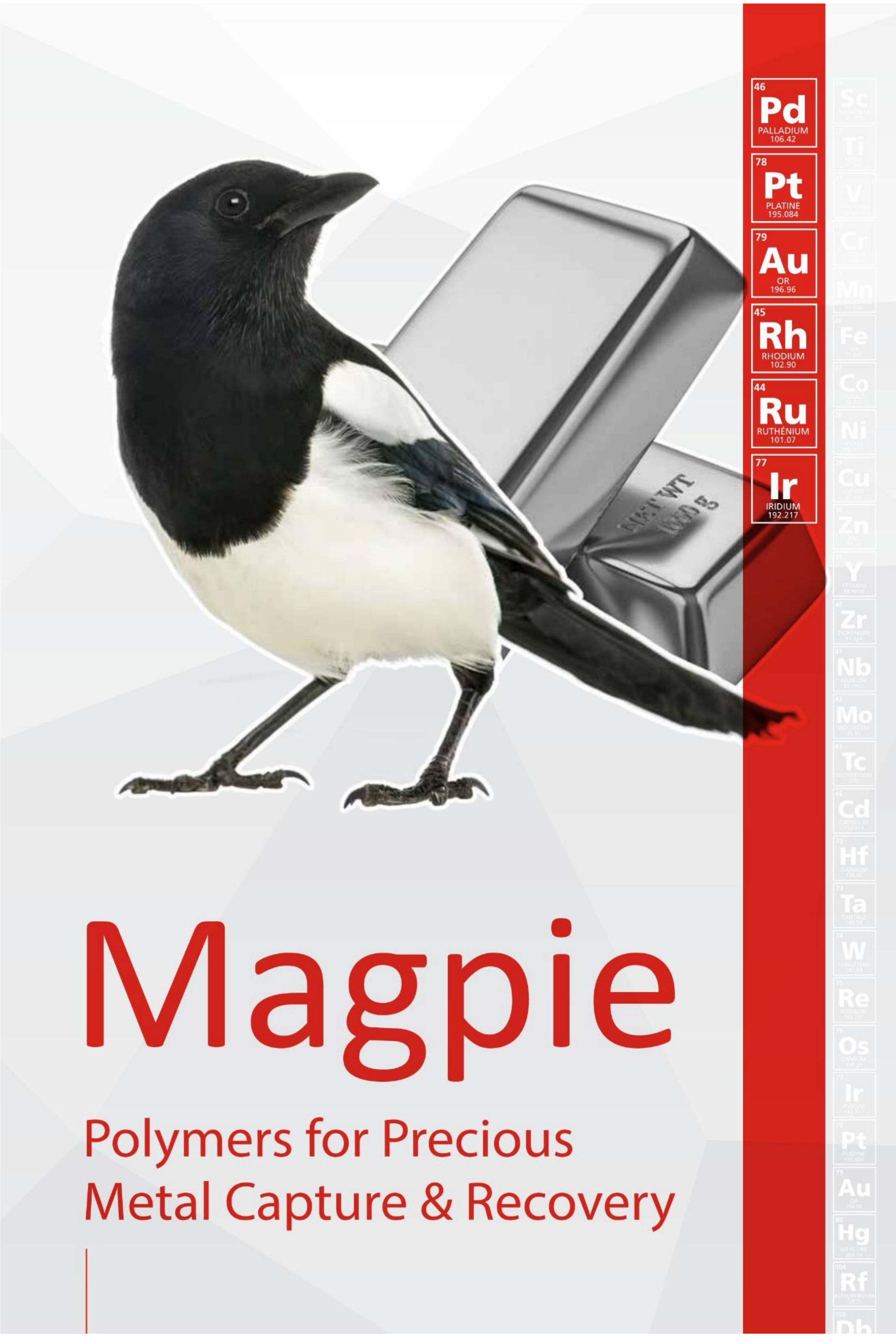

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They cover a wide temperature range from –180 °C to 2800 °C with a wide range of techniques such as thermogravimetry, calorimetry, DSC, thermal conductivity, specific heat, thermal expansion and DMA measurements, MS / FTIR / GC / MS couplings.

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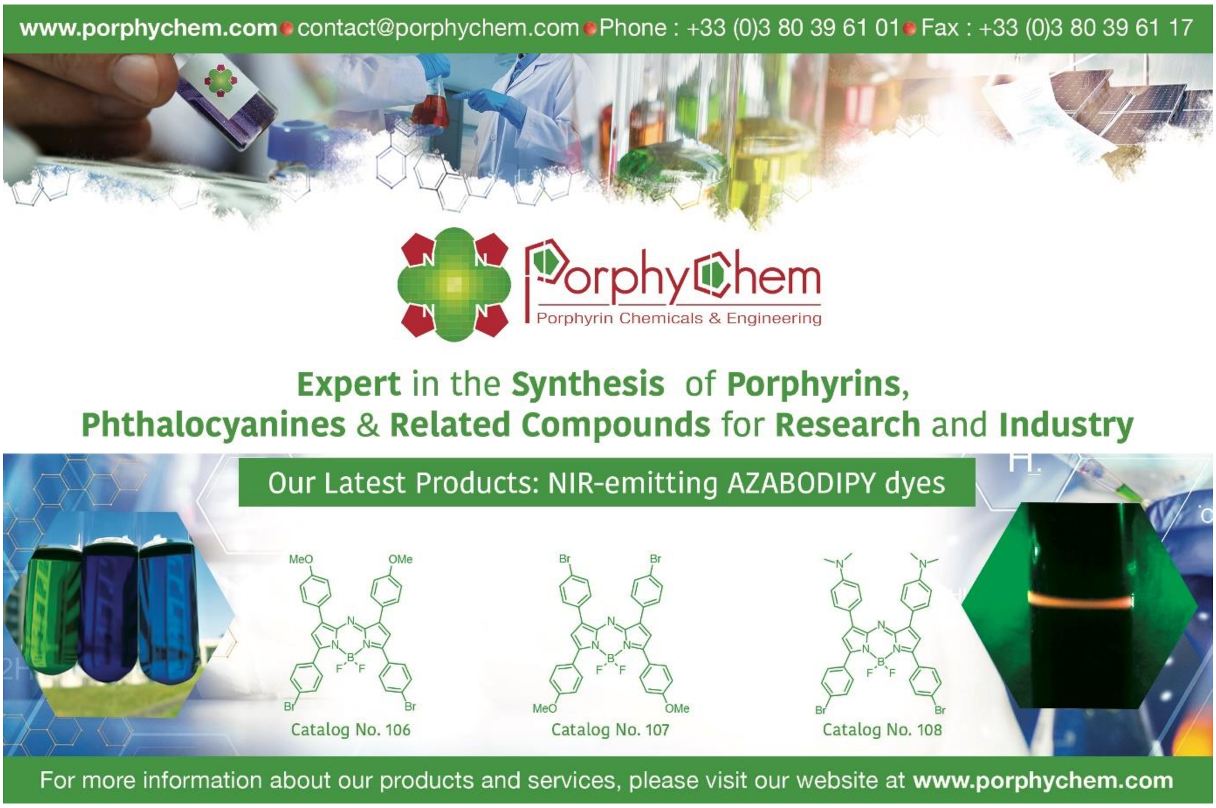
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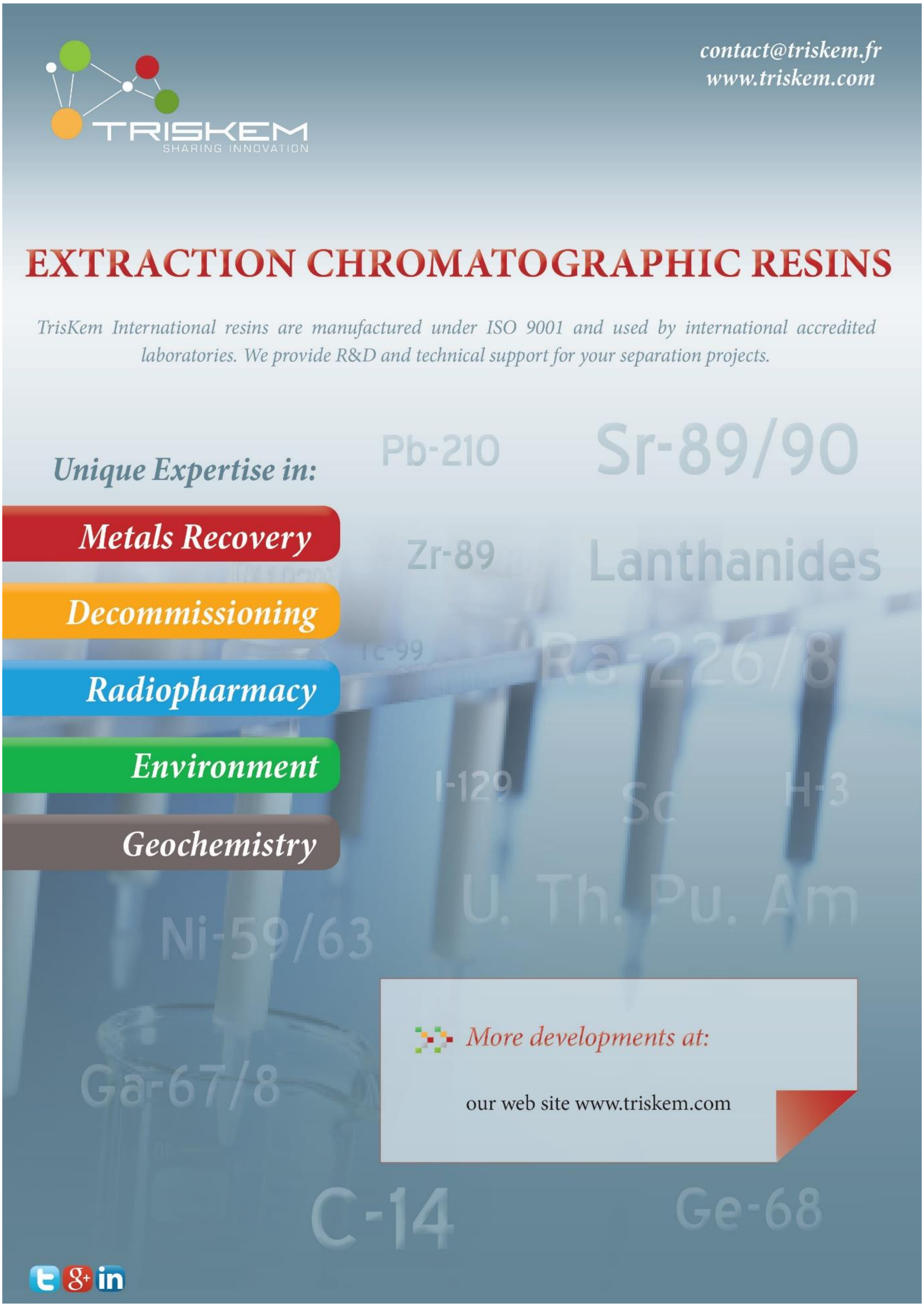
Pb-210
Sr-89/90
Zr-89
Lanthanides
Tc-99
Ra-226/8
I-129
Sc
H-3
U, Th, Pu, Am
Ni-59/63
Ga-67/8
C-14
Ge-68

Restauration
Traiteur
Hébergement
Séminaire
Tourisme
hotels bourgogne qualite

Presenting author index

		Sunday 11/06	Monday 12/06	Tuesday 13/06	Wednsday 14/06	Thursday 15/06
8:30	8:45		Opening ceremony	PL2 M. BOTTA	PL3 Y. LE MEST	
8:45	9:00					
9:00	9:15		Nobel lecture J.-P. SAUVAGE			PL4 G. LAURENCZY
9:15	9:30			OC10 K. DJANASHVILI	OC22 Y. FERRAND	
9:30	9:45			OC11 M. VISIGALLI	OC23 H. DEKKICHE	
9:45	10:00		Pulidori lecture: S. ADONIN	OC12 G. TIRCSO	OC24 S. TUNIK	OC29 M. KLEPKA
10:00	10:15		OC1 W. S. ABDUL-HASSAN	Agilent/Glindemann	Magpie/Micromeritics	OC30 C. SGARLATA
10:15	10:30		Coffee break	Coffee break	Coffee break	Coffee break
10:30	10:45					
10:45	11:00		KN1 P. PALLAVICINI	KN4 J. HAMACEK	KN8 P. HERMANN	OC31 A. LELIAS
11:00	11:15					OC32 O. FEDOROVA
11:15	11:30		OC2 X. YI	OC13 E. PUIG	OC25 T. GAJDA	OC33 A. ESEOLA
11:30	11:45		OC3 N. MORENO-GOMEZ	OC14 M. HAUKKA	OC26 E. FARKAS	OC34 L. GIRARD
11:45	12:00		KN2 R. ABERGEL	KN5 S. KUBIK	OC27 V. PATINEC	KN9 I. BANYAI
12:00	12:15				OC28 M. A. SANTOS	
12:15	12:30					
12:30	12:45		Lunch	Lunch	Lunch	Lunch
12:45	13:00					
13:00	13:15					
13:15	13:30					
13:30	13:45					
13:45	14:00			GTC Meeting		
14:00	14:15		PL1 R. MARTINEZ-MAÑEZ		Excursion to Beaune	KN10 G. BLONDIN
14:15	14:30					
14:30	14:45					OC35 G. JACKSON
14:45	15:00		OC4 I. GRABCHEV	KN6 R. BIESUZ		OC36 G. LEFEVRE
15:00	15:15	Registration at the Maison Internationale	OC5 R. BAKER			OC37 D. MILEA
15:15	15:30		Poster session	OC15 J. I. LACHOWICZ		OC38 M. VALIENTE
15:30	15:45			OC16 M. LARI		Coffee break
15:45	16:00			OC17 L. GUIJARRO		
16:00	16:15		Coffee break	Coffee break		OC39 A. MONCOMBLE
16:15	16:30					OC40 P. LUBAL
16:30	16:45		KN3 M.-C. CHARBONNEL	KN7 B. KERSTING		OC41 W. HUMMEL
16:45	17:00					OC42 H. SIGEL
17:00	17:15		OC6 M. R. BECCIA	OC18 S. El SAYED		Award ceremony
17:15	17:30		OC7 C. LUCHINI	OC19 A. MELCHIOR		Closing ceremony
17:30	17:45		OC8 A. MUSINA	OC20 N. VEIGA		
17:45	18:00		OC9 C. LEFEBVRE	OC21 Y. GAYFULIN		
18:00	18:15		Transfer to the City Hall	Triskem/Dostal		
18:15	18:30			Announcement ISMEC 2018		
18:30	18:45	Welcome party	Mayor's Reception (Palais des Ducs)	Poster Session		
18:45	19:00					
19:00	19:15				Banquet	
19:15	19:30					
19:30	19:45					
19:45	20:00					