COST Action CM1006

European f-Element Chemistry

EUFEN 3

April 14th and 15th 2014

HOLIDAY INN Nürnberg City Centre
Engelhardsgasse 12
90402 Nürnberg
Germany
COST Action CM1006

European f-Element Chemistry

Date: April 14th and 15th 2014

Meeting Place: HOLIDAY INN
Engelhardsgasse 12
90402 Nürnberg
Germany

Organisers: Dr. Christina Hauser
Prof. Stephen Liddle
Prof. Karsten Meyer

Timetable:

Monday 14th April
08.40 Start of Meeting
18.00 Poster Session
20.00 Conference Dinner

Tuesday 15th April
08.40 All Day Talks
17.30 Close of Meeting
Monday 14th April

0840-1020 Session 1. Chair – Steve Liddle

0845-0930 William Evans, University of California Irvine
"Recent Developments in the Chemistry of [K(2.2.2-cryptand)][Cp’3M] Complexes of the Rare Earths and Uranium"

0930-0950 Svetlana V. Eliseeva, CNRS Orleans
"Overcoming Low Quantum Yields of Near-Infrared Emitting Lanthanides(III): Metallacrowns and Polyamidoamine Dendrimers"

0950-1010 Leila R. Hill, University of Oxford
"Exploring Self-Assembly with Binuclear Lanthanide Complexes"

1010-1030 Christian Adam, Karlsruhe Institute of Technology
"Comparative NMR Study on Am(III) Complexes of nPr-BTP and C5-BPP"

1030-1100 BREAK

1100-1240 Session 2. Chair – Karsten Meyer

1100-1120 Stephen T. Liddle, University of Nottingham
"Recent Results in Uranium-Pnictide Multiple Bond Chemistry"

1120-1140 Floriana Tuna, University of Manchester
"Understanding the Magnetic Relaxation Properties of Dysprosium and Uranium Complexes"

1140-1200 Ulrich Kortz, Jacobs University
"Mono- and Di-Lanthanide Derivatives of 22-Tungsto-2-antimonate(III)"

1200-1220 Martina Delbianco, Durham University
"A New Very Efficient Class of Highly Emissive Lanthanide Complexes for FRET Applications"

1220-1240 Jessica A. Higgins, University of Sussex
"Uranium(IV) Mixed-Sandwich Complexes for Small Molecule Activation and Insertion"

1240-1340 BREAK

1340-1540 Session 3. Chair - Marinella Mazzanti

1340-1400 Matthew P. Blake, University of Oxford
"Rare Earth- and Alkaline Earth-Transition Metal Complexes"

1400-1420 Robert J. Baker, Trinity College Dublin
"Uranyl Minerals as Models for the Long Term Storage of Spent Nuclear Fuels"

1420-1440 Laurent Maron, INSA Toulouse University
"Theoretical Study of CC Coupling Reaction Mediated by Divalent Lanthanide Complexes"

1440-1500 Peter Harvey, University of Manchester
"Functionalisation of Rare-Earth Upconversion Nanophosphors with Enzymes"
Andrew Kerridge, University College London
"f-Orbital Covalency in the Actinocenes (An = Th-Cm): Multiconfigurational Studies and Topological Analysis"

Jun Okuda, RWTH Aachen University
"Molecular Hydrides of Rare Earth Metals"

BREAK

1610-1755  Session 4. Chair – Robert Baker

Pekka Pyyskkö, University of Helsinki
"Examples on the 32-Electron Principle"

Přemysl Lubal, Masaryk University
"Kinetic Studies of Lanthanide(III) Complexes of Mono(pyridine-N-oxide) Analogue of H_4dota"

Loic J. Charbonnière, CNRS Strasbourg
"Supramolecular Dimeric Lanthanide Capsules for Selective Fluoride Encapsulation and Sensing"

David L. Clark, Los Alamos National Laboratory
"Chemical Bonding in Molecules with Valence 5f-electrons"

POSTERS

DINNER

Tuesday 15th

0840-1030  Session 5. Chair – Louise Natrajan

Michel Ephritikhine, CEA Saclay
"Looking Back on Thirty Years of Uranium Chemistry"

Sébastian Georges, Université Lille Nord de France
"Facile Control of the Microstructure of Biobased Elastomeric Copolymers: Application of Coordinative Chain Transfer Copolymerisation (CCTcoP) to β-Myrcene"

Bernardo Monteiro, Universidade de Lisboa
" Dy_9(OH)_{20}Cl_4\cdot 6H_2O, The First Layered Lanthanide Compound with SMM Behavior"

Michel Meyer, Université de Bourgogne
"Siderophore-Mediated Transport of Uranium(VI): Structural, Equilibrium, and Kinetic Solution Studies"

BREAK

1100-1240  Session 6. Chair – Michael Patzschke

Oliver J. Cooper, CEA Grenoble
"The Cooperativity of Potassium on the Reactivity of Uranium(III) Complexes Towards Small Molecules"

Graeme J. Stasiuk, Imperial College London
"Molecular Imaging Agents for Formyl Peptide Receptor 1"
1140-1200 Nicole Bauer, Karlsruhe Institute of Technology
"Interaction of Trivalent Lanthanides and Actinides with Human Serum Transferrin Studied by TRLFS"

1200-1220 Michael Seitz, University of Bochum
"Non-Radiative Deactivation in Lanthanoid Luminescence – New Developments in Conceptual Understanding"

1220-1240 Margarida Henriques, University of Lisbon
"Tailoring the microstructure of UCₓ for improved radioisotope release of ISOL targets"

1240-1340 BREAK

1340-1540 Session 7. Chair – Robert Baker

1340-1400 Dominik P. Halter, University Erlangen-Nuremberg
"Structure and Reactivity of Uranium Monoarene Complexes Spanning the Formal Oxidation States of U(II) to U(V)"

1400-1420 Rik Van Deun, Ghent University
"Lanthanide-Doped Rare-Earth Tungstate Nano- and Microstructures with Multicolor Tunable Emission Properties"

1420-1440 Abdou Boucekkine, Université de Rennes
"Relativistic DFT Studies of the Reactivity of f Element Complexes"

1440-1500 Goran Angelovski, Max Planck Institute for Biological Cybernetics
"Towards the Visualization of Biological Processes Using Responsive MRI Contrast Agents"

1500-1520 Björn B. Beele, University of Heidelberg
"Modified Diglycolamides for Ln(III)/An(III) Co-Separation: A Complexation Study using TRLFS and Solvent Extraction"

1520-1540 Carlos Platas-Iglesias, Universidade da Coruña
"Macrocyclic Lanthanide(III) Complexes Containing Picolinate Pendants with High Stability and Kinetic Inertness"

1540-1610 BREAK

1610-1730 Session 8. Chair – Steve Liddle

1610-1630 Joy H. Farnaby, University of Edinburgh

1630-1650 Fabio Piccinelli, University of Verona
"Easily Achievable Ligands of Eu³⁺ Ion for the Luminescence Sensing of Anions in Acetonitrile Solution"

1650-1710 Gyula Tircsó, University of Debrecen
"Tuning the Formation Rates and Kinetic Inertness of Lanthanide(III) Complexes of Macrocyclic 1,4,7,10-tetraazacyclododecane Derivatives"

1710-1730 Ramanantoanina Harimbola, Université de Fribourg
"The Quest for Warm-White Light Using Combined Ligand-Field and Density Functional Theory"

1730 CLOSE
Plenaries
Recent Developments in the Chemistry of 
[K(2.2.2-cryptand)][Cp’3M] Complexes of the 
Rare Earths and Uranium

Megan E. Fieser, Christopher M. Kotyk, Matthew R. MacDonald, 
Jefferson E. Bates, Brandon T. Krull, Joseph W. Ziller, Filipp Furche, 
and William J. Evans*

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Recent studies of dinitrogen reduction chemistry with the rare earth elements have led to the synthesis of a series of complexes, [K(2.2.2-cryptand)][Cp’3M] (Cp’ = C5H4SiMe3), which represent the first examples of molecular species of Y2+, Ho2+, Er2+, Pr2+, Gd2+, Tb2+, Lu2+, and U2+.1-4 These complexes along with the [K(18-crown-6)(Et2O)][Cp”3Ln] (Cp” = C5H3(SiMe3)2-1,3) and [K(2.2.2-cryptand)][Cp”3Ln] complexes of La2+ and Ce2+ reported earlier by Lappert et al.,5 demonstrate that the +2 oxidation state is available for all the rare earths and uranium. These complexes are unusual compared to complexes of the traditional six +2 rare earth ions, Eu2+, Yb2+, Sm2+, Tm2+, Dy2+, and Nd2+, in that the bond distances are only slightly larger (ca. 0.03 Å) than those of their +3 analogs. This small change in size is more characteristic of d orbital transition metal complexes than f orbital species that often have 0.1-0.2 Å differences in bond lengths for analogous +2 and +3 species. Although there are extensive structural data on complexes of the traditional six Ln2+ ions, data on the direct analogs of the new complexes were not available. To make direct comparisons, the [K(2.2.2-cryptand)][Cp’3M] versions of La and Ce and the traditional six rare earths have now been made so the structural features and UV-vis spectra of the traditional six can be compared with those of the new nine Ln2+ ions in a single homologous set of complexes. The surprising results of this study and the implications in f element chemistry will be discussed along with density functional analysis of the data.

Chemical Bonding in Molecules with Valence 5f-electrons

David L. Clark*

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The covalent sharing of electrons between elements to form chemical bonds is a fundamental concept in chemistry that pervades our fundamental descriptions of the nature of chemical bonding. Concepts of covalency are routinely used to describe chemical reactions and chemical bonding interactions in s-, p-, and d-block elements of the periodic table. There has been an ongoing debate regarding the extent of covalency in f-block metal-ligand bonds, and unraveling the nature of bonding in f-element systems remains a computational and experimental challenge. It is important to emphasize that the debate is usually about the degree of covalency in a particular actinide metal-ligand bond, rather than whether or not it exists.

The renewed interest in covalency stems from the role of soft donor ligands in separating the heavier trivalent actinides from trivalent lanthanides in nuclear fuel cycles. This has led to introduction of more advanced theoretical and experimental studies, and extension to include heavier congeners Np, Pu, Am, Cm and Cf. The body of work reveals that the lighter actinides in their highest oxidation states (V and VI) can form unusually strong and covalent An=O bonds with significant 6d and 5f orbital interaction and covalency. For the heavier actinides that show a preference for trivalent oxidation states, the primary actinide metal-ligand bonding takes place through the agency of virtual 6d orbital interactions with filled ligand lone pair orbitals, with the 5f orbitals playing only a minor role. As these studies have been extended to the heavier elements, many workers have found the unexpected result of an increase in the 5f orbital mixing into occupied metal-ligand bonding orbitals. The mixing of atomic orbitals of neighboring atoms is covalent mixing by definition. A potential misunderstanding has arisen regarding the connection between this evidence of increasing covalency and the relative strength of these bonds with increasing atomic number.

We have employed Ligand K-edge X-ray Absorption Spectroscopy (XAS) and hybrid density functional theory (DFT) calculations on a series of simple metal complexes of general formula MCl₆²⁻, MO₂Cl₄²⁻, M(NR)₂Cl₄²⁻, (η-C₅Me₅)₂MCl₂, and M(η-C₈H₈)₄ for a series of transition metal and actinide ions (M = Ti, Zr, Hf, Th, U, Np, Pu) to assess the relative trends in covalency between d- and f-block elements. New insights into the nature of chemical bonding in f-block elements emerge from such studies, including the possibility of both overlap and near-degeneracy driven covalency and the need to quantify their relative contributions in actinide metal-ligand bonds.

We gratefully acknowledge support from the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, US Department of Energy. Cleared for unlimited release as LA-UR-13-29372.

In addition to the search for applications, particularly related to the topical problems of environmental remediation, the advances in molecular actinide chemistry are clearly motivated by its fascinating fundamental aspects. Uranium complexes became much more attractive in view of their structures which were unsuspected or reputed non accessible. The characterization of compounds with unprecedented coordination geometry, unusual oxidation state or novel functional groups, together with the remarkable improvements in computational investigations, give a better insight into uranium bonding, with the assessment of the covalent contribution to the metal-ligand bond and the role of the f electrons. The complexes also attract much attention for their efficiency in the activation of small molecules, their utility in organic synthesis and catalysis and the discovery of their peculiar magnetic properties.
Talks
Overcoming Low Quantum Yields of Near-Infrared Emitting Lanthanides(III): Metallacrowns and Polyamidoamine Dendrimers

Svetlana V. Eliseeva,* Evan R. Trivedi, Alexandra Foucault-Collet, Chad M. Shade, Vincent L. Pecoraro, Stéphane Petoud

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A number of modern advanced technologies rely on unique spectroscopic properties of lanthanide(III) ions. In particular, their ability to generate characteristic sharp emission bands in the near-infrared (NIR) range has a particular interest in view of numerous exciting applications in biosciences, telecommunications and solar energy conversion. The main fundamental challenges in design of NIR-emitting lanthanide(III) compounds are: (1) efficient sensitization through appropriate chromophores, and (2) good protection from non-radiative desactivations through O-H, N-H and C-H vibrations.

Here, we present two strategies to overcome low quantum yields of NIR-emitting lanthanide(III) compounds. The first, a direct one, is taking advantage of the unique structure of the "encapsulated sandwich" metallacrown (MC) complexes of the form \( \text{Ln}^{III}[12-\text{MC}_{2}\text{Zn(II)},\text{quinHA}^{-4}]_{2}[24-\text{MC}_{3}\text{Zn(II)},\text{quinHA}^{-8}] \) (\( \text{Ln}^{III} = \text{Nd, Yb, Er} \)) in which the MC framework is formed by the self-assembly of Zn\(^{II}\) ions and tetradentate chromophoric ligands, quinaldichydroxamic acid (quinHA). Such structure allows to locate lanthanide ions at a predetermined and relatively shielded position to achieve high quantum yields. The second, indirect approach, is based on combination of a large number of chromophores and lanthanide(III) ions within one macromolecule, generation 3 polyamidoamine dendrimer. The latter allows to increase the number of photons per unit volume even if the compound itself has a low quantum yield. Generation 3 polyamidoamine dendrimers functionalized with thirty-two 1,8- or 2,3-naphthalimide chromophores and incorporating eight lanthanide(III) cations will be described. Finally, the suitability of the probes for biological imaging applications will be evaluated and several examples presented.
Self-assembly of binuclear lanthanide complexes with 3,5-aryldicarboxylic acids presents us with an opportunity to explore the generation of new and complicated architectures for sensitised luminescence, and also allows us to explore the role of conformational space in the self-assembly process.

In this presentation, we will show how multimetallic d-f hybrids can be prepared, characterised and exploited through luminescence spectroscopy.

We will also demonstrate how remote substituents can be used to control available conformational space, and thus tune the affinity of complexes for anionic guests.

Comparative NMR Study on Am(III) Complexes of nPr-BTP and C5-

Christian Adam\textsuperscript{a,b,*}, Björn B. Beele\textsuperscript{b}, Peter Kaden\textsuperscript{a}, Andreas Geist\textsuperscript{a}, Lisa Böringer\textsuperscript{a}, Julia Schäfer\textsuperscript{a}, Petra J. Panak\textsuperscript{a,b}

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Partitioning and transmutation (P&T) is a strategy of reducing the long term radiotoxicity and thermal power of spent nuclear fuel.\textsuperscript{[1]} It involves separating the chemically similar trivalent lanthanides (Ln) from trivalent actinides (An). While feasible with some ligands, little is known about the molecular origin of these ligands’ selectivity. Our studies aim at a fundamental understanding of the reasons for the observed selectivity, which in turn should allow the design of improved extraction ligands.

\textbf{Figure 1:} nPr-BTP (left) and C5-BPP (right) ligands with the used numbering scheme.

In a study with partially \textsuperscript{15}N labelled nPr-BTP (2,6-Bis(5,6-dipropyl-1,2,4-triazine-3-yl)pyridine) we found spectroscopic evidence for an increased covalence in the metal-ligand bond.\textsuperscript{[2]} We have now extended our studies to C5-BPP (2,6-Bis(5-(2,2-dimethylpropyl)-1H-pyrazol-3-yl)pyridine).\textsuperscript{[3]} This ligand has similar complexation properties, like forming stable ML\textsubscript{3} complexes, yet shows significant differences in extraction and solution behaviour. Contrary to the notion that Am(III) has a diamagnetic \( J = 0 \) ground state\textsuperscript{[4]} we were able to detect a very weak paramagnetism in the Am(III) complex, similar to results for BTP complexes. Partial \textsuperscript{15}N labelling in positions N\textsubscript{8} and N\textsubscript{9} again revealed a tremendous highfield shift for Am(C5-BPP)\textsubscript{3}(OTf)\textsubscript{3} on the coordinating nitrogen atom N\textsubscript{8}, but not on the neighbouring N\textsubscript{9}. Using \textsuperscript{1}H,\textsuperscript{15}N-HMQC spectroscopy, this influence is found on N\textsubscript{1} as well. We will discuss these results, its origins and contributing factors and present conclusions to the binding mode in Am(III) complexes with N-donor ligands.

Recent Results in Uranium-Pnictide Multiple Bond Chemistry

David M. King, Benedict M. Gardner, Ashley J. Woonles, Peter A. Cleaves, Floriana Tuna, Eric J. L. McInnes, Jonathan McMaster, William Lewis, Alexander J. Blake, Stephen T. Liddle

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There is currently great interest in the nature and reactivity of actinide-ligand multiple bond linkages in a molecular context. Molecular uranium nitrides are of particular interest because of their relevance to uranium nitride materials which may form the basis for alternative nuclear fuel cycles. In particular, uranium nitride is often cited as providing materials with improved melting points, densities, and thermal conductivities in comparison to uranium oxides. Furthermore, uranium-ligand multiple bond linkages are of interest in terms of the extent of 5f/6d orbital participation and covalency and, by extension, applications in atom efficient catalysis and small molecule activation. However, little is known of the intrinsic nature of U≡N bonds, yet this information is crucial to understanding the inherent physicochemical properties of these linkages.

We will present our recent work describing the isolation of terminal uranium nitrides(see figure),\(^1,2\) and other uranium pnictide linkages.

Understanding the Magnetic Relaxation Properties of Dysprosium and Uranium Complexes

Floriana Tuna,a,* David M. King,b Robin Blagg,a David Collison,a Eric J.L. McInnes,a Richard Winpenny,a Stephen T. Liddleb

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In recent years remarkable results have been obtained from studies of the magnetic relaxation of f-block metal complexes. Terbium phthalocyanine complexes were reported to have energy barriers for loss of magnetisation as high as 800 K, which are an order of magnitude larger than those found in d-block single molecule magnets, while dysprosium and terbium complexes bridged by an N$_2$$_3$ radical ligand show magnetic hysteresis to 13 K. In addition, new physics were discovered for {Dy$_3$} triangles, while studies of uranium complexes led to the observation of single-molecule and single-chain magnet behaviours in uranium(V) [1] and uranium-manganese [2] compounds with energy barriers to loss of the magnetisation near 150 K and magnetic hysteresis up to 6 K.

Here we discuss the relaxation properties of several Dy(III) and U(V) complexes studied in our laboratories [1, 3]. Relaxation mechanisms were found to be different amongst complexes. Magnetic hysteresis (a) and ac susceptibility studies (b), as well as ab initio calculation, were involved to study the dynamics of the magnetisations and understand the relaxation mechanisms.


Mono- and Di-Lanthanide Derivatives of 22-Tungsto-2-antimonate(III)

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Polyoxometalates (POMs) are discrete metal-oxides and their large structural and compositional versatility gives rise to potential applications in different fields such as catalysis, medicine, analytical chemistry, and material science. POMs containing lanthanides are also known and of interest in areas such as photoluminescence, catalysis, electrochemistry, and magnetism. Our group has also been active in studying the synthesis, structure and physicochemical properties of lanthanide-containing POMs.

Here we report the synthesis and characterization of five mono- or di-lanthanide-containing 18-tungsto-2-antimonates(III) based on the dilacunary \([\text{Sb}_2\text{W}_{20}\text{O}_{70}]^{14-}\) unit \((\text{Sb}_2\text{W}_{20})\). The latter is either coordinated to a lanthanide and a tungsten ion, resulting in \([Ln(H_2O)_4\text{Sb}_2\text{W}_{21}\text{O}_{72}(OH)]^{10-}\) \((Ln = \text{Yb}^{3+}, \text{Lu}^{3+})\) with \(C_5\) symmetry, or to two lanthanide ions, leading to \([Ln_2(H_2O)_8\text{Sb}_2\text{W}_{20}\text{O}_{70}]^{8-}\) \((Ln = \text{Yb}^{3+}, \text{Lu}^{3+}, \text{Y}^{3+})\) with idealized \(C_{2h}\) symmetry. These polyanions were synthesized in acidic medium, and the pH was found to play an important role in directing the formation of the respective species. All compounds were characterized in the solid state by FTIR, single-crystal XRD, TGA, and elemental analysis.


A new very efficient class of highly emissive lanthanide complexes for FRET applications

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Fluorescence Resonance Energy Transfer (FRET) is a process in which the excited-state energy from an excited donor (D) is transferred to an acceptor (A). Because of the strong dependence on the distance between D and A, FRET can be used to estimate distances between two locations within or between macromolecules. The extremely long luminescence lifetime and sharp emission bands of lanthanide complexes make them ideal candidates to act as donors in FRET applications.

Herein, a new class of highly emissive europium complexes has been designed, synthesised and the photophysical properties analysed. In particular, synthetic work has focused on the development of complexes that possess appropriate photophysical properties to be suitable as donors in FRET applications with cyanine dye acceptors. In addition, functional groups that encourage high water solubility and a linkage point for conjugation with biomolecules have been incorporated into the complex structure.

Photophysical studies show promising behaviour, including high quantum yields (up to 30%), long luminescence lifetimes (1.1 ms) and excellent efficiency in energy transfer (> 90%).

Uranium(IV) Mixed-Sandwich Complexes for Small Molecule Activation and Insertion

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Recent work has shown the ability of uranium(IV) mixed-sandwich complexes of the form U(COTIPS2)Cp*R (where COTIPS2 = C8H6(SiPr3-1,4)2; R = alkyl, hydride, amide) to either react with or insert small molecules into the U-R bond, such as CO, CO2, H2 and NH3 (Figure 1).[1]

![Figure 1: Mixed-sandwich complex insertion chemistry](image)

Of particular interest is the reaction of the monomeric hydride complex, U(COTIPS2Cp*H, with CO, which results in the formation of a dimeric cis-enediolate (Figure 2). This talk will address this reaction and other, related, small molecule insertions.[2-4]

![Figure 2: Formation of a cis-enediolate complex](image)

Rare Earth- and Alkaline Earth-Transition Metal Complexes

Matthew P. Blake‡, Nikolas Kaltsoyannis, Philip Mountford*

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Metal-metal bonded molecular compounds have been an essential part of the development of inorganic chemistry for decades. However, there remains relatively little experimental or theoretical information regarding direct bonds between the alkaline earth and rare earth metals and the transition metals when compared to those between transition metals exclusively.

We recently reported that the reaction of calcium or ytterbium amalgam with [CpFe(CO)$_2$(Fp)$_2$]$_2$ gave the isostructural alkaline earth or divalent rare earth compounds [M(Fp$_2$(THF))$_2$ (M = Ca or Yb) containing two direct Ca-Fe or Yb-Fe bonds, providing the first direct comparison of M-TM bonding for an alkaline earth with its rare earth counterpart. Reaction of [Yb(Fp$_2$(THF))$_2$ with Yb(dippNacNac)Fp(THF) gives [{Yb(dippNacNac)(THF)}$_2$(µ-YbFp$_4$)] containing the first example of a lanthanide bound solely to four transition metals. In addition, reaction of alkaline earth or rare earth amalgams with [Co(CO)$_3$(PCy$_3$)]$_2$ gives complexes with alkaline earth- or rare earth-cobalt bonds. The complexes [M{Co(CO)$_3$(PCy$_3$)}$_2$(THF)$_3$]$_x$ (M = Sr or Eu) were found to have side-on carbonyl interactions between the metal centres, unprecedented for any alkaline earth or lanthanide complex.

Based on these findings we have sought to further increase the number of these metal-metal bonded structures and investigate their potential for the activation of small molecules and their application in catalytic transformations. In this presentation we report our recent work in these areas.

Storage of Spent Nuclear Fuels (SNF) in geological repositories is the favoured method for a number of EU countries. Under moist oxidising conditions, UO$_2$ will oxidise to uranyl compounds via a number of phase changes. These have been characterised on the weathering of uranium ores and the surface of UO$_2$ and SNF. These phases can sorb radionuclides such as neptunium and therefore alter the migration rates into the near-field.

We will present our recent work on the characterisation of selected minerals using solid-state electrochemistry and X-ray spectroscopy (EXAFS and HR-XANES). The electrochemical results suggest that uranyl minerals such as uranyl (oxy)hydroxides, uranyl carbonates and uranyl phosphates are redox non-innocent that may have implications for Np migration.

We will also discuss the use of Eu as a model for Am in the sorbtion onto the surface of selected minerals using emission spectroscopy.

The reaction mechanisms of CC coupling between terminal alkyne mediated by organometallic divalent lanthanide complexes have been investigated. Unlike the uranium(III) catalysed reaction, H₂ production is experimentally observed. The reactions mechanism have been computed for U(III) and Sm(II) complexes and will be compared. It will be shown that in both cases the mechanism involves the formation of bimetallic intermediate but the subsequent step are different for the two f metals. Interestingly, it will be demonstrated that for Sm(II) the reaction involves the formation of a dimeric alkylidyne complex that undergoes rapid C-C coupling. Such reactivity was already reported by Evans and Teuben groups while starting from the alkylidyne complex.
Rare-earth upconversion nanophosphors (UCNPs) are rapidly emerging as an important class of nanoparticles with potential applications in imaging, lighting, and other areas.\textsuperscript{1} When UCNPs are excited with NIR light, they exhibit efficient photoluminescence in the visible spectrum due to photon upconversion (UC). This UC process, which can be tuned by doping the UCNPs with various lanthanides, is a non-linear process involving the absorption of two or more low energy photons, leading to the population of a real, long-lived ($\mu$s), metastable excited state, rather than to a virtual excited state as in two-photon absorption.\textsuperscript{2} As a consequence of their UC, UCNPs are particularly promising as bioimaging probes as they exhibit no autofluorescence and NIR photons can penetrate far deeper into biological tissue than visible photons. It is also possible to synthesise and functionalise water-soluble nanoparticles and there has been some success in covalently coupling them to peptides/antibodies.\textsuperscript{3}

We will present our findings related to exploration of the behaviour of UCNPs with flavin-containing enzymes. As the spectral absorption properties of enzyme chromophores change during enzyme turnover, the FRET efficiency of the UCNP-enzyme conjugates are sensitive to the presence of enzyme substrates. Initial work involved investigation of the behaviour of the free flavin chromophoric co-factors with the UCNPs in aqueous solution. Efficient FRET was observed between the UCNPs and the flavin, even without covalently linking the two species. This FRET is then quenched by reduction of the flavin, meaning the system is able to report on enzyme turnover. FRET interactions between transitions metals and lanthanide coordination compounds with these UNCPs will also be discussed as emissive probes for detection of (trace) amounts of toxic metals in solution. Moreover, since the system exhibits multiple bands in the UCNP emission spectra, FRET changes are reported by ratiometric methods.

\begin{itemize}
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f-orbital covalency in the actinocenes (An=Th-Cm): multiconfigurational studies and topological analysis

Andy Kerridge*

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The quantification of covalency in f-element complexes is of both fundamental scientific interest and critical industrial importance. In this contribution the CASSCF methodology is used to calculate the ground state electron densities of a series of seven actinocenes, AnCOT₂ (An = Th-Cm, COT = \(\eta^8\)-C₈H₈). The multiconfigurational character of these complexes is found to be substantial and topological analysis of the electron density via the QTAIM approach is therefore chosen in order to investigate the electronic structure in more detail. Topological analysis reveals increased values of the electron density at the An-C bond critical point for An = Pa-Pu, suggesting enhanced covalent character in metal-ligand bonding for these complexes. In order to investigate the origins of this covalency, integrated one- and two-electron properties are evaluated. A trend for increased electronic charge, spin density and electron localisation on the An centre as one traverses the actinide series is found. The difference between atomic number and the electron localisation index is considered and found to correlate well with the expected oxidation state in these complexes, with a tendency towards trivalent character for the later actinides. Total and orbitally resolved delocalisation indices are evaluated, and increased electron delocalisation is found for the complexes containing Pa-Pu centres. It is shown that, while 5f contributions to covalency in these complexes are smaller in magnitude than 6d contributions, the variation in covalency is almost entirely accounted for by the variation in the 5f contribution.

Molecular Hydrides of Rare Earth Metals

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Solid state interstitial hydrides with the composition LnHₓ (x < 3) command some attention as hydrogen storage materials such as LaNiH₅. Obviously, simple molecular hydrides of the composition MHₓ (n = 2, 3, 4) of rare earth metals are not isolable under standard conditions. When stabilized by suitable ancillary ligands they could give valuable insights into the molecular processes associated with hydrogen uptake, activation and release. Coordinative saturation achieved by metallocene scaffolds (h⁵-C₅R₅)₂M resulted in a rich chemistry of group 3 metals hydride complexes. The use of polydentate ligands such as Me₃TACD or Me₆TREN has allowed the preparation and isolation of several new types of molecular hydrides of, the lanthanides.

The absence of sterically bulky and electron donating cyclopentadienyl ligand results in a more ionic metal-hydrogen bonds that along with the large metal size results in aggregation to give polynuclear species. The introduction of cationic derivatives gave relatively discrete units and led to the observation of dihydrogen activation reaction that involves intramolecular C-H bond activation of the ligand’s peripheral substituents.

The idea of special, magic electron counts goes back to Lewis’ octets or Langmuir’s 18-electron principle. The actual interpretation may involve kinetic-energy effects, due to the number of nodes, and not necessarily all of the ns, np and (n-1)d orbitals of the central atom, see [1] and references there.

Can we take the next step, and add a filled f-like shell, taking the total electron count to 18+14=32? We have so far found three such isoelectronic series. The first one was the Pu@Pb_{12} series [2, 4]. The second one, U@C_{28} [3] is actually experimentally known but had not been recognized as a 32e species. The third series is that of [U@Si_{20}]^{6-} [5].

A further series would be that of the [Th(BH_{4})_{6}]^{2-}, produced and identified as a 32e species by G. Girolami [6].

Kinetic Studies of Lanthanide(III) Complexes of Mono(pyridine-N-oxide) Analogue of H₄dota

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Ln(III) complexes of H₄dota and its derivatives are utilized in many areas of medicine (e.g. complexes of metal radioisotopes as ⁹⁰⁰Y, ¹⁵³Sm, ¹⁶⁶Ho, ¹⁷⁷Lu in nuclear medicine, Gd(III) complexes as MRI contrast agents, Eu(III) or Tb(III) complexes as luminescent probes).

In this contribution, kinetic properties of Y(III) and Ln(III) complexes (Ln = Ce, Eu, Gd, Yb) of the mono(pyridine-N-oxide) H₄dota analog¹-³ were studied by molecular absorption and emission spectroscopies (in UV/VIS region, luminescence, TRFS). The mechanisms of complex formation (pH = 5.0–6.0, t = 25 °C, I = 0.1 M KCl) and acid-assisted complex dissociation (t = 25–70 °C, I = 3.0 M (Na,H)ClO₄) were proposed. In the Ln(III) complex formation of study, HL²⁻ was determined as the reactive species and complex formation rate increases with decreasing ionic radius of the metal ions and follows a trend along the Ln(III) series (6.30 × 10⁵ (Ce) – 2.74 × 10⁶ (Yb) M⁻¹ s⁻¹). The same trend was observed for complex dissociation while LFER analysis of activation parameters proves that the reaction mechanism is the same for all studied Ln(III) complexes. The results were compared with data obtained for Ln(III) complexes of similar ligands, H₅do3ap and H₄dota. The results were utilized for development of sensitive determination of Ln(III) ions in mixture⁴.

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Supramolecular dimeric lanthanide capsules for selective fluoride encapsulation and sensing

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Because of its importance in health care, water pollution or positron Emission tomography, fluoride sequestering and sensing in aqueous solution is a topic of major interest in organic and coordination chemistry. In addition to a large solvation energy, a major difficulty of F⁻ coordination arose from the competition with the isoelectronic hydroxyde anion, which featured very similar ionic radius (1.285 Å for F⁻ vs 1.32 Å for OH⁻).

On the basis of our previous experiments, 1, 2 we have developed a ligand for lanthanide complexation that take advantage of the combination of synergistic weak interactions (n-n stacking and hydrogen bonding) to self-assemble into supramolecular dimeric capsules selectively sequestering fluoride anions in water.

The encapsulation of fluoride can be monitored by steady state and time-resolved luminescence spectroscopy. The detection is selective compared to other halogen and allows for submicromolar fluoride sensing in aqueous solutions.


Facile control of the microstructure of biobased elastomeric copolymers: Application of Coordinative Chain Transfer copolymerisation (CCTcoP) to β-Myrcene

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Coordinative Chain Transfer Polymerisation (CCTP) has known a growing interest in the last years\textsuperscript{1-3}. Such concept enables catalyst economy, molecular weight control, chain-end functionalization and the control of the microstructure of the polymer resulting. Chain transfer has the interesting ability to tune the microstructure of statistical copolymers when applied to certain statistical copolymerisation. In the particular case of conjugated dienes, applying this concept will allow a control on the composition of the copolymer and on the regioregularity in the case of conjugated dienes, as it was demonstrated for the statistical copolymerisation of styrene with isoprene\textsuperscript{4-5} and hexene\textsuperscript{6}.

Scheme 1: Coordinative Chain Transfer Polymerisation (CCTP). Polymer* represents a growing polymeric chain, $M$ the transition metal allowing propagation, $L$ a ligand and CTA the chain transfer agent

In order to provide facile access to partially biobased elastomeric materials of tunable microstructure, we applied that CCTcoP concept to β-Myrcene which is a renewable monomer of the family of terpenes. The statistical copolymerization of β-Myrcene mediated by the borohydrido half-lanthanocene Cp*La(BH\textsubscript{4})\textsubscript{2}(THF)\textsubscript{2} (Cp* = C\textsubscript{5}Me\textsubscript{5}), in combination with dialkylmagnesium and trialkylaluminum compounds as chain transfer agents, was achieved. The CCTcoP of β-Myrcene with styrene and isoprene was studied, together with the influence of chain transfer on the course of the terpolymerization of the monomers, leading to copolymers comprising different ratios of each monomer, different regioselectivity and molecular weight, depending on the lanthanum half-sandwich complex/dialkylmagnesium/trialkylaluminum combination.

Dy$_8$(OH)$_{20}$Cl$_4$·6H$_2$O, the first layered lanthanide compound with SMM behavior

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Layered materials with composition Ln$_8$(OH)$_{20}$Cl$_4$·nH$_2$O (Ln = Nd, Sm-Tm and Y) were originally prepared by Sasaki and coworkers.$^1$ A host-guest system with pure lanthanide cations in the layer allows us to combine the study of lanthanide chemistry with that of layered and intercalated compounds, providing advances in the field of new organic-inorganic hybrid materials and showing interesting properties derived from their potential as multifunctional materials. The optical properties of these compounds$^2$ attracted recently some attention but very little is known about their magnetism.

In this work the magnetic properties of the layered dysprosium hydroxide material Dy$_8$(OH)$_{20}$Cl$_4$·6H$_2$O (LDyH) were studied and revealed a slow magnetic relaxation behavior characteristic of single-molecule magnets.$^3$ The results obtained support the idea that the slow relaxation probably stems mainly from single ion effects, with the Dy–Dy interactions, although non-negligible, playing a secondary role in this magnetic behavior. In order to verify the influence of the non-negligible Dy-Dy interactions diluted solutions replacing the Dy cation by Y, as LYH::xDy, (x = 0.05, 0.1) were synthesized and their magnetic characterization performed revealing that the SMM behavior is maintained.

Figure 1. The Dy$_8$(OH)$_{20}$Cl$_4$·6H$_2$O unit cell viewed along the $a$ axis (right) and $c$ axis (left).

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Siderophore-Mediated Transport of Uranium(VI): Structural, Equilibrium, and Kinetic Solution Studies

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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.\textsuperscript{1} Because such data are scarce and often unreliable in the case of the transuranium cations, considerable research efforts are still required.\textsuperscript{2}

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.\textsuperscript{3}

The communication will focus on desferrioxamine B, an ubiquitous open-chain trishydroxamic siderophore which is present in soils at micromolar concentration levels. By combining classical potentiometric and UV-vis spectrophotometric titration techniques with capillary electrophoresis, EXAFS and RAMAN spectroscopies, the speciation of the uranium(VI)/DFO system could be unraveled and structures for the various complexes prevailing in solution proposed. Finally, the proton-assisted dissociation mechanism of the uranyl chelate will be discussed.

The Cooperativity of Potassium on the Reactivity of Uranium(III) Complexes Towards Small Molecules

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Over the last few decades, the activation of small molecules via uranium complexes has seen significant development.[1] Recently our group reported that the uranium(III) species \([\text{U\{OSi(O}^\text{tBu}\}_3\}_3\] can activate \(\text{CO}_2\) and \(\text{CS}_2\), generating a uranium carbonate and a \(\text{CS}_2\) bridged complex, respectively.[2] Furthermore, stark contrast was observed between the reactivity of \([\text{U\{OSi(O}^\text{tBu}\}_3\}_3\] and \([\text{U\{OSi(O}^\text{tBu}\}_3\}_4][\text{K18c6}]\) towards various azides. [3] This highlights the importance of coordination environment in influencing reactivity.

We will present the work of uranium(III) complexes mediating small molecule activation, and how the cooperation of potassium can influence the reactivity.

Molecular Imaging Agents for Formyl Peptide Receptor 1

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Formyl Peptide Receptor 1 (FPR1) is key in the signalling pathway of inflammation, and is found on leucocytes, in particular neutrophils. Inflammation is a major marker of many disease states in particular ischaemia-reperfusion injury and atherosclerosis.1 Identifying cells with high expression of FPR1 is important in the diagnosis and therapy of these diseases. A handful of molecules have been identified as targets for FPR1, in particular the peptide cFLFLFK.2 cFLFLFK is a hexapeptide with cinnamoyl group at the c-terminus, which acts as an antagonist for FPR1.

The cFLFLFK peptide has been modified with chelates that coordinate Gd (III) and Tb(III) to give MR and fluorescent imaging agents respectfully. The cFLFLFK peptide has also been conjugated with organic fluorophores to give dual-modal probes. The biological and chemical properties of the lanthanide analogues of these agents have been investigated, showing that they maintain specific binding to the FPR with $K_d = 4.5$ nM. MRI studies show that the Gd agent has excellent relaxivity $r_1 = 5.6$ mM$^{-1}$s$^{-1}$ (9.4T) and targets leukocytes during inflammatory response.3 The results obtained demonstrate that the FPR1 provides a viable target for visualising inflammation in disease, via MRI.


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Interaction of trivalent lanthanides and actinides with human serum transferrin studied by TRLFS

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In case of an accidental release of radionuclides actinides can cause a serious health risk upon incorporation. With regard to the development of potential decontamination therapies, a detailed understanding of the mechanisms of relevant biochemical reactions is necessary.\textsuperscript{1} Human serum transferrin, an iron carrier protein in the blood, is only saturated to 30% with iron indicating a high capacity for the complexation of other metal ions.\textsuperscript{2}

The complexation of Cm(III) with human serum transferrin is investigated in a pH range from 3.5 to 11.0 using time-resolved laser fluorescence spectroscopy (TRLFS).\textsuperscript{3} At pH \( \geq 7.4 \) Cm(III) is incorporated at the Fe(III) binding site of transferrin whereas at lower pH a partially bound Cm(III) transferrin species is formed. The fluorescence lifetime of the incorporated Cm(III) transferrin species correlates with two water molecules in the first hydration sphere resulting in a 4-fold coordination of Cm(III) via amino acid groups of the protein and coordination of three additional ligands (e.g. synergistic anions).

Furthermore, the complexation of Eu(III) with human serum transferrin was investigated at T < 20K using TRLFS. At high pH (pH 7.4/8.0) the spectra are characterized by a high fluorescence intensity and maximum splitting of the emission band indicating a highly unsymmetrical coordination environment of Eu(III) in the transferrin complex. The fluorescence lifetime indicates a sevenfold coordination of Eu(III) via amino acid groups of the protein and synergistic anions. This species corresponds to the incorporated Cm(III) transferrin species. The spectra at lower pH (pH 4.5/6.0) are less intense and show no visible splitting indicating the formation of an Eu(III) transferrin species with partial coordination of Eu(III) to the protein.

Further structural investigations were performed by EXAFS spectroscopy on Am(III) transferrin.\textsuperscript{3} They show the formation of an Am(III) transferrin complex at pH 8.5 which is characterized by a very short average distance of R = 2.38 Å in the first coordination shell. This indicates strong multidentate coordination of Am(III) as expected in case of coordination of Am(III) at the transferrin binding cleft. The presence of several shells at higher distances points to a well-defined bonding environment in the Am(III) transferrin complex.

Non-Radiative Deactivation in Lanthanoid Luminescence – New Developments in Conceptual Understanding

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Luminescent lanthanoids are prone to quenching by multiphonon-mediated relaxation. In these processes, the energy of a lanthanoid excited state is transferred onto vibrational overtones of surrounding oscillator moieties. Molecular lanthanoid complexes in solution are affected most severely, with high-energy oscillators like O–H, N–H, or C–H in the ligands and solvents being the main contributors to the overall quenching. Despite the central importance for lanthanoid luminescence, these phenomena are still ill-understood and synthetic work often characterized by trial-and-error approaches.

In this contribution, we will present our progress in systematically improving lanthanoid luminescence and investigating non-radiative deactivation by high-energy oscillators. In particular, we will discuss various aspects regarding our recent advances in understanding multiphonon relaxation, for example the role of vibrational anharmonicity, the importance of Franck-Condon overlap, or the suitability of the energy gap law for the quantitative description of the processes involved.

Tailoring the microstructure of UC$_x$ for improved radioisotope release of ISOL targets

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Radioactive ion beams (RIBs) are produced by interaction of a highly energetic proton beam impinging onto a thick target material. The isotopes created by nuclear reactions diffuse from the target and are ionized, accelerated and mass separated on line (ISOL) before delivered at the experimental stations. The target is a key component within this process. It works at high temperatures, undergoing fragmentation, fission and spallation, and it must assure an efficient and fast release of the short half life isotopes [1]. Uranium carbide-based targets are currently the reference material at ISOLDE - CERN. However, the need for improved and new RIBs should coincide with target developments. Desirable new and more intense RIBs might be expected if targets are achieved with permeable and porous submicron/nanostructures [2]. Therefore, the goal of the present study is the preparation of nanostructured U-based carbides to be tested as target materials.

For this purpose, three different approaches were tried. The first path was solid-gas reaction between metallic U and methane via UH$_3$ intermediate. In the second approach, precursor solutions of U acetate and acetylacetonate were prepared and processed by electrospinning. The third route was mechanical alloying of pre-alloyed UC with excess of graphite. The results have shown that nanostructured UC$_x$ materials can be successfully produced and batches of some of these materials are now under preparation for in-situ proton irradiation.


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Structure and Reactivity of Uranium Monoarene Complexes Spanning the Formal Oxidation States of U(II) to U(V)

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Uranium—arene interactions are known since the 1970’s,¹ however the characterization of uranium—arene bonds and neutral uranium monoarene compounds across the spectrum of uranium oxidation states is particularly limited.² Therefore our studies of structurally similar uranium-monoarene complexes in different oxidation states, including a divalent uranium complex deepen the understanding of 5f orbital extent and energy as well as the electronic structure and reactivity of uranium arene complexes. We will present recent work on trisaryloxide supported uranium—arene complexes accessible in the formal oxidation states from U(II) to U(V).³

Lanthanide-doped rare-earth tungstate nano- and microstructures with multicolor tunable emission properties

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Lanthanide-doped compounds of the rare-earth tungstate family have a long history of practical applications due to their unique luminescence properties originating from the electron transitions within the 4f shell, as well as high chemical and thermal stability. These materials have been used in phosphors, laser hosts, scintillation counters, and others. The “classical” rare-earth tungstates were most often prepared by employing the conventional solid state reaction or flux crystal growth. In the last few years there has been a large amount of interest in nano- and micro- sized rare-earth tungstate materials. These materials are most often prepared using hydrothermal synthesis or microwave assisted hydrothermal synthesis. It has been observed that by tuning the size, shape and dimensionality materials with new desirable luminescence properties can be obtained. Also it has been detected that by changing the doping concentration of the Ln3+ ions materials with various luminescence colors can be obtained [1].

Here we report various lanthanide-doped rare-earth tungstate materials with fascinating 3D architectures and very promising luminescence properties, which have been synthesized in our lab over the past 2 years [2]. It was observed that the shape of the nano building blocks, and therefore the architecture of the microstructures, could be tuned by controlling the reaction conditions, such as source of the rare earth, amount of surfactant and reaction time. By doping various Ln3+ ions into the tungstate matrix materials with a wide range of luminescence colors, including white light, were achieved.

2. A. M. Kaczmarek, Y.-Y. Liu, P. Van Der Voort, R. Van Deun Dalton Trans., 2013, 42, 5471-5479
Relativistic DFT Studies of the Reactivity of f Element Complexes

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Calculations of ionization energies and electron affinities of a series of biscyclopentadienyl imido-halide uranium(V) related to the U$^{IV}$/U$^{V}$ and U$^{V}$/U$^{VI}$ redox systems, were carried out for the first time, using Density Functional Theory (DFT) in the framework of relativistic ZORA coupled with the COSMO solvation model. Among the results which will be presented, a very good linear correlation ($r^2=0.993$) between calculated ionization energies at the ZORA/BP86/TZ2P level, and the experimental oxidation potentials.

Using the same computational methodology, insertion reaction of CO$_2$ and CS$_2$ in the U-S bond of a series of bisthiolato Cp$^*$$_2$U(SR)$_2$ with R= Me, tBu, iPr and Ph is under investigation. Our first results, via linear transit calculations, explain well the observed insertion.

Finally in relation with the Ln(III)/An(III) differentiation which is a crucial issue for the reprocessing of the used nuclear fuel, new computational results explaining the observed selectivity of the considered polyazine ligands, will be presented.
Towards the Visualization of Biological Processes Using Responsive MRI Contrast Agents

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Magnetic resonance imaging (MRI) has evolved into a powerful tool in modern biomedical research. Its signal specificity can be further improved using contrast agents and their application has largely contributed to the MRI development. We aim to develop new measurement techniques that would enable visualization of neuronal activity and better understanding of brain function by using responsive or 'smart' agents (SCA). These are biochemical markers that alter their MR signal upon a certain biochemical event due to changes in their microenvironment.

Calcium ions or amino acid neurotransmitters are excellent markers tightly linked to brain activation, and are typically been the preferred target for a number of optical imaging methods. To accomplish our goals, we synthesize and study SCAs, complexes that respond to differing concentrations of endogenous Ca$^{2+}$ or neurotransmitters by altering their magnetic properties.

Over the past years we have reported a number of Gd$^{3+}$ chelates linked to modified Ca$^{2+}$ chelators that act as smart MRI contrast agents.[1] Some of the agents exhibited remarkable sensitivity towards Ca$^{2+}$, dramatically altering their relaxometric properties. In a subsequent proof-of-principle study, we demonstrated the SCA response in a complex 3D cell culture model. Furthermore, we monitored the cellular signaling and Ca$^{2+}$ transport through the plasma membrane upon administration of the SCA and calculated of the possible T$_1$ values during the neuronal activity. The estimates of the actual T$_1$ values suggest that MRI signal changes could be detectable by modern instrumentation and imaging protocols.

We have also prepared a series of crown-ether containing SCA that are capable to sense amino acid neurotransmitters. Their relaxivity substantially reduces in presence of neurotransmitter molecule which is caused by the reduction in the hydration number of the studied complex. These are the first examples of the host-guest interaction between the lanthanide-based complexes and amino acid neurotransmitters.

Modified Diglycolamides for Ln(III)/An(III) Co-Separation: A Complexation Study using TRLFS and Solvent Extraction

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In order to achieve separation of trivalent actinides, An(III) and trivalent lanthanides, Ln(III) numerous processes based on oxygen and nitrogen-donor ligands have been developed.\textsuperscript{[1]} Hereby diglycolamide ligands like TODGA (\(N,N,N',N'\)-tetraoctyldiglycolamide) are widely-used as efficient O-donor ligands for the actinide and lanthanide co-separation by solvent extraction.\textsuperscript{[2,3]} The extraction behavior of An(III) and Ln(III) and other fission products is significantly influenced by structural changes in the back-bone of the TODGA ligands.\textsuperscript{[4]} In this work, the TODGA molecule was modified by adding one or two methyl groups to the carbon-atoms in \(\alpha\)-position to the ether oxygen atom (see Fig. 1).

\begin{center}
\begin{tabular}{ccc}
\textbf{TODGA 1} & \textbf{Me-TODGA 2} & \textbf{Me\textsubscript{2}-TODGA 3} \\
\includegraphics[width=0.3\textwidth]{TODGA1} & \includegraphics[width=0.3\textwidth]{MeTODGA2} & \includegraphics[width=0.3\textwidth]{Me2TODGA3}
\end{tabular}
\end{center}

\textbf{Figure 1:} Structures of TODGA 1, Me-TODGA 2, and Me\textsubscript{2}-TODGA 3.

In liquid-liquid extraction studies using TODGA 1 and the methyl-substituted derivatives Me-TODGA 2 and Me\textsubscript{2}-TODGA 3 a distinct influence of the degree of substitution on the extraction performance is observed: Significantly lower distribution ratios for Ln(III) and An(III) are found using 2 or 3 in comparison to 1. In order to obtain information about the complex stoichiometry and thermodynamic data of the complexation reactions the complexation of Cm(III) and Eu(III) with 1, 2 and 3 is studied by Time-resolved laser fluorescence spectroscopy (TRLFS).\textsuperscript{[3]}

Conditional stability constants of the final and intermediate complex species were determined and followed the order \(\beta_{\text{TODGA-complex}} > \beta_{\text{Me-TODGA-complex}} > \beta_{\text{Me2-TODGA-complex}}\). Furthermore, our studies show that separation factors calculated from TRLFS data (\(SF_{\text{Cm(III)/Eu(III)}} = \beta_{3,\text{Cm(III)}} / \beta_{3,\text{Eu(III)}}\)) are in excellent accordance with the experimental values obtained by extraction experiments.

Macrocyclic Lanthanide(III) Complexes Containing Picolinate Pendants with High Stability and Kinetic Inertness

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Lanthanide(III) coordination chemistry in aqueous solutions is currently receiving a great deal of attention due to the important biomedical and bioanalytical applications of these complexes. Indeed, stable Gd$^{3+}$ complexes with polyaminocarboxylate ligands are commonly used as contrast agents in Magnetic Resonance Imaging (MRI), while luminescent complexes of Eu$^{3+}$ and Tb$^{3+}$ have found application in fluorinmunoassays and as luminescent probes for optical imaging. These applications require a very stable complexation of the metal ion in highly competitive biological media. This is normally achieved with the use of macrocyclic ligands based on 1,4,7,10-tetraazacyclododecane (cyclen) such as DOTA [1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid], which forms lanthanide complexes of exceptionally high thermodynamic stability and kinetic inertness. Herein, we report a new series of lanthanide complexes based on cyclen, cyclam and reinforced cyclam platforms that contain picolinate pendant arms and present very high stabilities (see Figure).

The synthesis of the ligand and metal complexes and the assessment of their thermodynamic and kinetic stabilities will be presented and discussed. Furthermore, we have performed a detailed structural study in the solid state (single crystal X-ray diffraction) and in solution. The solution structures were established on the basis of DFT calculations and the analysis of the Ln(III)-induced paramagnetic NMR shifts.


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The design of simple, molecular systems that bind or combine one or a few actinide cations, in chosen oxidation states, is an area in its infancy. In our group we have had much success with the tetraanionic Schiff-based ‘Pacman’ macrocycle.[1] Very recently, we have extended our research in this area and synthesised the first mono- and dinuclear actinide complexes of the small-cavity, dipyrrolide, dianionic macrocycle trans-calix[2]benzene[2]pyrrolide (L)2-.[2]

The conformational flexibility and switchable π-coordination of this macrocyclic ligand provides a unique and well-defined molecular environment in which to study the interaction of uranium(III) ions with soft, arene-containing ligands and gain insight into actinide covalency, of relevance to the separation of minor actinides from nuclear waste mixtures.[3]

Here we show how the bonding, structure, and reaction chemistry of actinide complexes of this ligand, offer an ideal chance to explore the subtleties and differences in actinide-arene bonding.

Easily achievable ligands of Eu$^{3+}$ ion for the luminescence sensing of anions in acetonitrile solution

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Recently, the interest in Ln(III) compounds possessing chiral properties increased, as a result of the possibility to take advantage of the chiral feature introduced in the design of the complex [1]. In particular, Ln(III) compounds, where the chirality is “introduced” through the use of chiral ligands, have led to the development of new chiral sensing/recognition applications, such as luminescence sensing of anions [2-5] and of chiral biological substrates [3, 6-8].

In this contribution, we will present our recent work on the luminescence spectroscopy of several Eu$^{3+}$ complexes of a new family of organic ligands (Fig. 1). We will show how the Eu$^{3+}$ luminescence deriving from these complexes, can be effectively exploited for the detection of several kind of anions in aprotic polar solvents, such as acetonitrile. In this context, both the sensitivity and the selectivity of the technique can be tuned simply by changing the nature of the heteroaromatic ring within the ligand backbone.

![Figure 1](image)

Tuning the Formation Rates and Kinetic Inertness of Lanthanide(III) Complexes of Macrocyclic 1,4,7,10-tetraazacyclododecane Derivatives

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The complexes of trivalent lanthanides formed with some polyaza-polycarboxylate ligands and the analogous amide, phosphonate and phosphate derivatives attracted considerable attention during the last three decades due to their successful application in medical diagnosis and therapy.[1] Diagnostic applications such as Magnetic Resonance Imaging (MRI) rely on the use of complexes of paramagnetic ions (mostly Gd(III)) while chelates with radionuclides emitting positrons (66/68Ga, 86Y) or gamma photons (67Ga, 111In, 177Lu) are employed in Positron Emission Tomography (PET) or Single-Photon Emission Computed Tomography (SPECT), respectively. These applications require very stable and very inert complex of the metal ion in highly competitive biological media. In general two different types of ligands, the open-chain DTPA and the macrocyclic DOTA and their derivatives applied routinely to bind the metal ions. The complexes of the DTPA and its derivatives form fastly (this explains why the given ligand class is highly preferred in radiopharmaceutical applications) but the dissociation of the complexes of DTPA is also faster in comparison to the corresponding DOTA complexes. This was evidenced lately in patients with severe renal failure or following liver transplantation where the prolonged retention of some Gd(III) based contrast agents resulted in Gd(III) deposition giving a birth to a disease called Nephrogenic Systemic Fibrosis (NSF). The presentation intends to focus on the results of ligand design, synthesis, equilibrium (stability constants of the complexes of biogenic Mg2+, Ca2+, Zn2+, Cu2+ and Ln3+ ions) and kinetic (formation and dissociation) studies performed with two 1,4,7,10-tetraazacyclododecane derivatives that were designed 1. to form kinetically more inert complexes or 2. to form complexes considerably faster than the DOTA does.

Acknowledgement
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Old theory along modern quantum chemistry tools enhances the understanding of the chemistry of lanthanides. We discuss the applicability of Ligand-Field-Theory or Angular Overlap Model (AOM) combined with Density-Functional-Theory (DFT) to evaluate the electronic structure of lanthanide compounds, which are currently the subject of incredible interest in the field of luminescent materials. The functioning of phosphors is well established by the f-d transitions, which requires the investigation of both the ground 4fⁿ and excited 4fⁿ⁻¹5d¹ electron configurations of the lanthanides. The computational approach to the problem is based on the effective Hamiltonian adjusted from non-empirical DFT calculations. The given model contributes to the understanding of lanthanides in modern phosphors with high or low site symmetry and presents a non-empirical approach using less sophisticated computational procedure for the rather complex problem including both 4f and 5d open shells.

POSTERS
The development of sophisticated reporter probes for in vivo imaging of anatomy and physiology has become a very active field of research.\(^1\) On the other hand; design and synthesis of fluorescent signalling systems is highly topical in supramolecular chemistry.\(^2\)

Herein the design synthesis and properties of novel supramolecular lanthanide complexes will be reported.

**References**

Block Copolymers of A New Lanthanide Complex

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The design and synthesis of novel polymeric systems is an active field of research. Lanthanide based complexes have been widely used in a variety of applications like sensing, imaging and assay related ones.\(^1\) In particular, the incorporation of luminescent lanthanide complexes in solid matrices with a well defined structure has recently attracted considerable attention in materials science.\(^2\) However, block copolymers of lanthanide based monomers have been rare.

Herein the synthesis and properties of novel block copolymers of a lanthanide based complex will be described.

References

Luminescent Properties of Uranium Complexes

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The development of reprocessing strategies and long-term management programs for nuclear waste requires a detailed understanding of actinide behaviour in the environment. While the use of radiometric counting techniques is well developed as a means of following actinide migration, techniques based around the photophysical properties of uranium are relatively under-utilised. This is despite the potential for luminescence spectroscopy to provide valuable information regarding the oxidation state and speciation of uranium ions in solution. Here we present our efforts to study underexplored aspects of the green LMCT fluorescence of the U(VI)O$_2^{2+}$ species$^1$ as well as the first experimental studies of the f-f transitions of the U(IV) ion.$^2$ We also look at the little-known uranium(VI) terminal oxo complex UOCl$_5$ with the aim of furthering the knowledge of the non-trivial oxidation redox properties of uranium species in solution.

Small Molecule Activation by Lanthanides(II) Supported by Siloxide Ligands

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Promoting the activation of small molecules (CO$_2$, N$_2$) is an important goal in contemporary catalysis. Complexes of divalent lanthanides are ideal for promoting CO$_2$ reduction because of their oxophilicity, Lewis acid character and high reducing ability. However, only few examples of Ln (II) mediated CO$_2$ reduction have been reported.\textsuperscript{1, 2} The supporting ligand plays an important role in the reactivity of f elements with small molecules. While most previous work has been centered on carbocyclic ligands we have recently shown that terbutoxysiloxide are effective ligands in U (III) mediated reduction of carbon dioxide. We have now isolated stable lanthanide (II) complexes with siloxide ligands for Yb, Eu, and Sm. We will present the structure of these complexes together with their reactivity with different substrates.

Magnetic Characterization of a Single-Ion Uranium(III) Complex with a One-Electron Reduced Bypiridine

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Molecular compounds that present slow relaxation of the magnetization at low temperature, known as single-molecule magnets (SMMs), have been a topic of intense research over the last two decades due to their potential applications in data storage, quantum computing and spin-based electronics. 1 Recently, a few mononuclear systems based on actinides, mainly with uranium, have been identified. 2,3 Following our interest in the chemistry of uranium(III), and motivated by the outstanding challenges in this research field, we have reported the magnetic properties of two uranium(III) compounds, [U(TpMe2)2(bipy)]I and [U(TpMe2)2]I (TpMe2 = hydrotris(3,5-dimethylpyrazolyl)borate; bipy = bypiridine), revealing two new SMMs based on uranium. 3 In this communication, we report our latest studies within this family of complexes, by presenting the magnetic properties of the compound [U(TpMe2)2(bipy)], 4 a complex containing a radical monoanionic bypiridine as co-ligand. AC and DC magnetization measurements, at different temperatures, frequencies and magnetic fields, have been performed and revealed slow magnetic relaxation with an effective relaxation barrier (Eeff) of 22.6 cm−1 and a pre-exponential factor (τ0) of 4.7×10−8 s. The results obtained, particularly the effect of the presence of a radical ligand, are discussed on the basis of quantum chemistry calculations.

Cerium in its tetravalent state has a high reduction potential (+1.61 V vs NHE for Ceric Ammonium Nitrate (CAN)) which makes it a powerful one-electron oxidant. The reduction potential, however, strongly depends on the cerium(IV) coordination environment as has been demonstrated for CAN in various solvents. Organocerium(IV) redox chemistry is still in its infancy, while weakly nucleophilic alkoxide ligands provide the most stabilizing coordination environment. The syntheses of cerium(IV) alkoxides like cerium(IV) pentamethylethanolate, Ce$_2$(OCMe$_2$iPr)$_8$, is routinely accomplished by applying CAN-based protocols. We have recently described the synthesis and structural characterization of the homoleptic cerium(IV) bis(dimethylsilyl)amide, Ce[N(SiHMe$_2$)$_2$]$_4$, to be exploited as synthesis precursor according to silylamine and silylamine elimination protocols. Herein, we wish to report the synthesis of a series of cerium(IV) alkoxides, via protonolysis, utilizing Ce[N(SiHMe$_2$)$_2$]$_4$ and the respective pentafluorobenzyl alcohol, pentamethylbenzyl alcohol, and neopentanol (Scheme 1).

Scheme 2. Synthesis of cerium(IV) alkoxides according to the silylamine elimination of Ce[N(SiHMe$_2$)$_2$]$_4$.

New developments in the chemistry of Actinocenes

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The discovery in 1968 of uranocene, \((\eta^8-C_8H_8)_2U\), the first linear sandwich complex of an f element, was a milestone in the history of actinide chemistry and boosted the development of organo f-element chemistry.

For 45 years, most of the works dedicated to the \([(\eta^8-C_8H_8)_2M]^{q-}\) species \((q = 0, 1; M_f = \text{lanthanides and actinides})\), and in particular to \((\eta^8-C_8H_8)_2U\), the most stable of them, evidenced their poor reactivity and absence of coordinating properties. This relative inertness was explained by the inaccessibility of the metal center to supplementary ligands due to the steric constraints imposed by the two \(\eta^8\)-C\(_8\)H\(_8\) rings.\(^1\)

It was then a generally accepted idea that a bis(\(\eta^8\)-C\(_8\)H\(_8\)) complex could not adopt a bent geometry.

In 2008, by using the extremely coordinating cyanide ion (\(-CN\)), we characterized the first actinocene compound with a bent geometry, eg \([(\eta^8-C_8H_8)_2U(CN)]^-\.\(^2\)

We presented here the influence of the actinide An\(^{4+}\) ion (uranium and thorium) in the reactivity of the actinocenes \((\eta^8\)-C\(_8\)H\(_8\))\(_2\)An toward a series of anions and neutral molecules.\(^3\)\(^\text{-}^5\)

Synthesis and Applications of a New Luminescent Macromolecular Material

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The use of supramolecular chemistry to control the properties of the materials is a key aspect for the future of nanoscience and nanotechnology. In this respect, design and synthesis of novel functional organic compounds have attracted considerable attention since they lead to a variety of advanced technological applications in the field of molecular electronics, sensors, imaging agents, light emitting diodes, photovoltaics, electrochromics, data processing and storage media, molecular logic gates and so on.

Herein, a novel luminescent macromolecular material will be designed, synthesized and characterized spectroscopically. Furthermore, some applications of this novel macromolecular material in analytical, bio- and nanotechnological and/or materials science will be investigated.

References

Multiconfigurational Studies for Single-Molecular Magnets Based on Lanthanide Ions

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Beside single-molecular magnets (SMM) based on 3d metal ions also complexes with 4f ions are of great interest. The latter show high total spins $S$ and allow higher coordination numbers as compared to 3d metal ion. This can affect the axial magnetic anisotropy and, hence, cause slow magnetic relaxation. The corresponding thermal spin relaxation barrier depends on the square of the total spin $S$ and linearly on the so-called zero-field splitting (ZFS) parameter.

Figure 1: Molecular structure of the dinuclear gadolinium (III) complex $[\text{Gd(HSabhea)NO}_3]_2$

With increasing computational power and new developments in the field of theoretical chemistry the impact of quantum chemical calculations rises. With the help of density functional theory (DFT) and ab initio methods it has become possible to study challenging electronic structures of inorganic compounds. Although DFT is a widely used method for transition metal complexes, it is not applicable to investigate and explain magnetic properties of lanthanide complexes that require the treatment of interactions with near degenerated magnetic states.

Several lanthanide complexes have been studied for their SMM behavior with the multiconfigurational CASSCF/RASSI method as it is implemented in the MOLCAS² 7.8 program package.

Probing the Effective Charge Density of Uranyl, UO$_2^{2+}$, in the Gas Phase

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In this work, we used electrospray ionization quadrupole ion trap mass spectrometry (ESI-QIT/MS) to probe the effective charge density of uranyl, UO$_2^{2+}$, in the gas-phase.

Ethanol solutions of uranyl, divalent alkaline-earth (A = Ca, Sr, Ba) and trivalent lanthanide (Ln = La, Ce, Pr, Eu, Tb, Ho, Tm, Lu) nitrates readily yielded, in the negative ion mode, species of the type [(UO$_2^2$)(NO$_3$)$_x$]$^{2-}$, [A(NO$_3$)$_x$]$^{2+}$, and [Ln(NO$_3$)$_x$]$^{3+}$, where $x=1,2,\ldots$. With solutions of two metals in equimolar amounts, we observed the formation of the mixed species [A(UO$_2$)(NO$_3$)$_5$]$^-$, [Ln(UO$_2$)(NO$_3$)$_6$]$^-$ and [ALn(NO$_3$)$_6$]$^-$. Collision induced dissociation (CID) experiments in the QIT of the [A(UO$_2$)(NO$_3$)$_5$]$^-$ species showed only the formation of the [UO$_2$(NO$_3$)$_3$]$^-$ ion (Fig. 1A). CID of [Ln(UO$_2$)(NO$_3$)$_6$]$^-$ showed a preferential formation of the [UO$_2$(NO$_3$)$_3$]$^-$ ion for the Ln with larger ionic radii (Fig. 1B) and a preferential formation of the [Ln(NO$_3$)$_4$]$^-$ ions for the smaller Ln. CID of [ALn(NO$_3$)$_6$]$^-$ yielded the [Ln(NO$_3$)$_4$]$^-$ ions exclusively (Fig. 1C).

![Fig. 1 ESI-QIT/MS(-) CID spectra of: A. [CaUO$_2$(NO$_3$)$_5$]$^-$; B. [PrUO$_2$(NO$_3$)$_6$]$^-$; C. [CaPr(NO$_3$)$_6$]$^-$.](image)

Computational studies (DFT) of the energetics of fragmentation of selected mixed species were in agreement with the experimental observations.

The overall results suggest that, in the gas phase, the effective charge density of the uranyl ion is closer to that of a trivalent metal ion than to that of a divalent metal ion. This ordering is similar to that derived from the complexation stability with different ligands in solution studies \cite{1}.


Acknowledgments: The ESI-QIT/MS is part of RNEM-Rede Nacional de Espectrometria de Massa, supported by Fundação para a Ciência e a Tecnologia (FCT). Additional support from FCT (PhD grant SFRH/BD/70475/2010 to A.F.L.) is also acknowledged.
Iminophosphoranes-containing ligands (N=P bond) are known for more than thirty years and have been applied to the f-element chemistry for either catalytic or conceptual applications.[1] However, there is only few examples of divalent lanthanides bearing iminophosphorane ligands and they are limited to anionic ones.[2]

We have developed two new classes of ligands based on the iminophosphorane moieties: a neutral one that combine a pyridine ring with hemilabile iminophosphorane arms (Scheme, left) and another one combining iminophosphorane moieties with phenoxide rings named phasasalen (Scheme, right). The latter coordinated to Yttrium was found extremely efficient for the polymerisation of lactides.[3a] Moreover it has been also shown to stabilize unusual oxidation states of d-transition metals.[3b]

We are now interested in developing new chemistry with these ligands and divalent lanthanides in the aim of studying their electronic structure and their reactivity toward small molecules. The syntheses, structures and reactivity studies will be further presented and discussed.

DO ELECTROSTATICS DETERMINE THE MAGNETIC ANISOTROPY OF LOW SYMMETRY DYSPROSIUM COMPLEXES?

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The difficulties associated with rational magnetic design employing Ln\textsuperscript{III} ions are rooted in their flexible coordination modes in tandem with their complex and subtle electronic structure. The shielded nature of the 4f orbitals gives rise to only weak interactions with the surrounding environment, yet these interactions often govern the magnetic properties of interest. \textit{Ab-initio} calculations of the Complete Active Space (CAS) variety have become a useful tool to model the orbital degeneracy within the 4f manifold and to accurately predict the electronic and magnetic properties of dysprosium(III)-containing complexes [1]. Studies employing the CAS methodology have been shown to be in extremely good agreement with experimental measurements, where the orientation of the magnetic anisotropy of the ground doublet and the energies of the ground multiplet can be accurately reproduced [2 – 4].

Recently we proposed a quantitative methodology not only for the rationalization, but also for the prediction of the main magnetic anisotropy axis of the ground state of low symmetry Dy\textsuperscript{III} complexes, under the empirically justified assumption of an \( m_J = \pm \frac{15}{2} \) ground state [5]. Our approach, based on electrostatic optimization of the aspherical electron density distribution of Dy\textsuperscript{III}, employed a minimal valence bond representation of the potential of the ligand environment. This model provided excellent agreement with \textit{ab-initio} CAS calculations (deviation angle on the order of 5 – 10\(^\circ\)), Figure 1. We have subsequently undertaken studies to extend the model to more complex ligand types and to include the effect of formally neutral species. We have also begun to examine its application to other Ln\textsuperscript{III} ions. Our approach continues to provide invaluable chemical insight into the nature of the magnetic anisotropy in low symmetry Dy\textsuperscript{III} complexes and highlights the opportunity to use this knowledge in the rational design of novel complexes.

\textbf{Figure 1.} Our model provides a quantitative rationalization of the magnetic anisotropy in \([\text{DyDOTA(H}_2\text{O)}\text{Na}_3]^{2+}\) [3]. The main magnetic axis of the ground state; green = electrostatic, dark blue = \textit{ab-initio} [5], red = \textit{ab-initio} [3] and pink = experimental [3].


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Following the initial report of the terminal uranium nitride species, \([\text{U(N)(Tren}^{\text{TIPS}})]\text{[Na(12-crown-4)}_2],^1 \) work has concentrated on investigating alternative synthetic routes towards UN triple bonds. Thus, we have recently investigated the effects of reducing a pre-installed azide group on a uranium(IV) precursor, namely \([\text{U(N}_3]\text{(Tren}^{\text{TIPS}})])\), by alkali metal reductants. This successfully led to the isolation of a range of uranium(V) nitrido dimers of the general formula \([\text{U(µ-N)(µ-M)(Tren}^{\text{TIPS}})\text{]}_2\) (M = Na, K, Rb, Cs). The respective metal cation can be sequestered and encapsulated with a suitably sized crown ether yielding the terminal uranium(V) nitride separated ion pair species, \([\text{U(N)(Tren}^{\text{TIPS}})]\text{[M(crown)}_2\) (M = Na, K, Rb, Cs).

Alongside the neutral uranium(VI) derivative \([\text{U(N)(Tren}^{\text{TIPS}})]\),^2 we have utilised this library of uranium-nitride complexes to ascertain the inherent reactivity of the UN linkage with respect to small molecules, in particular CO.

A few years ago a new class of mononuclear compounds was identified where, at low temperatures, the magnetization presents slow relaxation of purely molecular origin, the so called single-molecule magnets (SMM)\cite{1}. The first single-ion magnet (SIM) was based on complexes of lanthanide ions\cite{2} which may provide high effective barriers ($U_{\text{eff}}$), owing to their large magnetic moments and strong anisotropy, arising from their large unquenched magnetic moments. Blagg et al.\cite{3} reported a square-pyramidal pentametallic Dy$^{3+}$ cluster that showed slow magnetic relaxation at temperatures as high as 40 K with $U_{\text{eff}}=530$ K. Thus, $f$-block complexes seem the most promising in order to provide the high $U_{\text{eff}}$ required for potential applications of SMMs in information storage, spintronics and quantum computation.\cite{4}

We will present the magnetic properties, by means of AC and DC magnetization at different temperatures, frequencies and magnetic fields of some $\beta$-diketonate Er$^{3+}$ complexes that besides their luminescent properties in the solid state, emitting in the near infra-red region, they also display slow magnetic relaxation behaviour.\cite{5,6} [Er(thd)$_3$(bath)] was the first Er$^{3+}$ $\beta$-diketonate displaying SIM behaviour.\cite{5} AC susceptibility studies revealed the presence of slow magnetic relaxation induced by the application of a static magnetic field and two relaxation modes could be distinguished with energy barriers $U_{\text{FR}}/k_B=15.6$ and $U_{\text{SR}}/k_B=22.4$ K. We will also report the SIM behaviour in other three novel $\beta$-diketonate Er$^{3+}$ complexes with 2,4-hexanedione and different N,N-donors\cite{6} in order to study the effect of the capping ligand on the anisotropy barrier. We could verify that the complex with the bulkier capping ligand and a larger compression of the Er$^{3+}$ square antiprism along the approximated tetragonal axis exhibits the highest energy barrier ($U_{\text{eff}}=23$ K).\cite{7}


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Towards water soluble uranyl-salophen Schiff-base Complexes

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The use of hexavalent uranyl dication UO\textsubscript{2}\textsuperscript{2+} coordinated with different ligands either in reactions or separation processes as well as in supramolecular assemblies has challenged the deeper understanding of the nature of uranyl-ligands coordination and binding properties\textsuperscript{1}. The number of artificial receptors containing UO\textsubscript{2}\textsuperscript{2+} has increased remarkably in the last years and in many instances unsuspected structural and reactivity features were revealed. Salophens are a quite popular class of Schiff base ligands. They are obtained by a modular synthesis comprising the condensation of 1,2-phenylenediamine with two equivalents of salicylaldehyde. The two starting building blocks can be easily functionalized and this gives access to a large variety of ligands with subtle variations in steric and electronic configuration. The resulting coordination site, an N\textsubscript{2}O\textsubscript{2} binding pocket, is capable of bonding to uranyl cation in a tetradentate fashion. Such derivatives can be described as immobilized Lewis acids able to coordinate Lewis bases. Remarkably, the introduction on the ligand skeleton of additional, appropriate binding motifs for the substrate can lead to a well-defined pattern of intermolecular interactions that can enhance the efficiency and selectivity of the recognition processes. Recently, our research focused on the use of suitably designed uranyl-salophen complexes as "supramolecular” receptors for the recognition of anions in water\textsuperscript{2}. To improve the water solubility of these derivatives and to obtain a library of potential artificial receptors able to work in aqueous media, we developed simple and general protocols to obtain series of salicylaldehydes properly functionalized\textsuperscript{3}.

Here we will present the results obtained in the field and the behavior of such systems as anion receptors in water.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{structure.png}
\caption{Structure of uranyl-salophen complexes.}
\end{figure}

Acknowledgments

We thank COST Action CM 1006 for financial support.


We deal with the computational determination of the electronic structure of open-shell f and d electrons, based on Density Functional Theory (DFT) for the reliable calculation and description of the f→d transitions in some lanthanide doped phosphors. We will consider here the optical properties of lanthanide Pr$^{3+}$ embedded into various solid state fluoride host lattices, for the prospection and understanding of the so-called quantum cutting process, being important in the further quest of warm-white light source in Light Emitting Diodes.

We use the conceptual formulation of the ever-modern ligand field theory into quantum chemistry tools: LFDFT. [1] [2] We present methodological advances for the calculations of the Slater-Condon parameters, [3] the ligand field interaction [4] and the spin-orbit coupling constant, important in the non-empirical parameterization of the effective Hamiltonian adjusted from the ligand field theory.

The model shows simple procedure using less sophisticated computational tools, which is intended to contribute to the design of modern phosphors and to help to complement the understanding of the 4f$^{n}$ → 4f$^{n-1}$5d$^{1}$ transitions in any lanthanide systems.

Novel DOTA Based Supramolecular Systems

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The design and synthesis of novel supramolecular systems is an active field of research. Among supramolecular systems, lanthanide based complexes have been widely used in sensing, imaging and assay related applications.1 In particular, the incorporation of luminescent lanthanide complexes in solid matrices with a well defined structure has recently attracted considerable attention in materials science.2

Herein the synthesis and properties of some novel DOTA based supramolecular systems will be described.

References

Luminescence Quenching in Molecular Lanthanoid Complexes

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Lanthanoid luminescence has attracted considerable interest for a great number of possible applications. However, luminescence is prone to non-radiative deactivation processes (quenching), which are mainly caused by energy transfer from the metal’s excited state to high energy oscillators (O-H, N-H, C-H). Although quenching is responsible for considerable decrease of luminescence intensities, lifetimes and quantum yields, a detailed understanding of non-radiative deactivation processes is still in its early ages.

We will present our recent work on the quantification of luminescence quenching by aromatic C-H and C-D oscillators, which are present in many successful ligand architectures for the sensitisation of lanthanoid(III) ions. In particular, we will show that resonance between the oscillator’s overtones and the energetic levels of the lanthanoid are of particular importance for the quenching effect. This phenomenon has widely been neglected in the commonly used models for the quantification of non-radiative deactivation in lanthanoid complexes.

![Figure 1: Lanthanoid cryptates used for the quantification studies.](image)

Figure 1: Lanthanoid cryptates used for the quantification studies.

New Multimetallic Assemblies as Photoluminescent Materials

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The preparation of metal-coordination compounds between pybox (pyridine-bis-oxazoline) as the ligand and Eu(III) and Tb(III) ions has recently attracted great interest.\textsuperscript{1,2} The resulting complexes exhibit the characteristic luminescence properties of the lanthanide ions both in solution and the solid state. High quantum yields and efficient ligand-to-metal energy transfer make pybox-related ligands good sensitizers for lanthanide emission.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic presentation of the preparation of lanthanide coordination networks with pybox-related ditopic ligands.}
\end{figure}

However, the research in the field to date, has shown that modifications of the pybox ligand do not result in remarkable changes of the photoluminescent properties, limiting the diversity of these complexes for potential applications. The main focus of this project is therefore the synthesis of new dumbbell-shaped bis-tridentate ditopic ligands and the subsequent preparation of photoluminescent lanthanide coordination networks (Figure 1). So far two new types of pybox-ligands, which also show blue luminescent properties, have been synthesized under improved cross-coupling reaction conditions. Coordination of these ditopic ligands with Eu(III) and Tb(III) in different stoichiometries resulted in photoluminescent materials which are also soluble in common organic solvents. The ultimate goal of the project is the synthesis of multimetallic networks and the preparation of photoactive devices by utilizing both the luminescent properties of the uncoordinated ligands as well as behaviour resulting from lanthanide coordination.

Preparation of Intermetallic compound nanoparticles by Electrospinnig

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Intermetallic compounds (IC) have a crystal structure and chemical formula well defined¹ and being for their use as structural materials, magnetic properties, the ability to reversibly absorb hydrogen¹, etc. Electrospinning is a technique that has been originally developed to produce ultra-fine polymer fibers ²,³. This route enables low cost production of nanometer scale fibers with tunable surface properties. Such fibers have extremely high surface area, very high porosity, high permeability, low basic weight, the ability to retain electrostatic charges, among others properties⁴. The purpose of this work was to apply electrospinning for the preparation of IC nanofibers/nanoparticles containing f-block elements. Moreover, the expected high surface area can bring benefits to the catalytic properties of these materials, which will be the aim of future studies. Preliminary results showed that IC nanoparticles containing f-block elements as LaNi₅, SmCo₅, LaCu₂, and DyFe₃ can be successfully produced by this technique, which, to our knowledge, happens for the first time. The XRD pattern and a SEM image of LaNi₅ IC nanoparticles are presented in Figure 1.


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Low Oxidation State Actinide Chemistry: From Fundamentals To Future Applications

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The decision to include nuclear power as a central part of the planned future energy portfolio has seen an increased interest in actinide chemistry.¹ Aspects of the nuclear fuel cycle: from mining and extraction, to reprocessing and disposal; sees the actinides encounter a range of elements across the periodic table under a variety of conditions.

Greater fundamental understanding of actinide bonding regimes is essential in enabling prediction of their behaviour in terms of speciation and reactivity, especially under unnatural or harsh environmental conditions. The chemistry of uranium in its +3 oxidation state has been well studied in recent years,² however that of other actinides in low-valent states is relatively unexplored.

Analysing the reactivity of subvalent actinides with environmentally relevant small molecules will deepen our understanding of their fundamental chemistry. Given that the Th(IV) → Th(III) standard reduction potential (E⁰ ≈ −3.7 V) is far greater than its U(IV) → U(III) counterpart (E⁰ ≈ −0.6 V),³ a rich small molecule activation chemistry of Th(III) can be anticipated.

It has been shown that the use of hexadentate ‘Werner-type’ ligands can stabilise uranium in the +3 oxidation state, so it follows that a similar structural motif employing hexadentate ligands could stabilise thorium(III) complexes. Various systems from Meyer,⁴ Marques⁵ and Mazzanti⁶ have proven that this motif is employable in uranium and lanthanide chemistry, so thorium and potentially other transuranics are therefore also feasible. This work will present our recent attempts to stabilise low-oxidation state actinides using sterically demanding hexadentate ligands.

6. M Mazzanti et al., Chem. Sci., 2013, Accepted manuscript
Cerium(IV) Alkoxides according to the CAN Protocol

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In 1985, Gradeff et al. described the synthesis of tetravalent Ce(IV) alkoxides utilizing Ceric Ammonium Nitrate (CAN) and sodium alkoxides (methoxide, n-octyloxide) as precursors. Several years later, Evans et al. explored this salt metathesis protocol in detail for tert-butoxide derivatives, by varying the molar ratios of the educts. Accordingly, a series of heteroleptic Ce(IV) tert-butoxides was obtained, which also revealed different degree of aggregation (clustering). Until now, crystallographically authenticated Ce(IV) alkoxides originating from the CAN protocol comprise OtBu, OiPr, and OCMe2iPr derivatives.

\[
(NH_4)_2Ce^{(IV)}(NO_3)_6 + x NaOR \rightarrow \]

\[
Ce^{(IV)}OR_{x-2}(NO_3)_{6-x} + 2 NH_3 + x NaNO_3 + 2 HOR
\]

\[
x = 4 - 6
\]

Following the original CAN protocol, the present study deals with the synthesis and characterization of Ce(IV) neopentoxides.

Uranyl-Salophen Complexes as Ditopic Receptors for Ion Pairs

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Metal-salophen complexes, 1, can be easily synthesized starting from two molecules of salicylaldehyde and one of o-phenylenediamine in the presence of the corresponding metal salt. In recent years it has been demonstrated that these derivatives have interesting applications in the field of material chemistry; behave as versatile tectons to build up supramolecular architectures; effectively act as electrophilic catalysts; work as ion-pair receptors.

A receptor designed for this last purpose should consist of at least two subunits, each capable to bind one of the partners of the salt. According to this strategy we carried out the synthesis of 2x and 3x. These uranyl-salophen complexes are able to recognize anions by Lewis acid-base interactions, and to bind the counterion through an aromatic pendant or a polyoxyethylenic chain respectively.

In this communication we describe the synthesis of complexes 2x and 3x and their behaviour as ditopic receptor for tetraalkylammonium halides, investigated both with UV-Visible and ¹H-NMR titrations. The analysis of the latter showed that the addition of guest induces some variation in the receptors signals, suggesting conformational changes or dimers formation in the complexes.


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Molecular compounds containing direct metal-metal bonds have long been of interest in inorganic chemistry. Although there are numerous examples of compounds with bonds solely between transition metal elements, there exist relatively few compounds that exhibit bonding between transition metals and the lanthanides (Ln) or alkaline earth (Ae) elements.

Mountford et al. have recently reported several compounds containing alkaline earth-transition metal bonds. The reaction of Mg(NacNac)I(THF) with K[CpFe(CO)2] (K[Fp]) afforded Mg(NacNac)Fp(THF) (Mg–Fe = 2.6326(4) Å). This was shown to react with TolN=C=NTol to afford Mg(NacNac){(NTol)2CFp}; the first net insertion of an unsaturated substrate into an alkaline earth-transition metal bond. The heavier alkaline earth and f-element congeners [Ca(NacNac)Fp(THF)]2 and [Yb(NacNac)Fp(THF)]2 were also synthesised but were shown to be unstable in non-donor solvents.

In an effort to further this chemistry we are developing species of the form M{RC(NR')2}M'(OEt2) (M = Ae or Ln, M' = CpFe(CO)2, CpRu(CO)2 or Co(CO)3(PCy3), R = mes, R' = Cy or iPr), which feature fewer carbon atoms in the ligand backbone. The reduced bite-angle offered by these ligands provides reduced steric protection of the Mg atom, compared with the NacNac analogue, potentially increasing the reactivity of these species.

Here we report our recent work in this area.

References
A Cerium(IV) Carbon Multiple Bond

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Metal ligand multiple bonding is an important chemical concept but one area that is not well-developed is that of the lanthanides. One of the most successful strategies in the stabilisation of lanthanide carbenes has involved the use of chelating phosphorano arms, such as \([C(PPh_2NR)_2]^{2-}\) (R=SiMe_3, BIMP_TMS) or \([C(PPh_2S)_2]^{2-}\), which provide both electronic stabilisation and steric protection. With the exception of neutral datively bound N-heterocyclic carbenes, all previous investigations of lanthanide carbone complexes have involved the use of trivalent lanthanides and the use of tetravalent lanthanides has not been investigated.

Our group have recently reported the synthesis of the heavy group 1 salts of the BIMP_TMS ligand \([M(BIMP_{TMS}H)]\) (M = Rb and Cs), which provide access to the previously inaccessible cerium(III) methanide complex \([Ce(BIMP_{TMS}H)I_2(THF)]\), 1. Treatment of 1 with \([K(Bn)]\) affords the cerium(III) carbene complex \([Ce(BIMP_{TMS})I(DME)]\), 2. Further treatment of 2 with two equivalents of \([K(ODipp)]\) (Dipp = 2,6-diisopropylphenyl) results in the formation of the anionic “ate” complex \([\{Ce(BIMP_{TMS})(ODipp)_2K(THF)\}_\infty]\), 3. Subsequent oxidation of 3 with \([Ag(BPh_4)]\) affords the cerium(IV) carbene complex \([Ce(BIMP_{TMS})(ODipp)_2]\), 4, which is the first structurally authenticated example of a cerium(IV) carbon multiple bond. Whilst the bonding in 4 is predominantly electrostatic, theoretical calculations reveal modest covalent character in the Ce=C bond with σ- and π-multiple bond components present, which is consistent with the spectroscopic and reactivity data.

Synthesis of High Affinity Agents for Targeted MR Neuroimaging

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Magnetic resonance imaging (MRI) has become one of the essential noninvasive diagnostic techniques for soft tissues and diseases. Contrast agents (CAs) are used to produce additional contrast and increase the signal intensity for MRI [1]. The commonly available monomeric CAs have disadvantages such as non-specificity, fast renal excretion, low contrast efficiency and therefore they require higher dosage. To overcome this problem, we use multivalent, highly-branched dendrimeric molecules that are capable of carrying large number of CAs and hence the amplification of MRI signal [2].

Here we report the development of a new type of target-specific contrast agents (TCA). We took advantage of the highly specific interaction of the protein avidin with its ligand biotin and synthesized biotinylated monomeric and dendrimeric TCAs. These TCAs are additionally labeled with a fluorescent dye to achieve their multimodal detection by means of optical and MR-based techniques. The affinity assay showed that TCAs bind specifically to avidin-coated beads. The MRI phantom experiments exhibited approximately 5-fold better efficiency of the dendrimeric TCA when compared to the monomeric CA. In parallel, commercially available, non-targeted CA Dotarem® did not show the specific binding to avidin since no significant increase in the T1-weighted MRI signal was observed in samples treated with this CA.

References:

Supramolecular Assemblies with Lanthanides: Conception of Polyfunctional Systems

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Since several years we are interested in designing new tripodal ligands for assembling lanthanide-mediated polynuclear systems, whose helicoidal structure is reminiscent to biological motifs. In this contribution, we will present different aspects of the chemical design of suitable organic receptors (anchoring moiety, spacers) as well as structural and physico-chemical properties of various self-assembled three-dimensional edifices (tetranuclear, pentanuclear, ...), which were investigated by NMR, spectroscopy and other techniques. In addition, thermodynamic characteristics will be discussed with respect (i) to the control of self-assembly processes and (ii) to possible predictions in designing new supramolecular functional compounds.

Cyanide complexes of the f-element

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The cyanide ligand is one of the most widely used ligands in coordination chemistry of transition metals\(^1\). Numerous studies have shown the interest of cyanides complexes in various fields from biology to nanomaterials\(^2\). These compounds often exhibit interesting physico-chemical properties such as magnetism\(^3\), photoluminescence\(^4\) and conductivity\(^5\). The low number of cyanide complexes of lanthanides and actinides incited us to develop this field for both reactivity and theoretical aspects\(^6\). In this work, we investigated the reactivity of \(M_l(C_8H_8)_2\) and \(M_l(N^*)_3\) precursors toward the cyanide ion.

The discovery of the first bent "Uranocene"\(^7\) \(((C_8H_8)_2U(CN))^-\) led us to focus our interest on the thorocene analogue in order to compare the reactivity between \(U^{4+}\) and \(Th^{4+}\) ions which adopt distinct electron configuration (respectively \(5f^2\) and \(5f^0\)). The goal is to evidence the role of the \(5f\) orbitals and the number of \(5f\)-electrons on the accessibility to bent actinocene complexes. The \((C_8H_8)_2Th\) was reacted with the cyanide anion and distinct products were isolated depending on the nature of the cyanide salt\(^8\).

This study clearly illustrates the distinct chemical behaviour of thorocene versus uranocene.

Amides complexes \(M_l(N^*)_3\) \((M_l = U, Ce ; N^* = N\{SiMe_3\}_2)\) and their metallacycle derivatives have gained considerable interest these last years for their particular reactivity and the capacity of the \(N^*\) ligand to stabilize both low and high oxidation states. We recently focused our interest on the reactivity of these compounds with cyanide ion which will be presented.

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\(^7\) J. C. Berthet, P. Thuéry, M. Ephritikhine Organometallics 2008, 27, 1664.
Tailored Hydrazone-Supported Tripodal \( \kappa^6 \text{N} \) Donor Ligands for the Coordination of \( f \)-elements

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Rare earth metal coordination compounds of \( N \)-donor ligands are of special interest because of their variety of applications, e.g. in catalysis [1] and medicine [2]. \( N \)-donor ligands play an important role in the reprocessing of spent nuclear fuels [3] by extracting the minor actinides (e.g. Curium, Americum) from high-level radioactive waste. In order to improve the performance of existing extraction ligands and to develop more suitable ones, a detailed understanding of the selectivity of existing extraction ligands for actinide over the chemically similar lanthanide cations is essential. Therefore, the characterization of the metal-ligand bond in the complex, the influence of counter anions, and the behavior of all existing species in solution are crucial factors. In order to investigate such tendencies, we prepared easily accessible, chelating tripod ligands, which provide intrinsically well-defined coordination geometries[4].

Several \( f \)-element compounds of the multifunctional ligand (S)P[\( \text{N}^{\text{Me}}\text{NC(H)Py} \)]\(_3\) [5, 6] and its derivatives will be presented. The electronic and structural properties of these complexes have been characterized by several spectroscopic methods including X-ray diffraction on single crystals, NMR spectroscopy, and XAFS. Detailed insights of the species in solution, for instance aggregation, dynamic behavior and structural properties could be gained by several advanced NMR techniques.

Developing Rapid Radiochemical Separations of Americium from Actinides and Mixed Fission Products

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Analysis of americium is essential to determining the origin and intended use of unknown radioactive materials (nuclear forensics). However, americium separation from matrices containing actinides, lanthanides and fission products is challenging. Such separations require removal of competing ions from the matrix using anion exchange resins before separation of americium. Faster processes (aim <3 days) for the selective extraction of americium are therefore desired to enhance nuclear forensic investigations. Soft N-donor ligands showing high selectivity ($S_{Am/Eu} > 250$) for Am/Cm over lanthanides have recently been developed for use in a selective actinide extraction (n-SANEX) process.$^1$ These ligands are promising for the development of a selective americium extraction process.

Development of a rapid radiochemical separation process for Am from model nuclear forensic matrices is currently underway. The ligand CyMe$_4$BTPhen$^2$ 1 (Figure 1) has been synthesised and an optimised liquid-liquid separation procedure for $^{241}\text{Am}/^{152}\text{Eu}$ with quantification by gamma spectroscopy/ICP-MS has been developed. Application of the method to simulated matrices showed selective extraction of americium within a 24 hour timescale. After Am extraction, rapid radiochemical separation of U/Pu/Np isotopes from the matrix can be achieved, thus providing a rapid procedure for the purification of actinides important in nuclear forensics.

**Figure 1.** CyMe$_4$BTPhen

Sterically demanding monodentate aryloxide ligands have proven to be a versatile tool for the stabilization of Uranium coordination complexes. Furthermore, those complexes can participate in small molecule activation and show unique reactivity.

Recent work on a bulky 2,6-disubstituted phenolate as monodentate aryloxide ligand will be presented. Uranium coordination complexes in oxidation states ranging from III to V have been synthesized and characterized, and their reactivity towards small molecules explored.
Multicolour optical coding from a series of luminescent lanthanide complexes with a unique antenna

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Luminescent lanthanide complexes are used in numerous applications in fields as diverse as bio-medical diagnostics and analytical sensors, organic light-emitting diodes or optical communications and photonic devices. Ln$^{III}$ ions generate different luminescent f-f emissions ranging from ultraviolet to Visible and near-infrared ranges. As such they are particularly well suited for the development of multiplex assays and barcodes for security applications where an important requirement is simultaneous multicolour emission.

Here we present a bis-tetrazolate-pyridine ligand $H_2$pytz which sensitizes very efficiently the visible and/or near-IR luminescence emission of all lanthanide cations (Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb). The Ln$^{III}$ complexes present sizeable quantum yields in both domains with a single excitation source. The wide range of possible colour combinations in water, organic solvents and in solid state makes them very attractive for labelling and encoding. Luminescent polymer latexes based on lanthanide complexes are presented showing good stability over leakage.
Novel Lanthanide Based Macromolecules

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The design and synthesis of novel macromolecular systems is an active field of research. On the other hand, lanthanide based complexes have been widely used in a variety of applications like sensing, imaging and assay related ones.¹ It is envisaged that the incorporation of lanthanide based complexes in macromolecular systems might be useful.

Herein the synthesis and properties of a novel lanthanide based macromolecular system will be described.

References

Bioreduction of Uranium followed by Luminescence

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Understanding the chemistry of uranium within the environment is important due to the need for future geological disposal of spent nuclear fuel.\(^1\) Uranium (VI) as the uranyl form \{UO\(_2^{2+}\}\) is mobile within the environment.\(^2\) This causes problems during geological disposal as it relies upon the immobility of radioactive materials should they escape the multibarrier system. Another oxidation state of uranium that can be easily achieved is the U(IV) species, which is immobile within the environment. If this oxidation state could be achieved over the mobile U(VI) species then the uranium would be immobile within the environment and would pose less of a risk.

Certain bacteria have been known to gain energy by exploiting the reduction between these two forms of uranium. This process was first reported by Lovely et al in 1991,\(^4\) yet the mechanism for this process is still poorly understood. Luminescence can be used to distinguish between the oxidation states of uranium and has not been used to investigate this system before.

We have followed the bio-reduction using luminescence to observe the uranyl(VI) in the system. Preliminary results, seen below in figure 1, suggest the formation of an unstable uranyl(V) intermediate occurring after 3-4 hours followed by disproportionation to soluble uranyl(VI) and insoluble uranium(IV). Over a 24 hour period, all the uranyl(VI) is reduced to uranium(IV), resulting in a black crystalline solid, uraninite, a uranium(IV) rich mineral. These results are consistent with previous findings by Renshaw et al.\(^5\)

![Figure 1: Bio-reduction followed by luminescence over a 24 hour period.](image)

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Activation of Carbon Oxides by Uranium(III) Mixed-Sandwich Complexes Incorporating Heteroatoms

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Low-valent uranium complexes have shown remarkable reactivity with small molecules over the last decade, often yielding unexpected or otherwise inaccessible fragments under mild reaction conditions. The mixed-sandwich motif has featured prominently in this field, with reactions including the reductive oligomerisation of carbon monoxide, reductive disproportionation of carbon dioxide and hydrogenation of carbon monoxide to methoxide.

Current research has focused on altering the electronic properties of these uranium complexes by substituting the cyclopentadienyl ligand with a heterocyclic analogue (EC₄Me₄, E = N, P, As). Reactivity of these complexes with carbon monoxide gives rise to cleavage of the C≡O bond to give a uranium oxo species, and incorporation of the carbon atom into the heterocyclic ligand (Figure 1). Carbon dioxide activation has also been investigated and further illustrates the non-innocent behaviour of the heterocyclic ligand with formation of a carbamate and phosphacarbonate complex when E = N and P respectively.

![Figure 1 Reactivity of heteroatom-containing uranium(III) mixed-sandwich complexes with carbon monoxide](image)


A New Dual Channel Imaging Probe

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Dual modal imaging probes are widely used for their high capability to detect biologically and environmentally important ions and/or molecules. Furthermore they can be used for bioimaging analysis in living cells.\(^1\) Therefore the development of sophisticated reporter probes for in vivo imaging of anatomy and physiology has become a very active field of research.\(^2\)

Herein we report the synthesis and properties of a novel dual channel imaging probe.

References

A new family of imidazolin-2-iminato uranium complexes was synthesized using the homoleptic U(NMeEt)_4 and the neutral superbasic imidazolin-2-imines (Im_R^2NH). The complexes [U(NIm^Bu)_4] (1), [U(NIm^Mes)_3(NMeEt)] (2) and [U(NIm^Dipp)_2(NMeEt)_2] (3) were obtained selectively, depending on the steric demand of the substituents in the 1,3-position of the imidazole heterocycles. Surprisingly, the number of imidazolin-2-iminato ligands could not varied by adjusting the reactions conditions, or changing the stoichiometry of the reaction conditions, suggesting a thermodynamic control of the reaction.

The uranium complex [U(NIm^Dipp)_2(NMeEt)_2] showed an extraordinary high activity in the ROP of ε-caprolactone reaching a TOF of $7 \cdot 10^6$ g(PCL)·mol(3)^{-1}·h^{-1} even at room temperature. The synthetic approach and the mechanistic insights will be presented.
Intramolecular Hydroamination of Aminoalkenes Promoted by Rare-Earth Metal Amides

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Organorare-earth metal complexes display highly efficient catalysts for the intramolecular hydroamination/cyclization (IHC) of various C-C unsaturated compounds such as alkenes, alkynes, allenes, and dienes. Current research in this field puts main emphasis on ancillary ligand design for enantioselective IHC and the development of intermolecular variants. Although the catalytic activity of ancillary ligand-free rare-earth metal silylamide complexes has been reported several times, the effect of the type of amido ligand on a given IHC reaction has not yet been addressed.  
Herein we present the synthesis and solid-state structures of alkylamide complexes. Furthermore, the catalytic activity of alkylamide complexes is investigated for the IHC of selected aminoalkenes and compared with the performance of several silylamide complexes.

Kinetics of lanthanide complexation with DOTA-like ligands: effect of chelating pendant arms

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Many lanthanide radioisotopes are used as contrast agents in medical imaging techniques. Prior to application, 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.

To increase the complexation rate, we have synthesized DOTA-analogues with pendant arms bearing weakly chelating groups. We have evaluated complexation of lanthanides with respect to potential application as metal isotope carrier. In comparison with DOTA, the studied ligands show increased as well as decreased complexation rate. 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.

![Chemical structures of DOTA, DOTAM, DO3A-PIDA, DO3A-PBP](image-url)
Reduction and Oxidation Reactions of a Uranium(III) Monoarene Complex

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In uranium arene complexes, covalent δ bonding presents an opportunity to stabilize low formal oxidation states. Chemical reduction of [(Ad,MeArO)₃mesU] reveals the solid-state structure of a formal uranium(II) arene complex in crystals of [K(2.2.2-crypt)][(Ad,MeArO)₃mesU]. Room temperature reduction of [(Ad,MeArO)₃mesU] without a cryptand leads to hydride transfer from the doubly benzylic positions of the aryloxide ligand arms to either the uranium center - forming an anionic uranium (IV) hydride - or to the arene with the concomitant formation of a uranium (IV) complex. The choice of reducing agent and supporting ligand governs the preferred coordination geometry and hydride transfer site. Oxidation of [(Ad,MeArO)₃mesU] provides the isostructural uranium (IV) monohalide or uranium (V) monooxo complexes of the type: [(Ad,MeArO)₃mesU(X)(thf)] (where X = F, Cl, Br, I or O). If time and space allow, the electronic structure and reactivity of [(Ad,MeArO)₃mesU]¹⁻ will be presented.
Luminescent Gold Nanoparticles based on coating with Lanthanide Complexes

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Nanoparticles offer a unique opportunity to incorporate multiple molecular-scale lumiphores into a single nanoscale architecture for signal detection without engaging in lengthy synthetic procedures for the incorporation of multiple labels. Nanoprobes are also ideal as spatially localised cellular probes in luminescence imaging. Indeed, gold nanoparticles and quantum dots have been used for a plethora of biochemical and therapeutic applications. We have employed gold nanoparticles as a scaffold for luminescent metal complexes, so that the nanoprobes bear the distinct optical signature of the luminescent agent, independent of the properties of the particle. Such designed probes offer multimodal detection, taking advantage of gold’s high electron density without the blinking effect observed in quantum dots.

The preparation and properties of gold nanoparticles coated with lanthanide complexes (Figure 1) will be presented.

The photophysical properties of the nanoparticles are examined by steady state and time resolved luminescence spectroscopy. The effect of the distance of the lanthanide probe from the surface of the nanoparticle will be discussed.

Oxo-Exchange of Uranyl, Neptunyl and Plutonyl with Water and Methanol in the Gas Phase

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Activation of the strong An-Oyl bonds in actinyls is a challenge in synthetic actinide chemistry. A special case of Oyl activation is oxo-exchange with an O-atom donor. Oxo-exchange with water in solution is well established but the exchange mechanisms are unknown. Gas-phase actinyl oxo-exchange is a means to probe these processes in detail for simple systems, which are amenable to computational modeling.

In an initial report on this topic, the comparative exchange rates of bare UO$_2^+$, NpO$_2^+$ and PuO$_2^+$ ions with H$_2^{18}$O in the gas phase, studied by QIT/MS, were described and rationalized by computed (DFT) potential energy profiles (PEPs) [1]. In the present work, we used FTICR/MS to extend the experimental measurements to UO$_2^{2+}$, for a direct comparison with UO$_2^+$. Oxo-exchange with CH$_3^{18}$OH was also examined for comparison with the results for H$_2^{18}$O. We also report here the first quantitative values for the gas-phase oxo-exchange rate constants. PEPs computed by DFT were obtained for all of the studied oxo-exchange processes.

The experimental results indicate faster exchange of UO$_2^{2+}$ versus UO$_2^+$ (by at least 100 times) and faster exchange with methanol versus water; the faster exchange of UO$_2^+$ versus PuO$_2^+$ was quantified. Computed PEPs revealed similar mechanisms and were in accord with the observed kinetics, validating the utility of DFT to model these exchange processes. The experimental result and DFT prediction that oxo-exchange should be decreasingly efficient from UO$_2^+$ to PuO$_2^+$ can be taken to indicate greater covalency of the actinyl bonds upon proceeding across the actinyl series. Bonding analysis of the actinyl complexes is not fully conclusive but does provide indications of increasing covalency between uranyl and plutonyl.


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Formation and Competitive Dissociation of Uranyl-Amino Acid Complexes in the Gas Phase

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Actinides can interact with biomolecules and compete for the biological sites of essential metallic ions, exerting adverse effects on and altering the functions of enzymes, proteins or nucleic acids. The molecular mechanisms of biological action of actinides are not well understood, even for the most common case of uranium [1]. Gas-phase studies based on quadrupole ion trap mass spectrometry (QIT/MS) can provide information about the coordination of amino acids to metals and help to illuminate their interactions with protein binding sites. As the uranyl cation is the predominant form in vivo and in natural environments, studies of the competitive coordination of amino acids with UO$_2^{2+}$ in the gas phase are in progress in our group.

The following types of uranyl complexes with neutral and deprotonated α-amino acids, with different side chain functional groups (aspartic acid, histidine and cysteine), were produced by electrospray ionization of solutions of uranyl(VI) and mixtures of two amino acids in a 1:1 ratio: [UO$_2$(aa$^1$)$_2$(aa$^2$-$H$)]$^+$ or [UO$_2$(aa$^1$)(aa$^1$-$H$)(aa$^2$)]$^+$, [UO$_2$X(aa$^1$-$H$)(aa$^2$-$H$)], and [UO$_2$(aa$^1$-$H$)$_2$(aa$^2$-$H$)]$^-$ (X = Cl$^-$, NO$_3^-$).

Collision induction dissociation (CID) of the mixed-ligand species [UO$_2$(aa$^1$)$_2$(aa$^2$-$H$)]$^+$ or [UO$_2$(aa$^1$)(aa$^1$-$H$)(aa$^2$)]$^+$ primarily showed loss of a neutral aa (e.g., Fig. 1), followed by reaction with the background water in the QIT for some of the products. In the positive mode, competitive CID and hydrolysis seem to indicate that the strength of the (neutral aa)-UO$_2^{2+}$ interaction follows the order His>Asp>Cys; this is the same trend as the gas basicity of these amino acids.

In the negative mode, CID of [UO$_2$X(aa$^1$-$H$)(aa$^2$-$H$)]$^-$ complexes resulted mostly in loss of HX. In CID of the [UO$_2$(aa$^1$-$H$)$_2$(aa$^2$-$H$)]$^-$ species, preferential loss of the neutral amino acid was observed in the order His~Cys>Asp (e.g., Fig. 1), indicating particularly strong coordination of doubly-deprotonated Asp to UO$_2^{2+}$.

**Figure 1:** CID mass spectra of mixed Asp-His-UO$_2^{2+}$ complexes produced by ESI-QITMS


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Two-electron Versus One-electron Redox Reactions at U(III) centres

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Complexes of low-valent f-elements and of uranium in particular have been identified as excellent candidates for small molecule activation. Siloxides can be used to isolate stable U(III) complexes which act as two-electron reducing agents in the reaction with a variety of small molecules such as organic and inorganic azides.[1], [2] Siloxide ligands provide a versatile tool to modulate the sterical and electronic environment of low-valent uranium which allows the tuning of the metal reactivity leading to unusual compounds. Recent redox chemistry of U(III) complexes with azides and chalcogenides[3] carried out in our laboratory will be presented together with the structure and properties of original compounds.

**Bigger Than "Big N", Simple Silylamides and Coordinatively Unsaturated Thorium**

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The organometallic chemistry of uranium (III) has taken off in recent years, while the corresponding work has not often been successful for thorium (III). There are several explanations for this; Th(III) is less stable than and is more difficult to access than U(III).\(^1\) Th(III) starting materials are not readily accessible, whereas U(III) materials are easily made.\(^2\) Uranium research has historically been necessary due to the civil and military drive for nuclear power, while thorium is more of an afterthought currently.

U(III) organometallic complexes have been shown to activate normally sparingly reactive small molecules such as \(\text{N}_2\), \(\text{CO}_2\) and \(\text{CO}_3\); this gives encouragement to the idea that Th(III) could should very interesting fundamental chemistry if it can be isolated. The Th(IV)/Th(III) couple has a standard reduction potential of \(E^\circ\) –3.7 V, which is far greater than the U(IV)/U(III) couple of \(E^\circ\) –0.6 V.\(^1\)

To date there have been few studies involving the fundamental chemistry of coordinatively unsaturated Th, and less for "sub-valent" Th. Those that have been synthesised show reactivity toward \(\text{CO}_2\).\(^4\)

Simple silylamide ligands find a wide range of usage through all parts of chemistry, such as lithiation agents for the organic chemist to handy salt-metathesis activated ligands for the inorganic chemist. The simple design, which allows for fine-tuning of the steric bulk is attractive and allows for a wide range of scope. Seminal work on such ligands in 1974 shows the remarkable stability such ligands can offer metals, including Th.\(^5\)

We intend to prepare a wide range of Th(III) complexes and probe their reactivity profile with a range of substrates, eg. CO. Renewed calls to utilise Th as a nuclear fuel in developing nations now makes a fundamental understanding of bonding regimes for this element crucial.\(^6\)

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Synthesis, Stereocontrol and Structural Studies of Strongly Luminescent Lanthanide Complexes

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The chirality of biological systems can be probed using bright, enantiopure lanthanide complexes with the aid of circularly polarised luminescence\(^1\) (the emission analogue of circular dichroism) and emission spectroscopy. Such complexes can be synthesised through the incorporation of a remote chiral centre within the ligand which can preferentially stabilise a particular stereoisomer giving a complex with well defined helicity.\(^2\) Any change in complex helicity on binding to another chiral molecule can be observed using CPL.\(^3\)

A series of chiral lanthanide complexes, \([\text{LnL}^1]^{3+}\), has been synthesized. Each complex is based on an amide substituted 1,4,7-triazacyclononane system derived from either \(R\)-(+) or \(S\)-(-) \(\alpha\)-methylbenzyl amine. The stereochemistry of the amide moiety controls the helicity of the lanthanide complex, and one major diastereoisomer is formed for each lanthanide metal (varying from 9:1 to 4:1 from Ce to Yb). The absolute stereochemistry of the major diastereoisomer was determined by X-ray crystallography (\(S\)-\(\Delta\)-\(\lambda\lambda\lambda\) and \(R\)-\(\Lambda\)-\(\delta\delta\delta\)). A set of four analogous europium complexes, \(S\)-[\text{EuL}^{2a-d}]^{3+}\), containing \text{para}-substituted pyridinyl-aryl groups has been synthesised, existing as one major isomer in solution (15:1). The incorporation of aryl-alkynyl moieties into the ligand system enhances the brightness of the complexes, aiding sensitised emission, paving the way for applications in anion and protein sensing using CPL and emission spectroscopy.\(^5\)

Redox Reactivity in Organolanthanides

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The synthesis of new divalent lanthanide complexes is motivated by their high reactivity that is used in organic chemistry as well as in the popular small molecule activation area.1,2 Since the last two decades, the chemistry of these molecules have dramatically increased because of the easy access to the halide form of several divalent lanthanide and because the synthetic organometallic chemists have managed to increase their overall stability by suiting them with the right ligands.3 It is now clear that the sterics play a big role in the stability and reactivity of these complexes4 but the contribution of the electronics of the ligands should not be underestimated.5,6 In this context, phospholide ligands are very interesting because their steric modulation is easy and they are known to lead to stable divalent complexes.3 We have been engaged in the synthesis of new molecules in order to study in dept their electronic structure and have recently found very interesting redox reactivity with a complex of thulium bearing bulky phospholide ligands and bipyridine (scheme).

The synthesis, characterization of this complex will be presented and discussed as well as its very intriguing reactivity.

Scheme. Thulium complex bearing phospholide ligands and bipyridine

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Eu(III)-coated Si solar cells with improved quantum efficiencies

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The efficiency of traditional Si solar cells is limited by the large energy mismatch between the spectrum of solar radiation and the spectral response of crystalline silicon (c-Si) wafer. Their efficiency could be significantly increased by converting the high-energy photons (in the region of 300 to 400 nm) to lower energies were the efficiency of the semiconducting materials is optimal (above 500 nm).1,2 This process is often referred to as down-shifting (Figure 1).

Lanthanide complexes appended with strongly absorbing antennae are efficient energy converters through down-shifting, providing they display a high quantum yield. Here we report the properties of solar cells spin-coated with a Eu(III)-doped polymer film. The down-shifting of the protons in the 200 - 400 nm region is clearly observed and accounts for a significant improvement of the external and internal quantum efficiencies.

Figure 1: Non-absorbable UV-photons are modified through down-shifting, enhancing the solar cell efficiency.

The Synthesis of a Formal High Oxidation State Inverse-Uranium Sandwich Complex and Its Reactivity

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Complexes containing metal-metal bonds can display novel bonding and reactivity and advances in this area have resulted in major advances in the development of our understanding of chemical structure and bonding. Metal-metal bonds containing p-block and d-block elements are legion and well understood. However, metal-metal bonds involving f-block elements, specifically uranium, are rare. Therefore, there is a desire to explore uranium-metal bonding not only to improve our understanding of the chemical bonding of actinides but also to explore the intrinsic reactivity of such bonds. Despite the abundance of f-block–cyclopentadienyl, arene, cycloheptatrienyl and cyclo-octatetraenide complexes, cyclobutadienyl derivatives are unknown in spite of their prevalence in the d-block.

In this poster we will present the reactivity of a uranium(V)-inverted sandwich 10π-toluene tetra anion complex\(^1\) (1) towards the synthesis of metal-metal bonds\(^3\) (2) via a novel methodology and also the reductive [2+2]-cycloaddition reaction of diphenylacetylene with the same arene complex resulting in the isolation of an inverted sandwich cyclobutadienyl uranium (IV) complex\(^2\) (3).

Near-infrared Emitting Lanthanide Metal-Organic Frameworks for Live Cell Imaging

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Luminescence is a detection technique that possess important advantages for biologic imaging: high sensitivity, versatility and low costs of instrumentation. A common characteristic of biologic analytes is their presence in small quantities among complex matrices such as blood, cells, tissue and organs. These matrices emit significant background fluorescence (autofluorescence), limiting detection sensitivity. The luminescence of lanthanide cations has several complementary advantages over the fluorescence of organic fluorophores and semiconductor nanocrystals, such as sharp emission bands for spectral discrimination from background emission, long luminescence lifetimes for temporal discrimination and strong resistance to photobleaching. In addition, several lanthanides emit near-infrared (NIR) photons that allows for improved detection sensitivity due to the absence of native NIR luminescence from tissues and cells (autofluorescence).

A main requirement to generate lanthanide emission is to sensitize them with an appropriate chromophore (“antenna effect”). An innovative concept for such sensitization of NIR-emitting lanthanides is proposed herein; the current limitation of low quantum yields experienced by most mononuclear lanthanide complexes is compensated for by using a large number of lanthanide cations and by maximizing the absorption of each discrete molecule, thereby increasing the number of emitted photons per unit of volume and the overall sensitivity of the measurement. To apply this concept, we have created several metal-organic frameworks and succeeded in generating highly emissive NIR MOF reporters. We will discuss their synthesis, structures, photophysical properties and their applications for biological imaging in living cells with NIR microscopy.

This work is the first report of the use of NIR photons arising from lanthanide cations for cellular imaging using single photon excitation.

Theoretical comparison of bonding in two uranium complexes: $[\text{UO}_2\text{BTP}_2]^2+$ and $\text{UO}_2[22]\text{isoamethyrin}(1.0.1.0.0.0)$

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The presence of long-lived and highly radiotoxic actinides in spent nuclear fuel presents an ongoing challenge for the nuclear power industry. A deeper understanding of the nature of bonding interactions between actinides and soft N-donor ligands is vital, and may help with the design of ligands with improved selectivity for specific elements.

Here, the structures of $[\text{UO}_2\text{BTP}_2]^2+$ and $\text{UO}_2[22]\text{isoamethyrin}(1.0.1.0.0.0)$ have been optimised at the density functional theoretical level using version 6.4 of the Turbomole code with both the PBE and B3LYP exchange correlation functionals. Optimisations were performed in both the gas and aqueous phases, with solvent effects accounted for by using COSMO continuum solvent model. Calculated structures were compared to experimental data, and molecular binding energies calculated in order to assess stability. The quantum theory of atoms in molecules (QTAIM) was applied in order to compare various topological quantities at the U-N bond critical points. Such quantities may be considered signifiers of bond strength.

QTAIM analysis reveals that, although there is little covalent character in the U-N bonds, electron sharing between the U and N centres is present in both complexes, and is of comparable magnitude, suggesting that isoamethyrin and related ligands may be of use when employed in situation where selectivity is required.

Further work will involve investigations of $\text{NpO}_2^{2+/+}$ and $\text{PuO}_2^{2+/+}$ complexes of isoamethyrin and other expanded porphyrin ligands.
Pyridine tetrazolate based lanthanide complexes: versatility and high luminescence in just one coordination motif

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Lanthanides are a series of elements with unique physical properties such as narrow line luminescence emission ranging from UV-to NIR. Their incorporation in molecular complexes allows the luminescence sensitization at low energy. The choice of the ligand is fundamental for the sensitization of the metal center throughout the chromophoric properties of the organic framework (antenna effect). Lanthanides complexes emitting in the visible range are particularly attractive for application in materials science, and biomedical imaging. Of primary importance is the ligand tuning process to greatly enhance the properties, robustness, and practical applications of the emitting system.

Tetrazolate are groups with affinity for lanthanide ions similar to the ubiquitous carboxylate group (tetrazole is its bioisostere). They can act as chromophores with significant absorption in the UV range with good sensitization of lanthanide ions in pyridine tetrazolate based system.

Here, I will present our recent results on highly luminescent europium and terbium complexes based on differently substituted pyridine tetrazolate scaffolds. The synthesis, physical and chemical characterization and the emissive properties of the complexes will be described. We will also present a versatile route to the easy modification of the ligand framework leading to optimized luminescence and solubility in various media.


Lanthanide-transition metal bonded complexes

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Lanthanide-transition metal bonding (Ln-TM) represents one of the frontier fields in inorganic chemistry. The study of these interactions has furthered our understanding of both metal-metal bonding and the chemistry of the lanthanides in general.[1]

Recently, in our group, a methodology for the synthesis of cationic derivatives of some lanthanides along with the appropriate nucleophilic reagents, yielded the first reported Ln-B bond.[2] In addition, the formation of Yb-Fe bonds from the Yb/Hg amalgam reduction of [CpFe(CO)2]2 (Fp2) was achieved.[3] Herein we present our findings from the reaction of related lanthanide cationic derivatives bearing amidinate moieties with the transition metal anionic sources KFp, NaRp(THF) (Rp = CpRu(CO)2) and [K{Co(CO)3PCy3}(THF)2]x to form complexes of the type [Ln{(Me3SiCH2)C(NR)2}2M'] (R = alkyl, M' = Fp, Rp or Co(CO)3PCy3) (Fig. 1) via salt metathesis. The structural and spectroscopic properties for these complexes, as well as their reactivity are described. Compared to TM-TM bonding, little is known about the nature of the Ln-TM interactions, and only a handful of reports on this topic have been made. Current studies are underway to take advantage of the reactivity of these complexes for the activation of small molecules.

Lanthanide(III) Complexes of Rhodamine-DO3A Conjugates as Agents for Dual-Modal Imaging

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The combination of magnetic resonance imaging (MRI) and optical imaging offers synergistic advantages over either modality alone by bringing together the high special resolution and good soft tissue contrast of MRI with the high sensitivity of optical imaging. It is becoming increasingly important to detect the early signs of cancer and by designing a dual-modal MRI/optical probe that can respond to characteristic traits of tumour cells, improved diagnostic accuracy can be achieved.

Two novel dual-modal MRI/optical probes based on a rhodamine-DO3A conjugate have been prepared. The bis(aqua)gadolinium(III) complex Gd.L1 and mono(aqua)gadolinium(III) complex Gd.L2 behave as dual-modal imaging probes ($r_1 = 8.5$ and $3.8 \text{ mM}^{-1}\text{s}^{-1}$, respectively; $\lambda_{\text{ex}} = 560 \text{ nm}$ and $\lambda_{\text{em}} = 580 \text{ nm}$ for both complexes). The rhodamine fragment is pH sensitive and upon lowering of pH an increase in fluorescence intensity is observed.

Confocal imaging experiments were carried out to establish the localisation of Gd.L2 in HEK293 cells and primary mouse islet cells. Colocalisation with MitoTracker Green demonstrated Gd.L2’s ability to distinguish between tumour and healthy cells, with compartmentalisation believed to be in the mitochondria. Gd.L2 was also evaluated as an MRI probe for imaging of tumours in BALB/c nude mice bearing M21 xenografts. A 36.5% decrease in $T_1$ within the tumour was observed 30 min post injection, showing that Gd.L2 is preferentially taken up in the tumour. Gd.L2 is the first small-molecule MRI/optical dual-modal imaging agent to display off-on pH switch upon its preferential uptake within the more acidic microenvironment of tumour cells.

Forcing trigonal C$_3$-symmetric uranium complexes into eight-coordinate tetragonal ligand environments

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Trivalent tacn-anchored tris(aryloxide) uranium complexes [(R,R'ArO)$_3$tacn]U$^{III}$ (R = Ad, tBu; R' = tBu) react with 2,2'-bipyridine to form eight-coordinate uranium(IV) complexes. Investigations of the Electronic properties (EPR, UV/Vis) and molecular structures of the compounds confirm the +IV oxidation state of the metal center and the presence of a 2,2'-bipyridine radical.$^1$

Further reaction of the [(R,R'ArO)$_3$tacn]U$^{IV}$(2,2'-bipy) compounds with KC$_8$ and a cryptand or crown-ether lead to reduction of the 2,2'-bipyridine radical to an ylidene moiety.$^2$ Because uranium in the oxidation state +IV is rather unreactive, the bipyridine moiety gets reduced by KC$_8$ and the electron is stored in the delocalized π-system.

Additionally, we report the synthesis and electronic properties of uranium difluoride coordination compounds supported by the tacn tris(aryloxide) ligand system, which results in a cis-conformation of the fluoride atoms. Reaction of one equivalent XeF$_2$ with [(Ad,tBuArO)$_3$tacn]U$^{III}$ produces Xenon and an uranium(V) difluoride complex, which can be further oxidized by silver salts to an uranium(VI) compound.

Exploring photophysics with lanthanide containing self-assemblies

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Self-assembly with lanthanide complexes has been extensively employed in assays\textsuperscript{1}, in the preparation of coordination polymers\textsuperscript{2} and metal organic frameworks.\textsuperscript{3}

In this work, we build upon the observation that binuclear lanthanide complexes bind strongly to bridging dianions,\textsuperscript{4-6} and exploit this interaction in the study of self-assembled systems that contain bodipy (BDP) or rhenium chromophores. These represent an ideal tool for the study of photophysics. In the case of bodipy (BDP) chromophores, we can exploit the large singlet/triplet energy gaps to selectively observe either bodipy (BDP) or lanthanide emission. By contrast rhenium chromophores can be used to sensitise lanthanide emission in self-assembled systems.

2. Ward, M. D., Coordination Chemistry Reviews 2007, 251 (13-14), 1663-1677.
The trityl radical as excellent leaving group towards the synthesis of a uranium-nitride complex

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Uranium complexes with a terminal nitride bond are a fundamental target for the study of f-orbital participation in metal-ligand multiple bonding. But to date only one isolable example is known.1 A major difficulty in synthesizing a terminal nitride uranium complex is the insertion of the reactive nitride ligand into the supporting ligand system. With the new neopentyl-derivatized triazacyclononane-anchored ligand (nP,MeArO)_3tacn⁻ the stabilization of terminal oxo uranium complexes in various oxidation states has already been achieved.2,3,4 In order to isolate a terminal nitride uranium complex, the reaction of the uranium(III) complex [((nP,MeArO)_3tacn)U^{III}] with trityl azide was conducted. The resulting uranium(V) imido complex [((nP,MeArO)_3tacn)U^{V}(N-trityl)] can either be oxidized to the corresponding uranium(VI) imido complex [[((nP,MeArO)_3tacn)U^{VI}(N-trityl)][Barf]] or reduced to the corresponding uranium(IV) imido complex K[((nP,MeArO)_3tacn)U^{IV}(N-trityl)]. These complexes exhibit only minor differences from one another in the core structure. The addition of 2.2.2-cryptand to the uranium(IV) imido complex leads to cleavage of the imido ligand and formation of an unexpected trityl anion with a cryptanded potassium counterion and an as of yet unknown uranium complex.

Literature:

Divalent Samarium Complex Supported by a Tetraazamacrocycle Bis(phenolate) Ligand: Synthesis and Reactivity Studies

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Over the past few decades, there has been a growing interest in the search for alternative ligand sets which are able to satisfy the coordination requirements of the large lanthanide cations. In this context, we have recently demonstrated that a new bulky ligand derived from a tetraazamacrocycle, bis(phenolate) cyclam, is adequate for the stabilization of solvent-free yttrium(III) and lanthanide(III) complexes of general formula [Ln{ArBu₂O)₂Me₂cyclam}Cl] (Ln= Y, La, Sm, Yb).

As we are interested in redox events associated with small molecule or unsaturated substrates activation, we expect that the dianionic hexadentate ligand [(ArBu₂O)₂Me₂cyclam]²⁻ (Figure 1-a) will allow to stabilize divalent lanthanide metals.

In fact, the new divalent samarium complex [Sm{(ArBu₂O)₂Me₂cyclam}] has been synthesized by salt metathesis reaction between SmI₂(THF)₂ and the potassium salt of the ligand. The Sm(II) complex was characterized by elemental analysis, X-ray diffraction analysis and ¹H NMR. The XRD analysis revealed the formation of a mononuclear Sm(II) complex (Figure 1-b), with the macrocyclic bis(phenolate) acting as a hexadentate chelator. Here we report the synthesis, structural analysis and solution behavior of this new Sm(II) complex.

Figure 1

The reductive chemistry of the Sm(II) bis(phenolate) cyclam is currently in progress and the results will be also reported.


Acknowledgements: The authors are grateful to Fundação para a Ciência e a Tecnologia for funding (research project PTDC/QUI-QUI/109846/2009 and “Ciência 2008” Programme).
Commonly used non-invasive diagnostic method – magnetic resonance imaging (MRI) – is very useful in visualizations of anatomic and functional abnormalities in a human body. MRI brings opportunity to focus on some parts of scanned area but acquired MRI scan does not contain as much information as it could. Gd$^{3+}$, the lanthanide cation with maximum spin, possesses a high ability to increase the contrast of acquired images as it influences visualization of water molecules. Thus, this ion is the core of the most MRI contrast agents used in the medical practice. The presence of CA’s molecules in the body should be as short as possible due to toxicity of the heavy metal, which can dissociate off. Therefore, the new MRI contrast agents are designed and synthesized to achieve better contrast and lower toxicity in vivo.

The most abundant protein in blood – human serum albumin (HSA) – contains two hydrophobic cavities capable of carrying hydrophobic groups, for example, dibenzylamino group as used in our new MRI contrast agent. Therefore, a molecular tumbling of CA’s molecules is reduced and the relaxivity value increases. However, such binding to HSA leads usually to longer persistence the in blood pool system, which potentially counts for a higher toxicity of the CA. It is not the case of our novel CA, as it can be relatively easily protonated in slightly acidic medium (kidney), which results in unbinding the molecule from albumin, and the excretion is fast (compared with MS-325\textsuperscript{[1]}).

Slow magnetic relaxation in tris(diphosphanylamido) and tetra(phosphanoamido) dysprosium complexes

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Lately the interest in molecular magnets incorporating rare-earth metal ions has been revived and 4f coordination compounds have been extensively investigated for their single-molecule magnet (SMM) and single-ion magnet (SIM) properties.[1]

We recently reported the synthesis of two homoleptic phosphanylamido dysprosium complexes [Li(THF)₄][(Ph₂PNPh)₄Dy] (1) and [Dy{N(PPh₂)₂}₃] (2).

Both compounds have a highly symmetric arrangement of the ligand which is only slightly broken in the solid state by steric and packing effects as a result of the weak coordination of the phosphorus atoms to the metal center. The magnetic properties of both compounds were examined and the occurrence of slow magnetic relaxation was observed. Although the Dy(III) centers in both compounds are not in the same coordination environment and have different geometries, the general behaviour of both compounds is quite similar. Therefore, the presence of slow magnetic relaxation processes is likely to be correlated to the individual ion anisotropy of the Dy(III) center.[2]


Luminescent Cell-Penetrating Pentadecanuclear Lanthanide Clusters


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Today a range of lanthanide hydroxy clusters exhibiting various nuclearities have been established, highlighting the ease of preparation and good yields.[1] Although these compounds combine advantages such as well-defined composition, stability and the fact that their luminescence is not as prone to quenching effects compared to mononuclear compounds, the photophysical properties of only very few lanthanide hydroxy clusters were investigated.[2]

We recently reported the synthesis and characterization of a novel pentadecanuclear lanthanide hydroxy cluster \[
\left\{\text{Ln}_{15}(\mu_3-\text{OH})_{20}(\text{PepCO}_2)_10(\text{DBM})_{10}\text{Cl}\}_{14}\right\} (\text{Ln} = \text{Eu} (1), \text{Tb} (2)) \]
featuring the first example with peptoids as supporting ligands:

The solid-state structures of 1 and 2 were established via single-crystal X-ray crystallography. ESI-MS experiments revealed the retention of the cluster core in solution. Although OH groups are present, compound 1 showed intense red fluorescence with 16(1)% absolute quantum yield, whereas the emission intensity and the quantum yield of 2 were significantly weaker. In vitro investigations on 1 and 2 with HeLa tumor cells revealed an accumulation of the cluster in the endosomal–lysosomal system, as confirmed by confocal microscopy in the TRLLM mode. The cytotoxicity of 1 and 2 toward the HeLa cells were moderate.[3]

Assembly of Large Tungstogermanates Containing 12 Lanthanide(III) Centers

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The synthetic combination of 4f ions and multi-lacunary polyoxometalate (POM) precursors is a powerful strategy to form unprecedented discrete supramolecular species with large sizes and intriguing structural diversity.

We present herein our recent work on the 12-Ln\textsuperscript{III}-containing tungstogermanates (Ln = Eu, Gd, Dy), which were synthesized under mild heating conditions in slightly acidic aqueous media. Their structures can be viewed as large assemblies of six dilacunary POM building blocks connected by twelve Ln(III) ions. Interestingly, two Ge\textsuperscript{IV} guest ions were also encapsulated in the Eu- and Gd-containing compounds.

Study on Uptake and Separation of Eu-152 and Am-241 by α-Zirconium Phosphates

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Inorganic materials, different α- and γ-zirconium phosphates, have been synthesized and tested on suitability for trivalent lanthanide and actinide separations. Closely similar to each other europium and americium were selected as model elements of the groups. Based on preliminary distribution coefficient studies in nitric acid of 0-3 molar range, most promising materials were selected for further column separation tests. Ultimate aim of the work is to achieve either individual or group separation for multiple trivalent elements in lanthanide-actinide range, preferably in plain nitric acid.

Worldwide on-going research on partitioning and transmutation (P&T) is an attempt to advance nuclear energy industry by multiple means. The research aims to maximize fission energy gain from bulk nuclear fuel while minimizing long term radiotoxicity of nuclear fuel waste. New partitioning methods are also essential in the development of closed fuel cycles. By the means of P&T, it is possible to recycle a fraction of used fuel, to shorten the time for fuel to cool down in temporary waste storages by addressing nuclides generating large amounts of heat and to lessen the radioactivity in nuclear waste final repositories.

This study aims to develop hydrochemical separation methods based on inorganic ion exchangers. Inorganic materials offer a superior radiation resistance over organic counterparts. Ideally inorganic resin could offer a separation of either specific nuclides or groups of nuclides straight from spent nuclear fuel dissolved in nitric acid resulting in a more straightforward method free of complex organic ligands/solvents. Alternate use would be the treatment of secondary waste streams formed in hydrochemical partitioning methods currently in use. The aims are to develop exchangers capable of separating actinides from lanthanides, modeled by close counterparts americium and europium. Main advances that will be presented include revised synthesis of the ion exchangers of interest – varying α- and γ-zirconium phosphates, further structural investigation and column separation experiments in nitric acid.

High distribution coefficient (Kd) values were obtained in surprisingly acidic conditions of pH 0 to 3 nitric acid. Different materials show most promising separation factors in pH range 1 to 1.5, always having higher Kd for europium and a lower one for americium, most promising being one of the synthesized α-zirconium phosphates. Column separation tests show great promise.

The research presented here is continuation to the work shown last year at EUFEN2.
Synthesis and Properties of a New Tb(III) Complex

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The use of lanthanide luminescent probes mainly based on Eu (III) and Tb(III) ions. These lanthanide probes have some advantages over the conventional organic fluorophores; e.g. re-absorption, large emission signal, short-emission lifetime, photobleaching. Furthermore, Ln (III) luminescent probes display large Stokes shift (>200 nm), narrow emission peaks (<10 nm full width at half-height), long-emission lifetime, relative insensitivity to photobleaching.

Herein the synthesis and properties of a new Tb (III) complex will be described.

References

Ship-in-A-Bottle Strategy to Fabricate a Rare-Earth Metal Containing Organic-Inorganic Hybrid Material

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Rare-earth metal containing organic-inorganic hybrid materials have attracted considerable attention due to their excellent optical properties such as very narrow emissions and long lifetimes. [1] Optically active components are usually introduced into inorganic silica matrices by traditional strategies such as impregnation, grafting, and co-condensation. Alternatively, the ship-in-a-bottle strategy features a powerful method to assembly small molecules in hollow materials [2] such as hollow siliceous spheres.

Herein, an in situ synthesized functional polymer, poly(4-vinylpyridine) (P4VP), was trapped into hollow mesoporous silica nanoparticles (MSNs) [3] by the ship-in-a-bottle strategy to afford hybrid material P4VP@MSN. The functional groups of the polymer can capture rare-earth metal ions such as terbium(III) or europium(III) to generate rare-earth metal-incorporated organic-inorganic hybrid fluorescent silica materials designated as Tb-P4VP@MSN. The 1,10-phenanthroline (Phen) donor ligand can strongly bind to the metal centers yielding to Phen-Tb-P4VP@MSN with enhanced fluorescent properties.

Figure 1. The proposed molecular structure of the entrapped terbium complex.

Lanthanide Complexes with Triaminoguanidine Ligands Exhibiting Slow Magnetic Relaxation

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Triaminoguanidine-based ligands \( \{\text{H}_3\text{L}^\text{R}\} \) open up the perspective to build \( \text{C}_3 \) symmetric 3d transition metal complexes and coordination polymers.\textsuperscript{1-4} The central N–N bridging unit mediates strong antiferromagnetic exchange interaction and, hence, spin frustrated systems are obtained for metal centers exhibiting odd electron spin. Such systems are promising candidates for quantum bits or quantum gates. Furthermore, 3d transition metal complexes, especially 3d–4f compounds, feature interesting magnetic properties.\textsuperscript{5}

With triaminoguanidine-based ligands lanthanide complexes are accessible. AC-SQUID measurements reveal slow relaxation of magnetization for the appropriate lanthanide complexes. By varying the substituent R at the salicylaldehyde moiety different relaxation behaviour can be observed.

Synthesis and Properties of Uranium Complexes Starting from bis-1,3-Diketo- and bis-Pyrazole-based ligands with 2,6-Pyridinyl-spacers

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In earlier work, we demonstrated that bis-1,3-diketo anions (L)\(^2^-\) act as excellent ligands for the complexation of different transition metals and hence enable the construction of supramolecular aggregates via metal-assisted self-assembly.\(^1\) In this context, we reported on the synthesis of the metallocoronate \([\{\text{Ca}(\text{Cu}_2\text{L}_2)\}(\text{OAc})_2]\) and the 1D-coordination polymer \([\{\{\text{Cs}_2\text{C}(\text{Cu}_2\text{L}_2)_{\text{Cs}}(\text{OAc})_2\text{Cs}(\text{OAc})_2\text{Cs}\}_n\}]\(^2\) Starting from enantiomerically pure ligands (L)\(^2^-\), chiral coronands [M\(_2\)L\(_2\)] and cubanes [Cu\(_4\)L\(_2\)(OMe)\(_4\)] could be isolated and completely characterized by different spectroscopic methods.\(^3\)

Encouraged by these results, we explored the potential of these ligands in the complexation of 5f-elements, in particular uranium. On the poster we will report on the synthesis and properties of the new, dinuclear uranium(IV) cryptate \([\{\text{Cl}(\text{U}_2(\text{LH}^\text{N})_4)\}\text{[FeCl}_4\text{]}_3\) (Figure 1). In addition, modification of the ligand system allowed for the synthesis of new U\(^{IV}\) complexes [U(R\(_2\)L)Cl\(_4\)] based on bis-pyrazole donor ligands. The detailed characterizations of [U(R\(_2\)L)Cl\(_4\)] will be presented, too.

Figure 1. Molecular structure of the metallocoronate \([\{\text{Cl}(\text{U}_2(\text{LH}^\text{N})_4)\}\]\(^3+\).

Activation of Elemental Chalcogenides at Reactive Uranium Centers

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We report the syntheses, electronic properties, and molecular structures of a series of polychalcogenido-bridged dinuclear uranium species. These complexes are supported by the sterically encumbering but highly flexible, single N-anchored tris(aryloxy) chelator \((^\text{Ad} \text{ArO})_3 \text{N}^-\).

Reaction of an appropriate uranium precursor, either the U(III) starting material, \([(^{\text{Ad} \text{ArO}})_3 \text{N}) \text{U}(\text{DME})]\), or the dinuclear mono-chalcogenido-bridged uranium (IV/IV) compounds \[{((^{\text{Ad} \text{ArO}})_3 \text{N}) \text{U}(\text{DME})}]_2(\mu-\text{E})\] (E = S, Se), with elemental sulfur or selenium, yields new complexes with a variety of bridging chalcogenide entities \(\mu-\text{E}_m^{n-}\) (E = S, m= 2, n = 1 or 2 and E = Se, m = 2, 4; n = 2).

Activation of the heavy chalcogens typically requires either a coordinatively-unsaturated, strongly-reducing metal complex or a compound with a metal–metal bond. Since uranium complexes in the +IV oxidation state, are generally considered rather unreactive, the observed reaction of the here employed uranium (IV)/(IV) species with elemental chalcogens is fairly remarkable.

**Trans-stereospecific polymerization of butadiene and random copolymerization with styrene using borohydrido rare earths / magnesium dialkyl catalysts (P)**

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The coordination polymerization of conjugated dienes is a topic of premier importance for numerous industrial applications requiring high performance rubber.\(^1\) Whereas polyisoprene has seen a renewing interest during the last decade, polybutadiene still reached the highest industrial development. With the aim to obtain mechanical behavior that can compete with Natural Rubber, researches on polybutadienes have been oriented through obtaining highly cis-stereoregular polymers, using Ziegler-type catalysts in mild temperature conditions based on transition metals,\(^1\)\(^a\),\(^2\) but the rare earths were also early recognized as major elements to provide efficient and stereospecific catalytic combinations.\(^1\)\(^b\) The trans-polymerisation of butadiene has been less explored since the pioneer disclosures of Natta.\(^3\) It mainly involves metals from columns 4 and 5, rhodium, iron and chromium based-catalysts, and the polymers display good hardness and abrasion resistance. Among them, some catalysts based on rare earths, which can be efficient in the absence of aluminum co-catalysts, are of interest regarding the environmental impact.\(^4\)

We describe here an efficient dual borohydrido Nd/Mg catalytic system for the highly trans-selective homo-polymerization of butadiene, and its co-polymerisation with styrene. Poly(trans-1,4-butadiene)-co-(styrene) could be obtained with up to 17 molar % of styrene units inserted.\(^5\)

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