Session 2

Keynotes lectures
Utilization of Redox-Active Ligands in the F-Block: Broadening Redox Chemistry in the Actinide Series

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Redox-active ligands have been demonstrated to mediate multi-electron chemistry on a variety of transition metals and main group elements, promoting useful bond forming and activation chemistry. Our group has been exploring such frameworks for the elements of the f-block, in hopes to extend this methodology to generate elusive targets and control redox properties. Herein, we present our latest findings on the unique electronic structures of actinide complexes with these ligands. These unusual species have interesting chemical properties, and their study gives insight into redox chemistry associated with typically redox-restricted systems. Our complete study combining characterization by spectroscopic and structural methods will be presented, as well as a discussion of the role of the redox-active ligands in the observed chemistry.
Moving Non-Aqueous Chemistry a Bit Deeper into the Periodic Table

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This lecture will focus on recent efforts in my group directed toward the synthesis of plutonium, americium, and californium organometallic and coordination complexes. The initial focus of the talk will be on demonstrating the utility of straightforward routes from simple, hydrated, transuranium starting materials all the way to highly air-sensitive complexes with a variety of ligands that include cyclopentadienyl derivatives, cyclooctatetraenyl compounds, crown ether and cryptand coordination complexes, and finally a few surprises with complexes containing ligands that were previously unused in actinide chemistry. A secondary goal of this talk will be the demonstration of similarities and differences between these complexes and those that contain either ostensibly isoelectronic lanthanides or lanthanides that possess similar ionic radii. The talk will conclude by pointing out the need to go back and reinvestigate the chemistry and properties of complexes that were reported in the early years of transuranium chemistry.
Lanthanide complexes with dual activity

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Harnessing the luminescence of lanthanide ions by sensitizing through coordinated ligands provides unique opportunities. These ligands can be functionalized to tailor the chemical and photophysical properties of the resulting complexes. We have used this approach to synthesize complexes that can be used as imaging agents for cancer cells.1 By extending the conjugation of the ligand we shifted the excitation wavelengths into the visible and simultaneously isolated complexes that can be used as molecular nanothermometers.2 In addition, we used carbazole-based ligands that enabled excitation of the resulting complexes in the biological window by a two-photon process. Finally, we used oligothiophene-based ligands to isolate complexes that luminesce and can generate singlet oxygen.

Figure 1. Temperature-dependent emission spectrum of K3[Tb(dipicCbz)3]. Inset shows the intensity of the 5D4 → 7F5 transition as a function of temperature.2

References

Hybrid materials from the f-block: restricted speciation and supramolecular assembly

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The synthesis of f-element bearing hybrid materials has seen increased attention of late, owing largely to the tremendous structural diversity and potential applications from spent nuclear fuel stewardship to solid-state lighting. Many materials may be considered as coordination polymers wherein multifunctional organic ‘linkers’ assemble inorganic building units into extended architectures. Hydrothermal synthesis is a common route to the formation of these materials and metal ion hydrolysis often contributes to structural diversity by producing oligomerized metal centers. Whereas this is a productive route to new materials, the inability to control the extent of hydrolysis, and consequently what species manifest themselves in the solid state, provides a challenge to producing targeted topologies.

We have developed an approach of ‘restricted speciation’ wherein hydrolysis is minimized through the use of complexing ligands in either high-halide media, or via chelating species such as terpyridine molecules. Molecular species are produced in solution with appropriate functionality (halogens, H-bond donors/acceptors) to participate in non-covalent interactions. One then assembles these lower dimensional species through supramolecular synthons (pi-stacking, halogen bonding etc.) to produce extended architectures. Advantages include a greater degree of predictability of structural motifs, along with the ability to impart systematic substitutions to explore structure property relationships. Presented will be an overview of our efforts in the [UO₂]²⁺, [NpO₂]²⁺ and [PuO₂]²⁺ systems.1-3

References

RARE-EARTH SUPRAMOLECULAR ASSEMBLY

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Coordination supramolecular containers have potential applications in sensing, biomimetic catalysis, stabilization of fleeting species, drug-delivery et al. By employing the metal-driven assembly strategy, numerous of metalloycles/cages constructed with transition metals have been reported. While rare-earth ions have a lot of optical, electromagnetic and catalytic properties to offer to the aesthetically appealing 3D supramolecular edifices, directed-assembly with rare-earth metals is difficult due to their unpredictable and labile coordination numbers/geometries. We are interested in the rare-earth supramolecular chemistry, in particular the designed assembly and fine-tuned photophysical properties of multinuclear lanthanide-organic polyhedral (LOPs) complexes. Recently, precise synthesis of LOPs with different molecular composition and geometry has been accomplished in our group.[1-2] Photophysical including chiroptical properties of the LOPs have been investigated, with proof-of-concept applications such as high selective and efficient sensing toward biological relevant molecules/ions,[3-4] ion separation,[5] single-molecular ratiometric luminescent thermometers,[6] photosensitizers et al. We envisage these LOPs will find potential applications in the biomedical and material fields.

![Figure 1. Rare-earth supramolecular chemistry: Structure and function.](image)

References


Session 2

Invited lectures
Trivalent Lanthanide and Actinide Thiocyanate Complexes

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The coordination chemistry of the trivalent lanthanides and actinide elements are often considered to be quite similar owing to their similar +3 charges and ionic radii. However, in the study by Diamond et al., disparate chemical behaviors of the trivalent lanthanide and actinide ions were observed on chloride based ion-exchange resins and attributed to increased participation and hybridization of the actinide 5f orbitals in their chemistry in contrast to the localized 4f orbitals in the lanthanides.1 Though still poorly understood, this behavior has been exploited in the development of separations process for trivalent lanthanides and actinides both in chloride (TRAMEX) and the pseudohalide thiocyanate solutions, where preferential extraction of trivalent actinides over lanthanides is observed.2,3

In order to more fully understand the fundamental chemical differences between trivalent lanthanide and actinide thiocyanate complexes and the preferential separation of actinides versus lanthanides we have undertaken a comparative study of trivalent lanthanide and actinide thiocyanate chemistries building on our earlier studies with the tetravalent actinide thiocyanate complexes and the hexavalent actinides.4,5 We have been successful in synthesizing an isostructural series of lanthanide and actinide thiocyanate complexes (La-Lu (ex Pm), Am(III) and Cm(III)) for study using both spectroscopic and structural techniques. Structural studies reveal a change in the space group symmetry across the lanthanides occurring near Eu while the Am and Cm compounds show phase behaviours consistent with the lighter lanthanides. We have conducted studies exploiting Raman spectroscopy and UV-Vis absorption spectroscopy aimed at quantifying the effect of metal coordination on the thiocyanate electronic structure in both the lanthanides and actinides. These Raman studies have revealed largely ionic interactions between both lanthanide and actinide thiocyanate complexes. Additional studies exploiting solution based X-ray absorption spectroscopy will also be presented.

This work was performed at Argonne National Laboratory operated by UChicagoArgonne LLC for the United States Department of Energy, Office of Science, Office of Basic Energy Sciences, Heavy Elements Program under contract number DE-AC02-06CH11357.

References

The Effect of Iron Binding on Pentavalent Uranyl(V) Stability

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Pentavalent uranyl has been proposed as an important transient intermediate in the biological or abiotic mineral-mediated transformation of soluble uranyl(VI) compounds into the insoluble uranium(IV) dioxide (UO₂), a very important process for ground-water remediation.

Recent studies indicate that U(V) species are incorporated in iron oxo-hydroxide minerals such as goethite and magnetite and the presence of iron as second nearest neighbour has been identified.¹

Several heteropolymetallic uranyl(V) complexes stable in organic solution have been isolated in recent years 2,3, with only few examples of a $\text{UO}_2^{2+}$-$\text{Fe}^{2+}$ interaction 4,5. However, the role of iron binding to uranyl(V) species in their stabilization remains ambiguous in spite of its importance for the correct speciation of uranium in the environment.

Here we report the synthesis of stable complexes of pentavalent uranyl supported by the tripodal Schiff base ligand $\text{H₃trensal}$ (2,2',2″-tris(salicylideneimino)triethylamine). The reactivity, chemical as well as redox stability of potassium complex $[\text{UO}_2(\text{trensal})\text{K}]\text{K}$ and the iron(II) heterometallic uranyl(V) complexes $[\text{UO}_2(\text{trensal})\text{Fe}(\text{py})_3]$; $[\text{UO}_2(\text{trensal})\text{Fe}(\text{py})_3\text{U}(\text{trensal})]\text{I}$; $[\text{UO}_2(\text{trensal})\text{Fe}(\text{py})_3\text{U}(\text{trensal})\text{Fe}(\text{py})_3]\text{I}_2$ was investigated.

This study demonstrated that Fe²⁺ stabilizes the U(V) toward proton induced disproportionation and redox reactions. Moreover, cation-cation interaction between the uranyl(V) oxygen and the Fe²⁺ is essential for the stabilization of U(V) while the presence of a Fe(II) bound through the ligand has no significant effect on the redox properties of the uranyl(V).

Pyrazolates Advance Tetravalent Cerium Chemistry

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In the current flurry of/hype about Ce(IV) chemistry,[1] the understanding of the Ce(III)/Ce(IV) redox couple is of peak interest. In this regard, pyrazolates have excelled at providing a platform to not only investigate this redox couple,[1f] but also the reactivity of the Ce(IV) ion beyond unidirectional redox chemistry.[1g]

Herein, we present the exciting chemistry of tetravalent cerium complexes which bear classical 3,5-di-alkyl-pyrazolate ligands. The reactivity of the complexes was screened across cage formation, C=X bond activation, treatment with alkylaluminates, and β-hydride abstraction through Si-H cleavage, leading to a large array of new complexes.

Scheme 1. The reactivity of “[Ce(Me2pz)4]” across a variety of different systems (HqH2 = 1,4-hydroquinone, “Me2pz” = CeIII(Me2pz)3 or Li(Me2pz))

References

Lanthanide Complexes for Catch-and-Release of Phosphates and Anions

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As a key ingredient in fertilizers, significant concentration of phosphates can accumulate in agricultural runoffs. The resulting surplus of nutrients causes eutrophication of surface and coastal waters, boosts algal growth, and creates dead zones that have significant economic and health impacts. On an industrial scale, purification of water can be performed with porous membranes that can separate out a desired species. Unfortunately, such technology have yet to be successfully developed for inorganic phosphates. Part of the problem hindering their development arises from the general paucity of receptors that can sequester inorganic phosphates with sufficient affinity directly in complex aqueous media, with high selectivity over competing anions, and in a reversible manner such that both the device and the phosphates can be recycled. Our group is currently designing such lanthanide-based supramolecular receptors for phosphate remediation. The ability of these complexes to catch and release phosphate upon addition of a trigger such as pH makes them promising candidates for the development of recyclable membranes. Although complexes of lanthanide ions with open coordination sites are known to bind phosphates, they do not all do so with the same affinity and selectivity. Even minor differences in ligand can lead to substantial changes in anion recognition. Herein, we discuss how the structure of the ligand L, the geometry of the lanthanide complex, its charge, and the presence of a hydrogen-bonding network all affect anion recognition, binding, and selectivity and how to design a lanthanide complex for catch-and-release applications.
LUMINESCENT LANTHANIDE COMPLEXES AS REDOX ACTIVE PROBES FOR MEDICAL IMAGING

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The development of luminescent redox active probes is an exciting field of research due to their potential as useful tools in medical imaging for in vivo detection.[1] Lanthanide complexes possess fascinating luminescent and magnetic properties due to their unique configuration.[2] However, the lack of controllable changeable oxidation states hinders their use as redox active probes. Our approach focuses on the incorporation of redox active ligands which, when oxidised independently of the metal ion, produce an easily detectable change in the complex properties. This could lead the way in the development of new families of redox probes capable of detection in biological media.[3,4] We report a new family of lanthanide complexes whereby selective oxidation of the redox active unit induces the switching of the luminescence and relaxivity of the lanthanide ion. The properties of these redox active complexes have been studied by electrochemistry, UV-vis absorption and fluorescence spectroscopy and EPR.

References


RECENT RESULTS FROM USE OF FREE RARE EARTH METALS IN SYNTHESIS

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The most common synthetic routes to rare earth organometallic or metal-organic compounds (organoamides, organo-oxides etc) are salt metathesis reactions of rare earth halides and protolysis reactions of rare earth bis(trimethylsilyl)amides.

\[
\text{LnCl}_n + nML \rightarrow \text{Ln}(L)_n + nMCl \quad n = 2, 3
\]

\[
\text{Ln}[\text{N(SiMe}_3)_2]_n + nLH \rightarrow \text{Ln}(L)_n + n\text{HN(SiMe}_3)_2 \quad n = 2, 3
\]

However, syntheses based on free rare earth metals as the reagent are becoming increasingly competitive owing to their simplicity (only one air-sensitive reagent) and often ease of work up.¹

Metal-based reactions include direct reactions with weak protic acids, e.g. phenols, alcohols, amines, pyrazoles etc.

\[
\text{Ln} + nHL \rightarrow \text{Ln}(L)_n + n/2 \text{H}_2
\]

These may be promoted by heat and activation of the metal by mercury, by activation of the metal with iodine or, in limited cases, can occur unactivated in polar solvents.

Lanthanoid pseudo-Grignard reagents are another possible source through protolysis reactions

\[
\text{Ln} + RX \rightarrow \text{“Ln(R)X”}
\]

\[
\text{“Ln(R)X”} + HL \rightarrow \text{RH} + \text{Ln(L)X}
\]

In the latter case oxidation and Schlenk equilibria can lead to both divalent and trivalent products. Further routes include redox transmetallation

\[
\text{Ln} + n/2 \text{HgAr}_2 \rightarrow \text{LnAr}_n + n/2 \text{Hg} \quad n = 2, 3
\]

and the much more generally useful, redox transmetallation/protolysis reactions

\[
\text{Ln} + n/2 \text{HgAr}_2 + nLH \rightarrow \text{Ln}(L)_n + n/2 \text{Hg} + n\text{ArH}
\]

The lecture describes advances in some of these syntheses, particularly use of pseudo-Grignard reagents, and including attempts to replace mercury in RTP syntheses by silver.

References

1 For reviews:

SYNTHESIS AND REACTIVITY OF RARE EARTH COMPLEXES INVOLVING FORMAMIDINATES OF MODERATE STERIC BULK AND THEIR USE IN TISHCHENKO CATALYSIS

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Much attention has been paid to prepare rare earth-organic compounds using bis(aryl)formamidine ligands. These types of ligands can bind rare earth metals very well and there is the benefit of being able to vary the steric bulk and electronic functionality at the N donor atoms. The aim of this project was to reduce the steric effect of the final compounds by using formamidines of moderate steric bulk and make the metal center more accessible for catalytic reactions. This project involved using \( N,N' \)-di(diphenyl)formamidine (PhFormH) or \( N,N' \)-di(2,4-dimethyl)formamidine (DMFormH) ligands as the precursors in redox transmetalation/protolysis reactions in the synthesis of rare earth complexes. As a result, a series of RE-formamidinate complexes were synthesized and reactivities of these compounds were studies toward Tishchenko reaction. These results will be discussed.

![Figure 1. X-ray crystal structure of \([\text{Ho(PhForm)}_3](\text{thf})_2\). Hydrogen atoms removed for clarity.](image)

References

First Series of Tetravalent Thorium-, Uranium- and Neptunium-Amidinate Complexes

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Actinides (An) can possess a variety of different oxidation states, which typically range from +III to +VI for the early actinides Th-Cm.[1] They have unique electronic properties originating from the 5f-orbitals, what makes their coordination chemistry a fascinating area of research for both, the nuclear engineering but also for fundamental chemistry. Thorium (Th), uranium (U), neptunium (Np) and plutonium (Pu) can form highly charged cations with the oxidation state of four (An4+), which is the dominant one under reductive conditions. Furthermore, An(IV) are of particular interest for the coordination chemistry because of their strong interaction with ligands.

Hence, the overall aim of our investigations is a deep understanding of the interaction mechanisms between tetravalent An (An(IV)) and ligands bearing soft donor atoms, such as nitrogen (N). Thus, we focused on the synthesis and characterization of a series of An(IV) complexes with the N-donor ligand N,N'-Diisopropylbenzamidine (iPr2BA) (see fig. 1) both in solution and in solid state.

Figure 1. Schematic synthesis route for the An(IV) iPr2BA complex preparation.

The structures of the synthesised complex series were determined by single-crystal X-ray diffraction (SC-XRD), showing the An(IV) coordinated by three iPr2BA molecules and one chloro ligand in a monocapped octahedral coordination geometry (see fig. 2). This is the very first example of an An(IV) complex series including Np(IV) as a transuranium element with an amidinate ligand. The isostructural complexes allow a direct comparison of the binding situation of the An(IV) across the series. Quantum chemical calculation strongly supported the experimental results to further study the electronic structure of the complexes.

Figure 2. Thermal ellipsoid plots of [An(iPr2BA)3Cl] (An = Th, U, Np).

NMR-spectroscopic investigations of the dissolved complexes in toluene-d8 showed significant chemical shifts due to considerable effects of the paramagnetic metal centres U(IV) and Np(IV) compared to the diamagnetic reference [Th(iPr2BA)3Cl].

References
HIGHLY AXIAL LANTHANIDE COMPLEXES FOR OPTIMISED MAGNETIC PROPERTIES

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Single molecule magnets (SMMs) display magnetic hysteresis of molecular origin – a magnetic memory effect and a prerequisite of data storage – and lanthanide examples have exhibited this phenomenon at the highest temperatures to date. However, in nearly 25 years since the landmark discovery of SMMs hysteresis temperatures have only increased from 4 K to ~14 K (using a consistent magnetic field sweep rate of ca. 20 Oe s⁻¹). We have recently reported a hexa-tert-butyl dysprosocenium complex, [Dy(Cp₃ttt)₂][B(C₆F₅)₄] [1; Cp₃ttt = {C₅H₂tBu₃-1,2,4}; tBu = C(CH₃)₃], which shows magnetic hysteresis up to 60 K at 22 Oe s⁻¹. Guo et al. have also reported the synthesis and magnetic data of 1. Ab initio spin dynamics demonstrate that magnetic relaxation at high temperatures is due to local molecular vibrations, and thus indicate that with judicious molecular design, magnetic data storage in single molecules at temperatures above liquid nitrogen may become possible. Herein, we present our latest progress in the synthesis and analysis of isolated lanthanocenium cations, using the new methodology that we have pioneered.

Figure 1. (A) Synthesis and (B) molecular structure of 1

References
POLYPHENYL CYCLOPENTADIENYL LANTHANIDE COMPLEXES: SYNTHESIS, STRUCTURE AND APPLICATIONS

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Substituted cyclopentadienyl ligands are widely used to stabilize heteroleptic cyclopentadienyl complexes. We have performed an attempt of systematic study of mono-, bis-, and tris- phenylcyclopentadienyl lanthanide complexes of Nd, Gd, and Tb. Synthetic routes to these compounds have been discovered along with the investigation of their structures and luminescent properties. We have also examined their use as precursors of catalytic ethylene oligomerization systems. We obtained a series of di-, tri-, and tetraphenylcyclopentadienyl complexes of Nd, Gd and Tb.

$$\text{LnCl}_3(\text{THF})_3 + \text{Cp}^{\text{Ph}}\text{K} \rightarrow [(\text{Cp}^{\text{Ph}})_n\text{LnCl}_{3-n}(\text{KCl})_x(\text{THF})_y], \quad \text{Ln} = \text{Nd, Gd, Tb}$$

New opportunities in design of lanthanide complexes are opening if the number of phenyl groups in Ph,C$_x$H$_{5-x}$ ligands is changing with simultaneous alteration of the number of Cp$^{\text{Ph}}$ ligands in the Ln$^{3+}$coordination sphere. Phenylcyclopentadienyllanthanides form a variety of structures: from coordination polymers to mononuclear complexes. (Figure 1)

![Figure 1. Molecular structure of $[(\text{Ph}_2\text{C}_3\text{H}_5)_2\text{Tb}(\text{thf})\text{Cl}_2\text{K}]_{\infty}$ (left) and $(\text{Ph}_2\text{C}_3\text{H}_5)_3\text{Tb}$ (right)](image)

Phenyl-substituted cyclopentadienyl ligands may serve as a “ligand-antenna” for lanthanide ions sensitization in lanthanide cyclopentadienyl complexes.

We thank Russian Science Foundation for financial support (grant No. 17-13-01357).
Session 2

Posters
Photo-physics and -chemistry of Variant Coordination Structured f-Element Complexes

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The visible and NIR emission of Ln(III) systems have been used in various potential applications such as biomedical probes, luminescent sensors, laser systems and organic light emitting devices (OLEDs).1 Recently, the Ln β-diketonates complexes in particular have been used as emitting layers in OLEDs. For such applications, the excellent photoluminescence quantum yield (PLQY) and stability are the two key points that can be achieved simply by selecting the proper organic ligands around the Ln ion in a coordination sphere. Regarding the strategies to enhance the PLQY, the most common is the suppression of the radiationless deactivation pathways due to the presence of high-frequency oscillators (e.g. –OH, –CH groups) around the Ln centre. Recently, a different approach to maximize the PLQY of Ln(β-DKs) has been proposed (named “Escalate Coordination Anisotropy”, ECA). It is based on the assumption that coordinating the Ln ion with different ligands will break the centrosymmetry of the molecule leading to less forbidden transitions (loosening the constraints of the Laporte rule). The OLEDs based on such complexes are available, but with low efficiency and stability. In order to get efficient devices, there is a need to develop some new Ln complexes with enhanced PLQYs and stabilities.

In this work, new complexes of variant coordination structures, both visible and NIR emitting, based on the various fluorinated/non-fluorinated β-diketones and O/N-donor neutral ligands were synthesised and fully characterised. Their photophysical properties were studied and best ones were selected to fabricate stable and efficient OLEDs. The results and the potential applications for OLEDs will be presented and discussed.

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References

Solution State Structure of Amide Appended LnDO3A Complexes with Slow Amide Bond Rotation

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Kinetically stable DO3A type lanthanide(III) complexes are of great interest due to their applications in bioimaging and as MRI contrast agents. [1] To investigate the inherent chirality of the DO3A ligand we have introduced a chiral amide arm which resolves the many conformations of the complex and illustrates the complicated speciation that must be taken into account when even simple DOTA-like complexes are used in an inherently diastereotopic biological medium.

![Figure 1: The eight resolved conformation of the complex.](image_url)

COMPLEXATION OF EUROPIUM WITH CHONDROITIN SULFATE

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Glycosaminoglycans (GAGs) are linear polysaccharides and highly negatively charged. GAGs are part of proteoglycans which are major components of the extracellular matrix. They are involved in binding cations (such as sodium, potassium and calcium) and water, and also regulating the movement of molecules through the matrix. Individual functions of proteoglycans can be attributed to either the protein core or the attached GAG chain. The GAG family consists of heparin/heparan sulfate, chondroitin sulfate (CS) and dermatan sulfate (DS). CS is composed of the disaccharide unit N-acetylgalactosamine (D-GalNAc) and D-glucuronic acid which can be sulfated at the C4 and C6 of GalNAc (CS4S and CS6S). DS is defined by presence of L-iduronic acid residues and is always sulfated at C4 at the GalNAc. The ability of the lanthanide ions, like Europium (Eu), which show luminescence properties, allowed studying the binding behavior of GAGs.

The behavior of the complex formation of Eu$^{3+}$/GAGs was analyzed under physiological conditions by several experimental methods such as time-resolved laser-induced fluorescence spectroscopy (TRLFS) and infrared spectroscopy (ATR-FT-IR), supplemented by theoretical calculations of the possible structures and resulting spectra.

All three GAGs (CS4S, CS6S and DS) caused an increase in luminescence intensity of the hypersensitive $^5D_{0} \rightarrow ^7F_{2}$ emission band of Eu$^{3+}$ due to complex formation, which was more pronounced for CS4S and DS compared to CS6S. The luminescence lifetimes increased with CS4S and DS up to 200-300 µs, corresponding to 2-4 remaining H$_2$O molecules in the first coordination shell of Eu$^{3+}$. With CS6S, the luminescence lifetime was even more prolonged up to ~650 µs (~1 remaining H$_2$O).

FT-IR showed that the binding of GAGs to Eu$^{3+}$ occurs not only via the carboxyl groups but also via the sulfate groups.

Even though the coordination behavior of GAGs towards Eu$^{3+}$ is in general quite similar, particular differences could be identified: GAGs with C4 sulfation seem to be stronger ligands, whereas C6 sulfation seems to be sterically more ambitious since it can replace more H$_2$O molecules from the first spherical coordination shell of Eu$^{3+}$ than C4 sulfation.
Solvent chemical potential: A key player in intermolecular association processes

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Thermodynamic laws treat solvent activity as a constant when binding equilibria occur in diluted solutions and any deviations are assumed to arise from some non-ideal behaviors of the reactants and products. However, a better modeling of the solvent molecules involved in solvation reactions may be beneficial to the rationalization of intermolecular association processes. In this context, Castellano and Eggers1 developed a novel approach, in which solvent molecules were introduced as chemical partners. In the chemical potential framework, the explicit consideration of solvent contribution to the complexation equilibria results in significant deviations of the law of mass action. Stability constants, which characterize the formation of coordination complexes, are therefore significantly altered. Bearing all these elements in mind, we established theoretical and experimental methods, which aim at separately evaluating solvent effects and “pure” binding affinity accompanying the reaction of neutral tridentate ligands (L1, L2 and L3) with neutral saturated trivalent lanthanide containers [Ln(hfac)₃(diglyme)]. Changes in ligand lipophilicities and in metallic sizes are investigated for decrypting robust trends in binding selectivity.2

![Chemical structures of tridentate ligands L1, L2, L3](image)

**Figure 1.** Chemical structures of tridentate ligands L1, L2, L3

References


TACN (1,4,7-TRIAZACYCLONONANE) BASED LIGANDS COMPARED TO CYCLEN DERIVATIVES AS CHELATORS FOR Er$^{3+}$

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Cyclen based ligands for lanthanide(III) ions are well known and their paramagnetic and luminescence properties make them appealing as MRI contrast agents and for bioimaging applications.$^1$

Synthesis and investigation of ligands based on the smaller 1,4,7-triazacyclononane ring (TACN) can, $^2$-$^3$ however, give an insight into how chelators with a lower symmetry than DOTA influence the properties of the lanthanide complexes.

The affinity of these ligands for erbium(III) was compared to DOTA and DO3A. The aim is to document that the tpatcn ligand (figure 1) is an effective chelator and can be modified in ways that allow it to form kinetically inert complexes with lanthanide(III) ions.

References


PUTTING SOME LIGHT ON SENSING OF BIOMARKERS

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Biomarkers are traceable molecules, which may indicate the presence of a disease when found at certain concentration in organisms. They are indeed a relevant target for medical diagnosis and become particularly interesting when we can detect and quantify them by using image diagnosis. Trivalent lanthanide (Ln(III)) complexes have extensively been studied and used as optical and luminescent sensors for biomedical imaging, due to their particular and convenient luminescent properties. 1,2 In order to assess the viability of a Ln(III) complex for its use on actual imaging applications it is of main importance to first establish its stability, speciation and structure in the adequate conditions. The complexes have to be stable in water, the concentration of light-emitting species has to be known and high at the established conditions, and the complex structure may leave some space for the entrance of the target biomarker into the inner coordination sphere.

We are particularly interested on deeply studying the stability, speciation and structure of some water-soluble Ln(III) (Ln = Eu, Tb) complexes with pyridine- and quinoline-based polyaminocarboxylate ligands (Fig. 1). Some of us have recently reported 3 a thermodynamic and spectrophotometric study about lactate sensing based on the Tb(III) complex with H2bpcd (Fig. 1). Lactate is a relevant biomarker, which may reveal sepsis, liver pathologies, Parkinson disease and some types of cancer. The chirality provided by the diaminocyclohexane backbone endows the ligand interesting chiroptical properties, which may be exploited by circularly polarized light luminescence for lactate sensing. Currently, we are studying Ln(III) complexes with H2bpcd, H2bQcd, H3PyC3A and H3Q3CA (Fig. 1) for the sensing of bicarbonate, a crucial biomarker for the early diagnosis of some severe kidney diseases.

Figure 1. Library of chiral ligands discussed in this communication

References


Implementing Room-Temperature Dual Emission in Molecular Erbium Complexes for Molecular-Based Upconversion

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Due to the wealth of regularly spaced excited spectroscopic levels which covers the entire near-infrared, visible and ultra-violet domain, trivalent Er(III) cations have been exploited as activators in linear optics for upconversion operating in doped ionic solids and nanoparticles and, sometimes in pure molecules. In order to explore the structural and electronic conditions required for the explicit induction of minimal dual visible/NIR emissions sensitized via ligand excitation in erbium coordination complexes, a series of mono- and dinuclear Er(III) complexes with polyaromatic tridentate ligands with variable aromaticities and ever-widening alkyl substituents has been synthesized and structurally characterized (Fig. 1a). Although the NIR emission arising from the Er(4I_{13/2}→4I_{15/2}) transition may be classified as ‘standard’, the ligand-sensitized nanosecond Er(4S_{3/2}→4I_{15/2}) green emission occurring at 540 nm observed in these Er(III) complexes is more challenging and rarely reported for coordination complexes possessing high-energy oscillators (Fig. 1b). The special conditions required for implementing Er-centered upconverted emission in coordination complexes following different mechanisms (ESA (= excited-state absorption) and ETU (= energy-transfer upconversion) in mononuclear and dinuclear complexes are discussed.

Figure 1. a) Molecular structure of complex [Er(terpy)_{2}(O_{3}SCF_{3})_{2}]^{+} (taken from the crystal structure of [Er(terpy)_{2}(O_{3}SCF_{3})_{2}]CF_{3}SO_{3}·1.5C_{6}H_{5}N) and associated b) visible (λ_{exc} = 350 nm at 7K) and c) NIR (λ_{exc} = 447 nm at 11K) emission spectra recorded in the solid state.

References
Three Dimensional, Layered, and Cation-Cation Interaction 
Structures Built from Phosphuranylite Units

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The phosphuranylite topology is abundant amongst naturally occurring and synthetic uranium containing materials and is built of chains of alternatng uranyl hexagonal bipyramids and pairs of edge-sharing uranyl pentagonal bipyramids. These chains are connected to adjacent chains through edge- and corner-sharing phosphate tetrahedra, and the orientation of adjacent phosphate tetrahedra (either pointing up or down from the plane of the phosphuranylite layer) influences the corrugation of the layers. Recently, these phosphuranylite type chains have been observed as building units in several new structures including those featuring three dimensional frameworks, two dimensional layers, and cation-cation interactions as seen in Rb$_3$[Al$_2$O(PO$_4$)$_3$][(UO$_2$)$_3$O$_2$], K$_3$[(UO$_2$)$_3$O$_2$(PO$_4$)$_2$], and Cs$_6$[(UO$_2$)$_3$O$_4$(PO$_4$)$_4$], respectively. Each of these structures has been synthesized by high temperature alkali chloride molten flux methods in alumina crucibles. By employing this synthetic method and introducing new building units, such as the [Al$_2$O(PO$_4$)$_6$]$^{14-}$ unit in Rb$_3$[Al$_2$O(PO$_4$)$_3$][(UO$_2$)$_3$O$_2$], a variety of new uranium containing materials may be synthesized and characterized. This presentation will focus on the synthesis, structure, optical characterization, and ion-exchange properties of these phosphuranylite based materials and related phases.

References


Figure 1. The construction of Rb$_3$[Al$_2$O(PO$_4$)$_3$][(UO$_2$)$_3$O$_2$] (left) and Rb$_3$[Al$_2$O(PO$_4$)$_3$][(UO$_2$)$_3$O$_4$(PO$_4$)$_2$] (right) from [Al$_2$O(PO$_4$)$_6$]$^{14-}$ units (middle) and phosphuranylite units. Uranium polyhedra in blue, aluminium tetrahedra in blue, phosphate tetrahedra in gray, and oxygen atoms in red. Rubidium cations are omitted for clarity.
Structural and spectroscopic studies of heavy lanthanide complexes with 1,10-phenanthroline and thiocyanate

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Spectroscopic and structural properties of lanthanide (Tb, Dy, Ho) complexes with 1,10-phenanthroline and thiocyanate have been investigated as a potential candidate for optical materials. Lanthanide (Tb3+, Dy3+, Ho3+) complexes were synthesized in solution and as crystals and were characterized by elemental and thermal analyses, XRPD method, FTIR and UV-Vis-NIR spectroscopy. The optical spectra of these two types of rare-earth compounds were performed at room and low temperatures in order to understand the electrostatic nature of the Ln3+-N coordination bonds.

The lanthanide (Tb, Dy, Ho) complexes are isostructural and crystallizes in a monoclinic system with space group P21/c and the following unit cell parameters: a= 8.476 (2) Å, b= 32.926 (4) Å, c= 10.417 (2) Å, β= 112.51 (2)°.

The intensities of electronic lines and the Judd-Ofelt parameters were calculated. In the absorption spectra, „red shift” was observed for hypersensitive transitions of the lanthanide ions. The variation of the spectroscopic parameters (β, δ) and their correlation with the nature of the Ln3+-N bond are discussed. The nephelauxetic ratio β and Sinha’s parameters δ suggested an increase in the ‘degree of covalency’ of the metal-ligand coordination bond from the Dy3+ crystals to the Ho3+ crystals. The photoluminescence of Tb3+ complex was investigated. The experimental data of the decay time of the 5D4 state of the Tb3+ ion for the title compound were fitted using single exponential (77K) and two exponential (293K) function. These data and their comparison with absorption spectra of the Ho3+ crystal recorded at room and low temperature suggests the presence of temperature dependence in crystals.
Polymorphism and luminescent properties of heteropolynuclear complexes containing oxydiacetate as linker

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Oxydiacetic acid (H$_2$oda) is a versatile flexible ligand. In the presence of a lanthanide ion (Ln) and a divalent cation (M), it has proved to form heteropolynuclear complexes of general formula [Ln$_2$M$_3$(oda)$_6$]ꞏxH$_2$O. These compounds exhibited interesting properties as catalysts. In this contribution, we present the synthesis and characterization of ten novel compounds of this series, with M = Zn. They were prepared by direct reaction of oda in aqueous solution with stoichiometric amounts of Zn and Ln salts, followed by slow organic solvent diffusion. Two different structures were obtained under the same stoichiometry. The lighter Ln ions (Pr, Nd, Eu) gave place to compounds belonging to the hexagonal system, space group P6/mcc. On the other hand, heavier Ln ions Ho, Er, Yb (and also Y) formed cubic systems, space group Fd3 c. In the case of Dy, the two polymorphs were obtained by slight variations of the synthetic conditions (Figure 1). The influence of Ln on phase change is discussed in comparison with previously reported compounds. Luminescence studies were carried out. Compounds containing Eu or Tb show the most intense luminescence, bearing also relatively long time decay for the excited state. Dy compounds belonging either to the hexagonal or the cubic system show very similar luminescence profiles based on the similar environment of the Ln having also the same point group symmetry.

Figure 1. Polymorphic compounds [Dy$_2$Zn$_3$(oda)$_6$]ꞏxH$_2$O. Hexagonal (left) and cubic (right)

References

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Design of chiral lanthanide helicates and tetrahedral cages with chiral optical properties

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“Supramolecular diastereoselective phenomenon” to engineer high order chiral self-assembly architectures is an important area of research especially in the design and development of chiral functional materials for applications such as for catalysis and sensing functions. This has been especially hard in the case with lanthanide ions due to the issues of variable coordination number, kinetic lability and poor stereochemical preference of the lanthanide ions.

In our study of the formation of lanthanide tetrametallic supramolecular tetrahedral cages, we discovered that significant diastereoselectivity (only ΔΔΔΔ− or ΔΔΔΔ− twisted conformation was observed with NMR) can be easily broken to significantly less diastereoselectivity (ΔΔΔΔ− and ΔΔΔΔ− twisted conformation) by slight alterations of (a) position or (b) steric bulkiness of point chirality at the ligands.

The self-assembly of europium (Eu) tetrametallic tetrahedral cages from three closely related chiral ligands based on the same diagonal 2,6-diaminoanthraquinone linked bis(pyridine-2,6-dicarboxamide) moieties is demonstrated to show very different supramolecular formation phenomenon. One ligand exhibits a high diastereoselective assembly of homochiral (either ΔΔΔΔ or ΔΔΔΔ) Eu tetrahedral cages whereas two other ligands, with two different approaches of loosened point chirality, leads to a significant break down of the diastereoselectivity to generate a mixture of (ΔΔΔΔ and ΔΔΔΔ) isomers in ~ 1:1.06 to 1:1.20 ratios. Highly emissive (quantum yields: 16 to 19%) with strong circularly polarized luminescence (|glm|: up to 0.22) are also observed for the first time with these tetrahedral cages. In further studies it is also identified in an unprecedented case, to correlate the nonlinear enhancement of the chiroptical response to a nonlinearity dependence on point chirality.

Figure 1. schematic diagram showing the self-assembly formation of the Eu tetrahedral cages

References:
Metal-organic coordination polymers based on dicyandiamide complexes of rare earth metals as precursors of bright luminescent materials

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The dicyanamide (DCA) ligand is frequently used for the design of metal-organic coordination polymers of transition metals but it is underappreciated tool in the rare-earth chemistry. In this work we have proposed method for design of one- and two- dimensional coordination polymers basing on the L2Ln[(N(CN)2)3, LLn[(N(CN)2)3(LLL’Ln[(N(CN)2)3 and LL’Ln[(N(CN)2)3] (L – bidentate N-containing heterocyclic ligand). Structural and optical properties of all synthesized compounds are analyzed (Fig.1).

Figure 1. The general view and crystal packing of Eu(phen)3(DCA)3(H2O).

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PYRIDINE/DIAZINE DERIVATIVES TO ACCESS A NEW LANTHANIDE LUMINESCENT MATERIALS

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Tris-N-heterocyclic ligands, such as 2,6-bis-(pyrazol-1-yl)pyridine derivatives, continue to be very widely used in lanthanide complexation chemistry due to they provide a cavity for lanthanide chelation, optimal for the enhancement of the luminescent emission properties of the ion by antenna effect.

The family of luminescent MOFs based on lanthanide ions (LnMOFs) has a great impact within hybrid materials since they combine typical MOFs’ properties such as porosity, with the good photophysical properties of lanthanide ions, greatly expanding the possible applications of these materials.

In this communication we will describe selected properties of new families of trisheterocyclic ligands based on pyridine and any of the three diazine rings, pyrazine, pyrazine and pyrimidine as central rings, flanked by two differently substituted pyrazol-1-yl rings. These polyheterocyclic frameworks give access to LnMOF’s with different luminescent and crystallographic behavior. The crystallographic and photophysical data obtained from these LnMOF’s let us to extract structure–property relationships.

![Image of trisheterocyclic ligands and LnMOFs structures]

**Figure 1.** Crystallographic-photophysical relationships.

References


Anticooperative lanthanide loading on tridentate oligomers

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Metal-containing (bio) organic polymers are a class of material that combines the electronic and optical properties of transition metals with the versatility of organic polymer. Their applications in energy storage and conversion, drug delivery, shape memory materials and photonic devices are continuously increasing.\cite{1} Despite these unique properties, the preparation of novel exploitable structures has remained a considerable challenge, particularly because the lack of rational control on metal loadings on multisite polymers limits their design to empirical and poorly reproducible materials\cite{2}. Considering this limitation, we applied thermodynamic models for rationalising the lanthanide loadings of linear multi-tridentate polymers\cite{3}, with the help of two parameters (i) the intrinsic affinity of Ln(III) for the tridentate binding sites and (ii) the intermetallic interactions \cite{4}. We exploit these two microscopic descriptors, for implementing selective lanthanide metal ions incorporation into multisite organic receptors. In this contribution the synthesis of new tridentate ligand and the thermodynamic properties of their reaction with [Ln(hfac)₃(diglyme)] containers will be discussed.

Figure 1. Chemical structures of tridentate ligands

References


Solution Structure of DO3A-like Lanthanide Complexes Investigated by \(^1\)H-NMR

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Kinetically inert lanthanide(III) complexes have many important applications in e.g. magnetic resonance imaging,\(^1\) bioassays\(^2\) or catalysis.\(^3\) The many applications have resulted in a large research effort and development of many kinetically inert lanthanide complexes derived from polydentate cyclen ligands. In spite of the rigid structure of these ligands, a complicated picture of dynamic processes is found for the lanthanide complex in solution as shown in figure 1. In some ligands, the exchange between different conformations may be slow as observed for [Ln.DOTA].\(^4\) However, other ligands may be locked in a single conformation, have rapid exchange between conformers, and in some cases specific exchange processes are prohibited.\(^5\)

Here, DO3A analogues have been synthesized in order to map the solution structure and exchange processes by paramagnetic \(^1\)H-NMR, and thereby investigate how the structure of the ligand may be used to control conformational flexibility.

**Figure 1.** Left: Conversion of stereochemistry of a lanthanide complex by arm rotation and ring inversion. Right: Possible conversion of conformers for benzyl-DO3A and pentylamid-DO3A.

Polynuclear Ln(III) complexes based on Pyridinephosphonate ligands with upconversion properties

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A series of polynuclear assemblies based on ligand L (Figure 1) has been developed. The coordination properties with LnIII (Ln = La, Eu, Tb, Yb, La) have been studied in water (pH = 7) and in D2O (pD = 7) by UV-absorption spectrometry, spectrofluorimetry, 1H and 31P NMR, DOSY, ESI-mass spectrometry and X-Ray diffraction. This nonadentate ligand forms highly stable mononuclear complexes in water and provide a very efficient shielding of the Ln cations, as emphasized by the very good luminescence properties of the Yb complex in D2O, especially regarding its lifetime (τD2O = 10.21 us) and quantum yield (τD2O = 0.42%). In the presence of excess LnIII cation, polynuclear complexes of [(LnL)2Ln]x stoichiometry (x = 1 and x = 2) are observed in solution. Single crystals of a dinuclear La(III) were also isolated and the X-ray structure, emphasized the presence of strong hydrogen bonding interactions between the La(H2O)93+ cation and the [LaL]- complex.1

Upconverted TbIII emission (Figure 1) was observed upon NIR excitation of the 2F7/2 → 2F5/2 transition of Yb at 980 nm of the heteronuclear [(YbL)2Tb] assemblies in D2O. Two photon UC mechanism was confirmed by monitoring the TbIII emission intensity as a function of the laser power. These results are the third evidence of up-conversion at the molecular level in D2O and at room temperature.2,3

References


Figure 1. Stepwise formation of mononuclear and polynuclear complexes with ligand L (X-ray structures) and upconversion spectrum recorded upon laser excitation at 980 nm of a D2O solution of [YbL] in the presence of 0.5 equivalent of TbCl3·6H2O (25°C, pD = 7.75, P = 1W).
Pressure-Induced Planarization of An(III) Complexes

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Low-coordinate U(III) complexes are rare and interesting because they offer opportunities for in-depth studies of their potentially unusual electronic structure [1]. Three-coordinate actinide (An) complexes almost exclusively adopt trigonal pyramidal coordination geometries rather than trigonal planar, but the influential factor that favours pyramidalization still remains unclear. Theoretical studies have shown that the energy difference between pyramidal and planar geometry is small [2]. Therefore, their geometries may be sensitive to factors such as steric effects and pressure [3]. Indeed, a totally planar U(III) amide was synthesized by exploiting steric repulsion of bulky ligands [4].

We will present the first studies of the effect of pressure on the geometry and electronic structure of U(III) complexes: the uranium(III) tris(aryloxide) complex [U(ODtbp)3] (ODtbp = O-2,6-(Bu2C6H3)2) 1, one of the most studied AnX3 complexes; and the only known sulfur analogue [U(SMes*)3] (SMes* = S-2,4,6-(Bu3C6H2)2) 2, [5].

The structures of 1 and 2 were determined at pressures up to 3.5 GPa and 5.4 GPa, respectively. 1 undergoes a phase transition at high pressure (ΣO-U-O = 324° at 3.5 GPa) (Figure 1). In sharp contrast, 2 becomes planar with increasing pressure (ΣO-U-O = 360° at 5.4 GPa), and shows acute U-S-C bond angles (av. = 79.6°) and short U···Ar distances (the shortest U···C₃ distance = 2.854 Å). Computational analyses of the pressure-induced planarization and the effect of these weak interactions will also be presented.

Figure 1. a) Compound 1 and its solid state structure at 3.5 GPa; b) Compound 2 and its solid state structure at 5.4 GPa.

References

The optical properties and potential practical applications of rare earth monocarboxylates depend on the character of the lanthanide–carboxylate oxygen bond, i.e., electron density distribution of the active metal ions, the binding site(s) of the ligand, and the metal–donor atom distance. These factors are affected by steric aspects relating to the structural characteristics of the ligand. The ─C=C─ double bond and length of the C-chain in the substituent of the carboxylate ions may influence the photophysical properties of lanthanide compounds, too. Spectroscopic investigations of two monocrystals: Er$_2$(CH$_2$=CH-(CH$_2$)$_2$-COO)$_6$·4H$_2$O (I) and Er(H$_2$C=CHCOO)$_3$·1.5H$_2$O (II), at room and low temperatures down to 4.2 K were performed to explain the electrostatic nature of Ln$^{3+}$–ligand bond. Crystals of Er$_2$(CH$_2$=CH-(CH$_2$)$_2$-COO)$_6$·4H$_2$O (I) are built of centrosymmetric dimer molecules. There are two erbium cations, which adopt a 9-coordinate geometry with seven oxygen atoms from carboxylate groups and two oxygen atoms from water molecules. The Er$^{3+}$ ions occupy low-symmetry sites in the dimeric structure of Er$_2$(CH$_2$=CH-(CH$_2$)$_2$-COO)$_6$·4H$_2$O. The single crystals of Er(H$_2$C=CHCOO)$_3$·1.5H$_2$O (II) are built of dimer molecules too, but there are two erbium cations with different coordination number (9 and 8). The Er$^{3+}$ ions occupy low symmetry sites in the both crystals. The spectroscopic parameters, determined on the basis of absorption spectra: the nephelauxetic ratio β and Sinha’s parameter δ and their variations for both the title compounds, point out that the degree of Ln$^{3+}$–L bond covalency is rather bigger for pent-4-enoate erbium (I) than for 2-propenoateerbium (II), i.e., for the compound with a shorter C-chain in the ligand. Spectroscopic measurements allowed us to compare the optical properties of the title compounds with other lanthanide carboxylates.
A Unique Synthetic Approach to Novel Materials Containing Uranium(V)

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Interest in remediating environmental impacts of nuclear waste production in addition to the continued efforts to expand upon our understanding of the nuclear fuel cycle has prompted extensive research focused on elucidating the role of uranium(V) in these processes. However, the stability of the +5 oxidation state of uranium is limited, thus there are few examples of materials containing pentavalent uranium relative to those which contain U(IV) and U(VI). Up to now, the primary preparative methods for these materials has been high temperature solid state and high temperature high pressure hydrothermal methods, which are either limited to the preparation of only thermodynamically-favored phases, or require expensive equipment and specialized laboratory settings to utilize. Recently, we have realized a new low temperature route to uranium(V)-containing materials. This method, which is carried out under hydrothermal conditions near the critical point of water, has resulted in a novel pentavalent uranium borate1 and several mixed-valent uranium silicates. This discussion will focus on the targeted synthesis of novel pentavalent uranium compounds and their unique structural features.

References

Amide and Siloxide Ligand Influence on f-Element Redox Chemistry

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Abstract

Understanding basic chemistry of f elements could improve materials development for more efficient nuclear and chemical energy conversion. Electron transfer reactions are fundamental to the synthesis of uranium materials, e.g. uranium containing ceramics for nuclear fuel applications and molecular complexes used to study f electron bonding and catalysis. Catalysis using f elements is less developed than with transition metals; however, the unique properties of f electrons could allow new types of transformations. We report work that examines influences of amide and siloxide ligands on the redox chemistry of uranium and the ability of its complexes to perform thermodynamically difficult transformations. Also presented is a new class of heterobimetallic complexes which combines f element redox chemistry with that of transition metals.

References

Structural and Spectroscopic Characterization of Novel Uranium (U^{4+}) and Uranyl (UO_2^{2+}) Sulfate-Chloride Materials

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Sulfate (SO_4^{2−}) containing uranium species are of fundamental interest due to their structural diversity, appearance in nature, and relevance to the nuclear fuel cycle. Research into these materials has led to the study and robust structural characterization of many synthesized uranyl (UO_2^{2+}) sulfate materials1 and uranium-sulfate mineral species2 over the past several decades. Efforts have focused on the coordination of sulfate to the environmentally relevant uranyl triatomic cation to explore the structural aspects of these materials. In general, sulfate-containing uranium species (both mineral and synthetic) crystallize into 1-dimensional chains or 2-dimensional sheets due to the oxophilic nature of uranium and the preferential coordination of ligands equatorially to the uranyl metal center. As such, very few of the materials are molecular.4 Here we present a new class of sulfate containing compounds with a series of molecular and 1-dimensional uranium (U^{4+}) and uranyl sulfate-chloride materials, wherein discrete molecular units are common due to reactions in a high chloride environment. This synthesis technique is well studied within our group5 and the benefits of high anion media and low pH are outlined as generating discrete, reproducible, and unhydrolyzed units with predictable solid-state speciation paired with protonated organic cations. We have used a multitude of pyridinium and bipyridinium cations to provide charge-assisted non-covalent interactions (NCIs) to stitch molecular and 1D uranium units into 2D or 3D supramolecular networks. The role NCIs play in the assembly of these materials has been analysed and the influence those interactions have on the luminescent properties of certain compounds has been explored.

Figure 1. Polyhedral representations of a uranyl (UO_2^{2+}, yellow) and a tetravalent uranium (U^{4+}, green) sulfate-chloride material. Sulfate oxoanions bridge uranium metal centers to form discrete units or 1D chains. Protonated bipyridinium cations provide charge balance and hydrogen based non-covalent interactions for assembly into 2D supramolecular networks.

References

Low-valent oxidation states of uranium with oxoanionic sulfur ligands

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In contrast to the well characterised uranium compounds containing the uranyl cation, UO$_2^{2+}$, low valent uranium chemistry is less developed. Herein we present our previous and ongoing research towards low oxidation state uranium compounds with redox innocent ligands, focussing on the oxoanions of sulfur. Sulfate complexes of hexavalent uranium have been investigated both computationally$^1$ and spectroscopically in aqueous solution$^2,3$. Their relative stability may be dependent on the water activity, and they may form different isomers with different coordination numbers. Here, we have reinvestigated sulfate complexes of uranium in non-aqueous, highly oxidizing media. Using concentrated H$_2$SO$_4$, oleum, SO$_3$ and CH$_3$SO$_3$H we have identified a range of new uranium complexes, and we will present the formation of low-valent uranium complexes from these solvents. In particular, we will present the synthesis and spectroscopic data of U(SO$_4$)$_2$, two modifications of U(CH$_3$SO$_3$)$_4$ and the mixed-valent sulfonate (UO$_2$)U(CH$_3$SO$_3$)$_3$CH$_3$SO$_3$H with special regard to its excitation and emission spectra. The spectra are strongly influenced by the presence of the UO$_2^{2+}$ ion in the compound. Not only the electronic transitions are seen but also the vibronic structure of these transitions could be identified and show the presence of both uranium(IV) and uranyl(VI) within the compound.

Figure 1. The U$^{4+}$ ion in U(SO$_4$)$_2$ is coordinated by eight monodentate sulfate ligands forming a square antiprism. The distances U–O range between 231 and 240 pm for U(SO$_4$)$_2$.$^4$

References

Dinuclear \([\text{Ln}_2(2-\text{FBz})_6\text{(terpy)}_2]\) compounds. SMM behaviour and luminescent properties.

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Lanthanide ions possess interesting luminescence properties, emitting light when appropriately sensitized by a ligand. The 2-fluorobenzoate ligand (2-FBz) interacts strongly with the \(\text{Ln}(\text{III})\) via the carboxylate group and possesses a conjugated aromatic ring that confers luminescence properties to the compounds it forms.\(^1\) Moreover, lanthanide atoms are also well known to exhibit large magnetic moments and strong magnetic anisotropy and therefore they are considered to be good candidates for the elaboration of Single Molecule Magnets (SMMs).\(^2\) The use of 2-FBz and \(2^\prime,2^\prime\prime,6^\prime,2^\prime\prime\prime\)-terpyridine (terpy) has led to a new family of isostructural homodinuclear compounds with general formula \([\text{Ln}_2(\mu_2-\text{FBz})_2(2-\text{FBz})_4\text{(terpy)}_2]\) (Ln(III) = La, Nd, Sm, Eu, Gd, Tb, Dy, Er and Yb). The dysprosium derivative (Figure 1) presents SMM behaviour at zero applied field and luminescence in the visible region. In this work, we present the magnetic and luminescent properties of this family of compounds.

![Diagram](image)

Figure 1. Structural representation (top centre), luminescence spectra (bottom left) and ac magnetic measurements (bottom right) of the dinuclear compound \([\text{Dy}_2(\mu_2-\text{FBz})_2(2-\text{FBz})_4\text{(terpy)}_2]\).

References


Design and Synthesis of MOF-Sensors for the Detection of Excess Fluoride Levels in Drinking Water

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Prolonged consumption of water contaminated with fluoride (F⁻) at concentrations exceeding 1.5 ppm can lead to considerable health implications, particularly in children and developing embryos. Various irreversible and often severe forms of fluoride toxicity, including skeletal fluorosis, are endemic in at least 25 countries. The most intensely affected populations have limited access to water testing facilities, and existing technologies are lacking in terms of specificity to F⁻ and sensitivity to the very low and narrow physiologically relevant concentration range of 0.5 – 1.5 ppm. Rapid, remote-access and reliable water sampling for F⁻ contaminations is thus an important goal. In this work, we present a rationally designed, lanthanide-based, luminescent metal-organic framework (MOF), named SION-105, for the selective detection of F⁻ ions in drinking water at concentrations as low as 500 ppb, with a 100 ppb limit-of-detection. The weak interactions between F⁻ ions and the Lewis-acidic B groups present within SION-105 allow the material to be regenerated and reused, thus setting it apart from most existing molecular F⁻ ion sensors, which are limited to one-time use by their reliance on irreversible covalent or bond-cleavage interactions. To demonstrate SION-105 as a candidate for the existing gaps in F⁻ sampling technology, we realized a portable, robust prototype device to be used with SION-105. This was used to measure F⁻ ion concentrations in natural ground water samples taken from three different countries, the results of which show excellent agreement with ion chromatography analysis.[1]

References

Chiral Ln(III) coordination compounds based on (R)- or (S)-(±)-2-(6-Methoxy-2-naphthyl)propionic acid: structural, magnetic and optical studies

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The (S)-(+)2-(6-Methoxy-2-naphthyl)propionic acid (S-HL), commonly known as Naproxen, is one of the most popular Nonsteroidal Anti-inflammatory Drugs which also exhibits analgesic and anti-herpetic properties. [1] In addition to medical applications, the deprotonated specie of the acid could easily coordinate to lanthanide trivalent ions [Ln(III)] via carboxylate group. The use of the enantiomeric R-HL and S-HL species and the N-donor ligand 1,10-phenanthroline (phen) led to the isolation of dinuclear compounds with formulae [Ln2(R-L)6(phen)2]ꞏ3DMFꞏH2O for Ln(III) = Nd (R-1), Eu (R-2), Gd (R-3), Tb (R-4) and Dy (R-5) and [Ln2(S-L)6(phen)2]ꞏ3DMFꞏH2O where Ln(III) = Nd (S-1), Eu (S-2), Gd (S-3), Tb (S-4) and Dy (S-5). These compounds present luminescence properties due to the sensitization of the f-f electronic transitions of the Ln(III) ions by the phen coordinated molecules, optical properties induced by the chiral carboxylate ligands and/or field induced SMM properties which arise from the magnetic anisotropy of the Ln(III) ions.

Figure 1. Top: Structural representation of dinuclear compound S-4. Bottom: Magnetic measurements (left), luminescence spectra (centre) and Circularly Polarized Luminescence spectra (right) of compounds [Ln2(R/S-L)6(phen)2]ꞏ3DMFꞏH2O.

References

Measuring the Effect of Ligand Backbone, Denticity, Functional Groups, and Solvent on the Formation of Gd(DOTA)$^-$ and Related Complexes

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Studies on the details regarding the complexation of Gd$^{3+}$ with macrocyclic ligands remains relevant as the body of evidence of Gd$^{3+}$ deposition in vivo grows. We have previously reported that the Gd$^{3+}$ ion forms a strongly-coloured complex with the dye xylene orange (XO), and that the Gd–XO complex can be used as a colorimetric probe to measure relative rates of complex formation with test macrocyclic ligands via a mechanism of ligand substitution. Indeed the method has been shown to discriminate between rates of complexation among ligands of different hydrophobicity, structural backbone (i.e., acyclic vs. macrocyclic) and degree of denticity, as well as acidity of functional group (i.e., phosphate vs. acetate vs. amide). More recently, we endeavoured to investigate the role of solvent polarity. Not only was solvent polarity found to have a pronounced effect on reaction rate but on the thermodynamics of complex formation as well, as measured by Isothermal Titration Calorimetry, under both aqueous and organic conditions. Our findings are important in the context of solvent choice in the preparation of related complexes.

References


