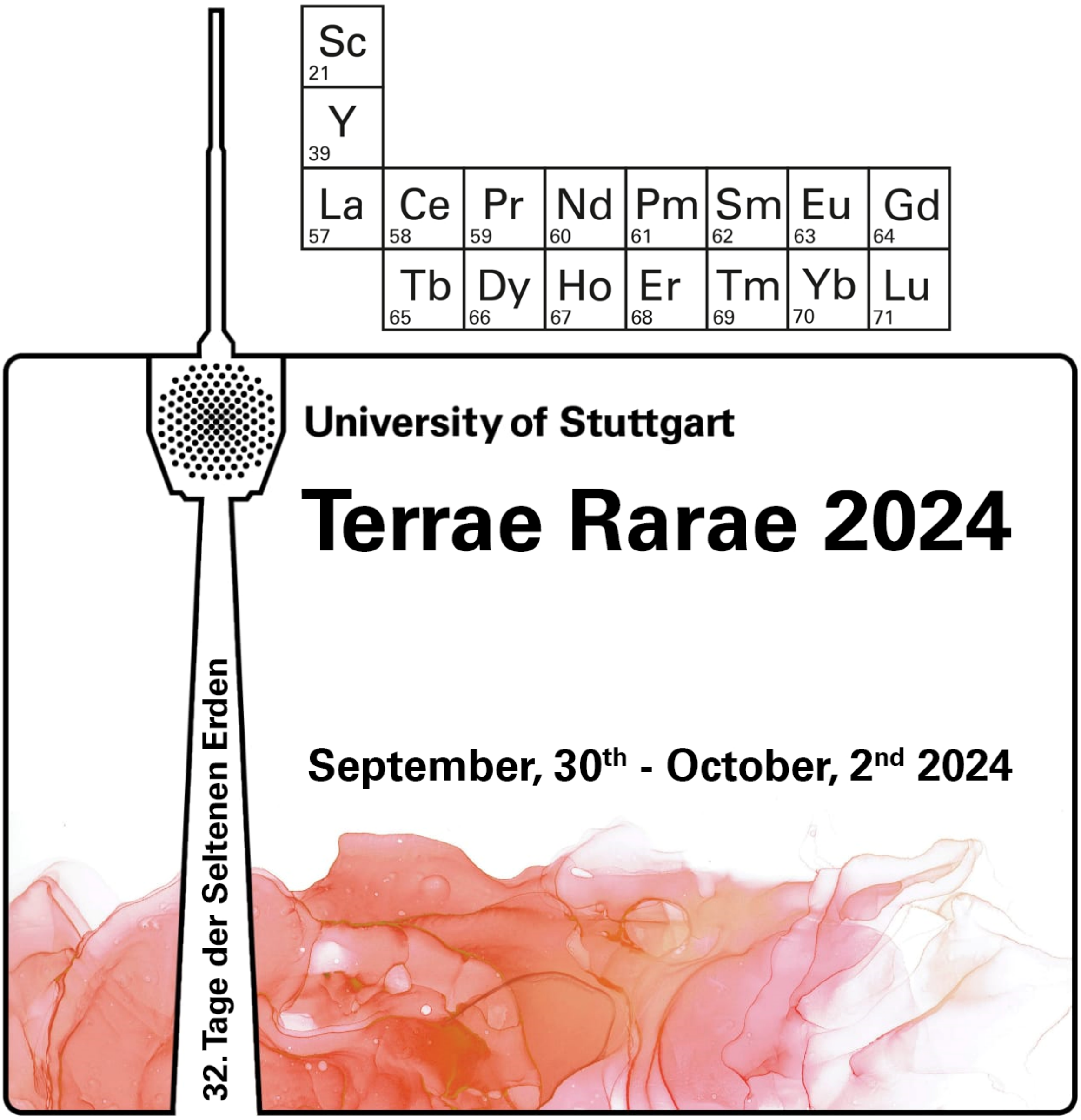
Book of Abstracts



University of Stuttgart

Terrae Rarae 2024

32. Tage der Seltenen Erden

September, 30th - October, 2nd 2024

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Contents

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Program

Monday, September 30th 2024

11:30 Begin registration

13:00 Opening

13:15 Plenary lecture: Dr. Florian Jaroschik − Twenty years of low-valent lanthanide chemistry with superbulky Cp ligands

14:10 Dr. Sandeep Kumar: Similarities and Differences in Benzene Reduction with Ca, Sr, Yb and Sm: Benzene^{2-} versus Benzene^{4-}

14:30 Dr. Salauat Kiraev: Photophysical Properties of Triazacyclononane Complexes with Thioanisolyl-Picolinates as a Function of the Lanthanide Ion

14:50 Dr. Dimitrii Roitershtein: N-Heterocyclic Tridentate Ligands for the Design of Rare Earth Complexes

15:10 − 15:40 Coffee break

15:40 Prof. Dr. Richard Layfield: The Pursuit of Exotic Oxidation States in Rare Earth Chemistry

16:00 Dr. Elisabeth Kreidt: Photoswitching lanthanoid luminescence with diazocines

16:20 Dina Akl: NIR-NIR Lanthanide Emitting Bioprobes for Invivo Imaging

16:40 Dr. Nicolaj Kofod: Non-Radiative Transitions in Lanthanide Photophysics

17:00 Nathan Alcock: Determination of actinide central-field covalency with 3d4f resonant inelastic X-ray scattering (RIXS)

17:20 Plenary lecture: Prof. Dr. Thomas E. Albrecht − Chemistry Beyond Plutonium

18:20 – 20:00 Poster session

Tuesday, October 1st 2024

09:00 Plenary Lecture: Prof. Dr. Susan Kauzlarich − Zintl Phases, Hydrides, and Electrides: Synthesis, Properties, and Applications

10:00 Dr. Svetlana Klementyeva: Lanthanide vertices in main group clusters

10:20 Villads Nielsen: Relating Electronic Structure with molecular structure of Neodymium(III) complexes

10:40 − 11:10 Coffee break

11:10 Dr. Jack Baldwin: Low-coordinate lanthanide complexes with bulky silylphosphide ligands

11:30 Dr. Sophie Corner: Rare Earth Diaza-diborolyl Complexes

11:50 Dr. Maxime Beauvois: Rare-earth-metal complexes bearing group 13 heterobenzene ligand

12:10 Dr. Johann Hlina: Towards Rare-Earth-Transition Metal Complexes for Application in Hydrofunctionalisation Catalysis

12:30 − 14:00 Lunch break

14:00 Plenary lecture: Prof. Dr. Peter Junk − Recent developments in redox transmetallation chemistry involving rare earth metals

15:00 Prof. Dr. Sjoerd Harder: Synthesis and Structure of a Mg(0)-Yb(II) Complex

15:20 Dr. Guillaume Bousrez: Using ionic liquid to generate anhydrous lanthanide Acetate Complexes

15:40 − 16:10 Coffee break

16:10 Prof. Dr. Anja-Verena Mudring: Molten Salts and Ionic Liquids for f-Element Chemistry

16:30 Prof. Dr. David Mills: Towards linear lanthanide single-molecule magnets

16:50 Prof. Dr. Gaël Ung: Circularly Polarized Luminescence of Curium and Americium molecular complexes

17:10 Prof. Dr. Thomas J. Sørensen: f-elements in solution, do we care?

17:30 Prof. Dr. Peter Roesky: Multidecker Sandwich Compounds

19:15 Conference dinner

Wednesday, October 2nd 2024

09:00 Plenary lecture: PD Dr. Oliver Janka − Rare earth based intermetallic aluminum compounds – structures and properties

09:55 Erich Turgunbajew: Rare Earth doped Borosulfates – Candidates for Quantum cutting?

10:15 Marvin Michak: In situ investigations on H/O exchange reactions in yttrium hydride oxide YHO

10:35 − 11:05 Coffee break

11:05 Prof. Dr. Stephan Hohloch: Putting the F in Phosphorus: Lanthanide Chemistry with Anilidophosphine Ligands

11:25 Prof. Dr. Fabrizio Ortu: New rare earth iminophosphoranomethanide complexes: synthesis, characterisation and applications

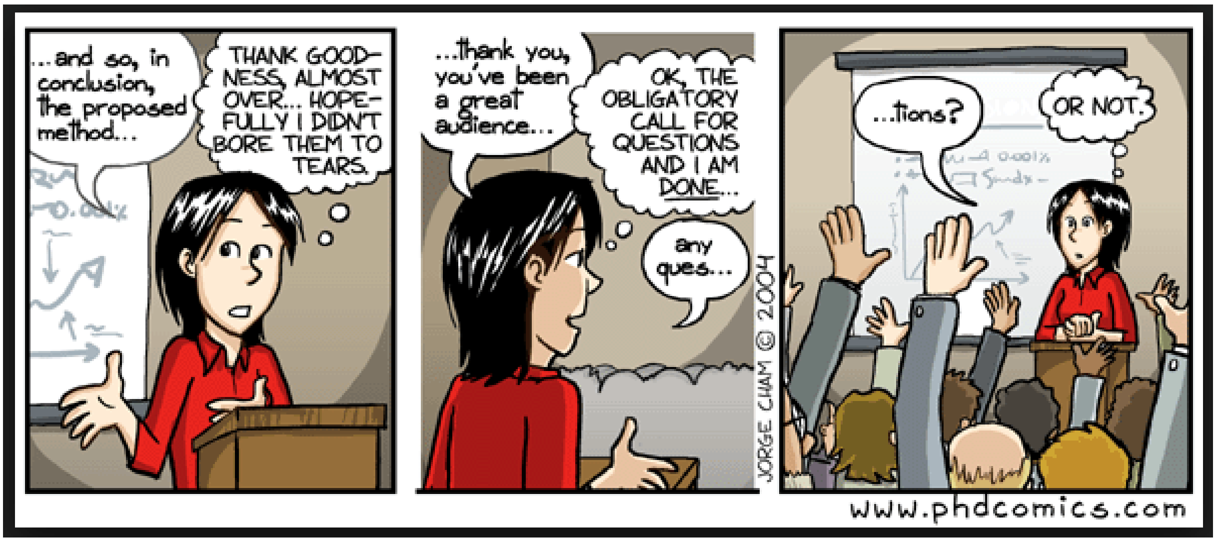
11:45 Jonas Malzacher: Donor-free samarium silylamides

12:05 Elias Alexopoulus: Phosphinoaryloxide Rare Earth Complexes for Frustrated Lewis Pair Chemistry

12:25 Prof. Dr. Gerd Meyer: Halides as Electrolytes for All-Solid-State Batteries

12:45 Uhr Closing remarks

Plenary Lectures



Twenty years of low-valent lanthanide chemistry with superbulky Cp ligands

Florian Jaroschik*

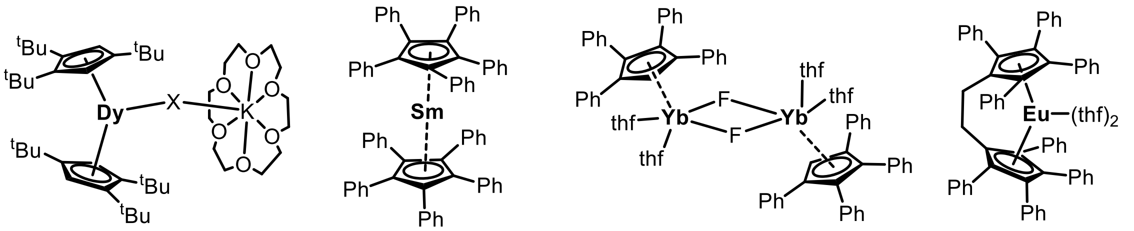
Institut Charles Gerhardt Montpellier, Univ. Montpellier, CNRS, ENSCM, 34090 Montpellier, France; E-Mail address: florian.jaroschik@enscm.fr

The seminal discovery of stable divalent organothulium complexes based on bulky cyclopentadienyl and phospholyl ligands in the early 2000s by Evans and Nief has triggered an immense development of "new" divalent lanthanide chemistry.[1] Nowadays, several ligand systems have provided divalent complexes for the whole lanthanide series (except radioactive Pm), unthinkable twenty years ago!

In this contribution, I will discuss recent discoveries and future directions on two very bulky ligand systems related to my personal experience:

(i) The highly sterically hindered 1,2,4-tris-*t*-butyl-cyclopentadienyl ligand (Cp^{ttt}) has played an important role in this emerging field of "new" divalent lanthanides, e.g. giving access to the first divalent Dy and Nd complexes.[1] This ligand is still under active investigation for small molecule activation with very reactive divalent lanthanide complexes.[2]

(ii) Superbulky polyarylCp ligands, such as C_5Ph_5 or C_5Ph_4H, are another very promising class of ligands for accessing divalent lanthanide complexes due to steric and electronic stabilization of the metal center.[3] Unfortunately, despite our efforts, "new" divalent lanthanide complexes have remained elusive with these ligands, so far. Nevertheless, unprecedented synthetic strategies to classical divalent lanthanide complexes starting from readily-available Ln(0) sources involving selective C-F or C-P bond activation, have been developed.[4,5] Other promising synthetic routes have also been explored, including Sterically-Induced-Reduction (SIR) methodologies and reductive dimerization of fulvenes.[6]



small molecule activation C-P activation SIR C-F activation reductive dimerisation

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Chemistry Beyond Plutonium

Thomas E. Albrecht

Department of Chemistry and Nuclear Science & Engineering Center, Colorado School of Mines,
Golden, Colorado 80401. tschoenzart@mines.edu

The elements in the actinoid series are firmly under relativistic control, but how do these effects manifest? In this talk we will explore the final elements for which macroscopic chemistry is possible – the late actinoids curium, berkelium, californium, einsteinium, and fermium – where relativistic effects might be most apparent. The combination of micro-scale synthesis and crystal growth with high-resolution, X-ray crystallographic measurements, a wide variety of spectroscopies, and relativistic theory has allowed us to better understand why the actinoids can deviate from the lanthanoids in structure, physical properties, and reactivity. The talk will conclude with current efforts to push the boundaries of the periodic table even further into the unknown.

Zintl Phases, Hydrides, and Electrides: Synthesis, Properties, and Applications

Susan M. Kauzlarich[1]*

[1]Department of Chemistry, University of California, Davis, CA 95616 United States
*Corresponding author's email: smkauzlarich@ucdavis.edu

Intermetallics, which combine two or more metallic or semimetallic elements, interest the solid-state community because of their variety of crystal structures. The requirements for efficient energy conversion from waste heat directly to electricity (thermoelectric property) for Zintl phases and our synthetic efforts with hydrides and electrides and their solid solutions will be presented. Zintl phases are a subset of intermetallics, compounds made from all metals. In the case of Zintl phases, they exhibit ionic and covalent bonding, resulting in semiconducting properties. Electrides are materials where an electron serves the role of an anion. I will provide the context of the important structural and electronic design of Zintl phases with the $Ca_{14}AlSb_{11}$ structure type, the utility of hydrides for synthesis of complex phases, introduce electrides, and the investigation of an electride-hydride solid solution.

Recent developments in redox transmetallation chemistry involving rare earth metals

Peter C. Junk

College of Science & Engineering, James Cook University, Townsville, Qld, 4811, Australia

Redox transmetallation has been a very versatile synthetic approach to organolanthanoid complexes. We have developed a very high yielding and simple approach using lanthanoid metals as starting materials and treating them with organomercury reagents such as $Hg(C_6F_5)_2$. These reactions generate $Ln(C_6F_5)_x$ (x = 2, 3 depending on the lanthanoid metal) and can be used to produce many other metal organic complexes of the lanthanoids by treatment with protic reagents such as acidic organics, amines and alcohols. Alternatively, the chemistry can be performed in a one-pot synthesis as a redox transmetallation/protolysis reaction where lanthanoid metal, $Hg(C_6F_5)_2$ and LH (protic reagent) can be added to produce LnL_x (x = 2, 3);

e.g. $Ln + Hg(C_6F_5)_2 + 2\,LH \rightarrow LnL_2 + Hg + 2C_6F_5H$ (for lanthanoid divalent metals)

While this chemistry works beautifully, as may be expected, it has attracted criticism for its involvement with the toxic mercury reagents, so more recently we have developed greener approaches in this synthetic endeavour. We have replaced the mercury reagents with organobismuth(III) and Ag(I) reagents in similar chemical pathways to synthesise the lanthanoid organometallics.1-3 The chemistry has required new approaches to organosilver reagents and has uncovered some unusual Bi chemistry. Most recent findings in this story will be covered in this presentation.

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Rare earth based intermetallic aluminum compounds – structures and properties

Oliver Janka*

Inorganic Solid State Chemistry, Saarland University, Campus C4.1, 66123 Saarbrücken, Germany, oliver.janka@uni-saarland.de

Intermetallic compounds are, especially with respect to their numerous applications in everyday life, an important class of materials. Amongst these, aluminum containing intermetallics are an interesting field of research, since aluminum is used as pure element or as alloys in all sorts of technical products. Amongst the many applications, the most important field is probably the transport sector. In the case of aluminum alloys, the handling during preparation and annealing plays an important role with respect to the mechanical properties of the final product [1]. Modern solid-state chemistry usually follows an opposing approach. Its goal is to synthesize novel binary, ternary or even multinary compounds and investigate their structures and physical properties.

The talk will cover our endeavors in the field of intermetallic rare earth aluminum compounds from different viewpoints, namely structural and crystal chemistry as well as spectroscopical and physical properties. These compounds exhibit a large structural diversity that can be examined with several different methods, addressing different aspects of the compound. X-ray diffraction methods can attribute the structural characteristics while quantum-chemical calculations can address the bonding. Solid-state ^{27}Al NMR spectroscopy for example can be used as an auxiliary tool to underline structure and bonding [2]. Especially the NMR spectroscopic studies, however, can only be conducted on the lanthanides without unpaired f-electrons.

The majority of the rare earth elements exhibit unpaired f-electrons, giving rise to a plethora of different physical properties such as heavy fermion behavior, superconductivity, intermediate valence or valence fluctuations. In order to investigate these properties, usually magnetic measurements are of key importance. While for most compounds, typical Curie-paramagnetic behavior alongside magnetic ordering can be observed, $Eu_2Al_{15}Pt_6$ [3] or $YbAl_3Pd_2$ [4] show a significantly different trend in their susceptibility measurements. By a combination of temperature dependent powder X-ray diffraction and physical property investigations, a temperature driven valence phase transition was established for these compounds, being a quite rare phenomenon in rare earth chemistry.

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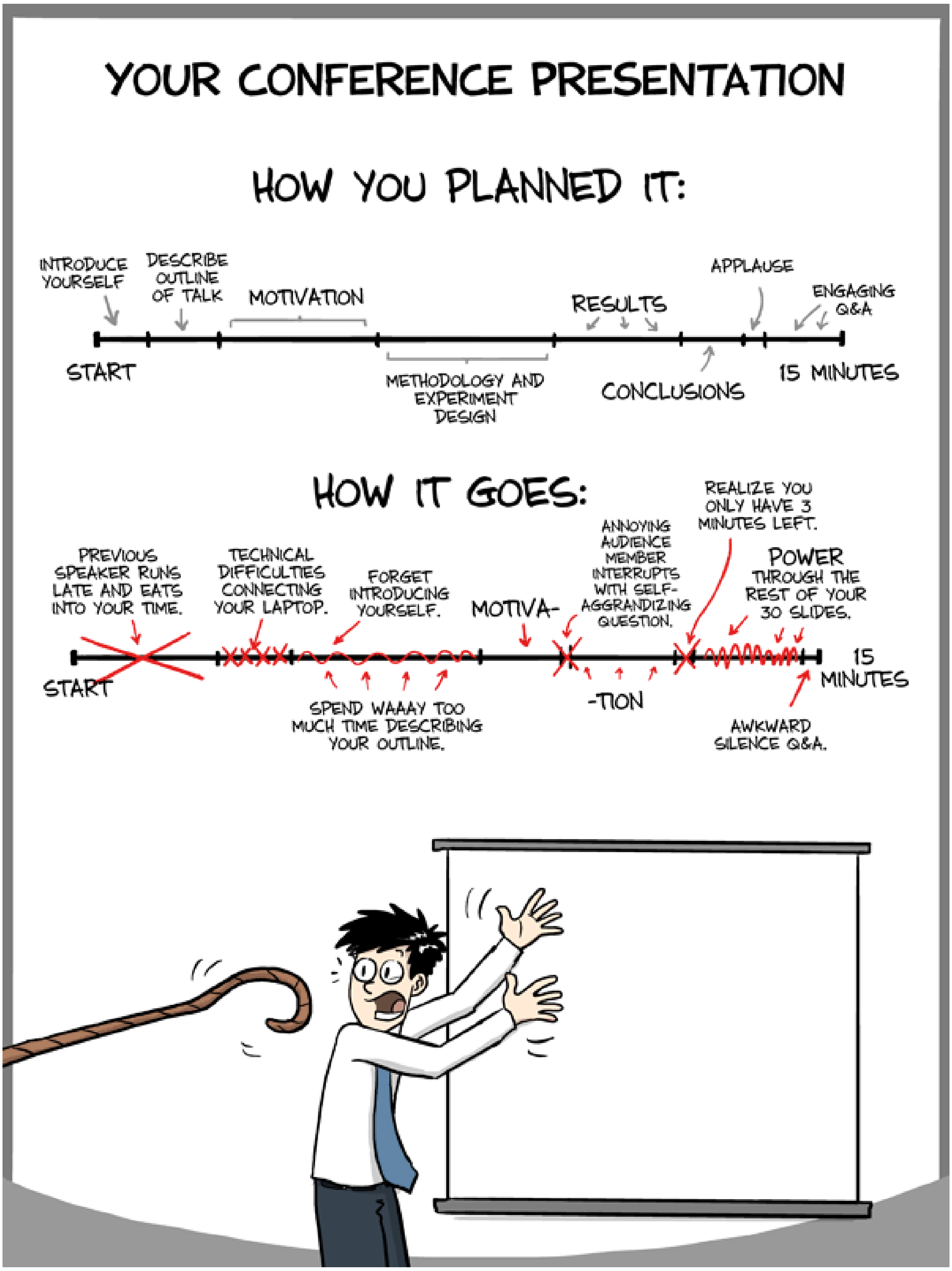
Short Talks


YOUR CONFERENCE PRESENTATION
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DESCRIBE OUTLINE OF TALK
MOTIVATION
RESULTS
APPLAUSE
ENGAGING Q&A
START
METHODOLOGY AND EXPERIMENT DESIGN
CONCLUSIONS
15 MINUTES
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TECHNICAL DIFFICULTIES CONNECTING YOUR LAPTOP.
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ANNOYING AUDIENCE MEMBER INTERRUPTS WITH SELF-AGGRANDIZING QUESTION.
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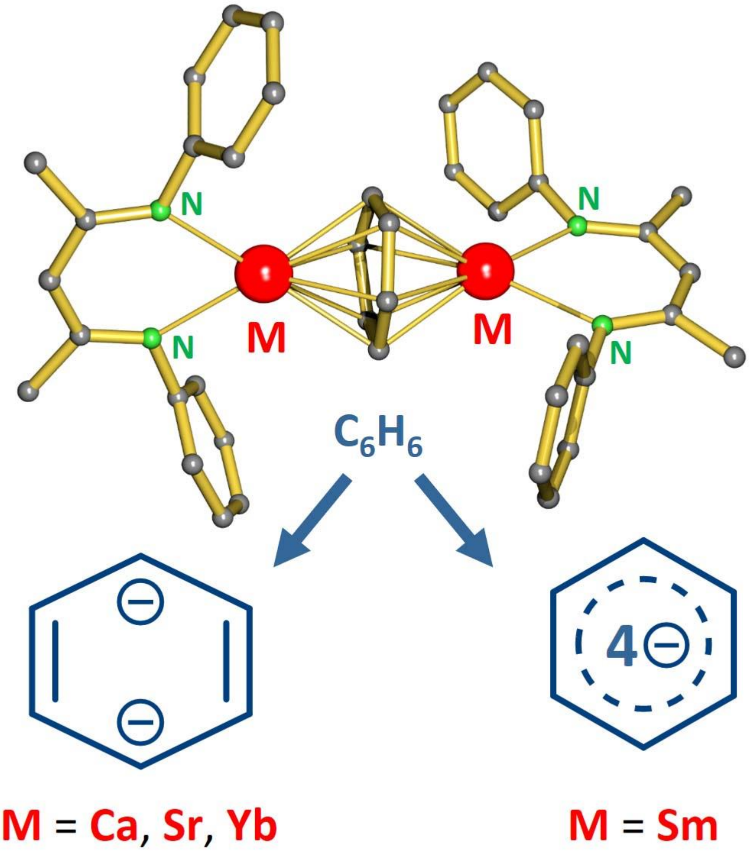
AWKWARD SILENCE Q&A.
15 MINUTES

Similarities and Differences in Benzene Reduction with Ca, Sr, Yb and Sm: Benzene^{2-} *versus* Benzene^{4-}

Sandeep Thakur Kumar, Nil Roig, Roger Monreal-Corona, Jens Langer, Mercedes Alonso and Sjoerd Harder*

Anorganische Chemie, FAU, Egerlandstrasse 1, 91058 Erlangen, GERMANY

Inverse sandwich benzene complexes are prone to metal oxidation state ambiguities. Based on comparisons between alkaline-earth and lanthanide metals, we now solve these oxidation state uncertainties by comparing structures of Ca/Yb and Sr/Sm pairs. The chemistry of Ca(II) is generally similar to that of Yb(II) and Sr(II) complexes match the corresponding Sm(II) and Eu(II) species [1]. However, comparing the inverse sandwich complexes of these four metals show remarkable differences [2]. This provides strong evidence for the formal formation of a Sm^{III}-benzene^{4-}-Sm^{III} complex, whereas a similar Yb complex should be regarded as Yb^{II}-benzene^{2-}-Yb^{II} species. We report syntheses, structure and a comprehensive DFT calculations.



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Photophysical Properties of Triazacyclononane Complexes with Thioanisolyl-Picolinates as a Function of the Lanthanide Ion

Salauat Kiraev[1]*, Dina Akl,[1] Lucile Bridou,[1] Maher Hojorat,[1] Guillaume Micouin,[1] François Riobé,[2] Sandrine Denis-Quanquin,[1] Akos Banyasz,[1] Olivier Maury[1]

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[2]Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB UMR 5026, F-33600 Pessac, France
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The molecular complexes of lanthanide(III) ions (Ln(III)) receive increased attention due to unique *4f-4f* emission properties. The Ln(III) luminescence consists of line-like transitions emitting in the visible and near-infrared (NIR) electromagnetic spectral regions with up to ms lifetimes. Such features offer detection in a time-resolved mode and an augmented signal-to-noise ratio useful for bioimaging applications. Ln(III) have similar coordination chemistry, allowing chelation with identical macrocyclic ligands, combined with the organic chromophores (antennae), that strongly absorb light and overcome the low Ln(III) extinction coefficient.[1]

One of the most ubiquitous chromophores for sensitising Ln(III) emission via one (1P) or two-photon (2P) absorption is the picolinate charge-transfer (CT) antenna with an electron donor on the *p*-position. The *p*-alkoxyphenyl derivatives efficiently transfer energy to the Eu(III) ions with emission quantum yields up to 48%, staining cells with optimal brightness.[2] However, the ethynyl-containing donor groups were shown to be unstable in the presence of trifluoroacetic acid[3] or undergoing a thiol-yne reaction during the peptide coupling.[4]

Thus, our objective was to prepare triple-bond deprived CT antennae by functionalising picolinates with thioanisolyl donors in a series of Ln(III) compounds with triazacyclononane (tacn, Figure 1) macrocycles. Tacn was alkylated with three thioanisolyl-picolinates, affording a new nonadentate ligand, which formed complexes with visible and NIR emitting Ln(III). The Eu(III) species had 44% quantum yield, while Tb(III) emission was quenched by oxygen due to thermal back energy transfer to the antenna triplet excited state. I will present the detailed results of Ln(III) spectroscopic studies, including transient absorption and nonlinear optics.[5]

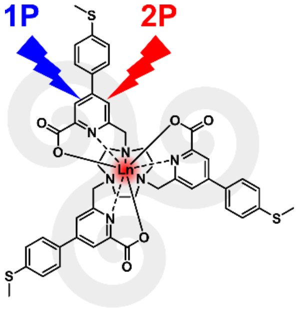

Figure 1. *The structure of target Ln(III) complexes of a new ligand with thioanisolyl-picolinate.*

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N-HETEROCYCLIC TRIDENTATE LIGANDS FOR THE DESIGN OF RARE EARTH COMPLEXEES

Dmitrii M. Roitershtein

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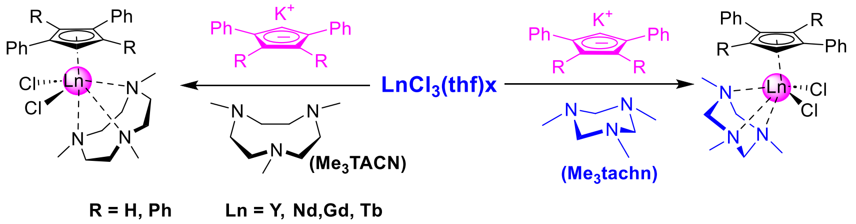
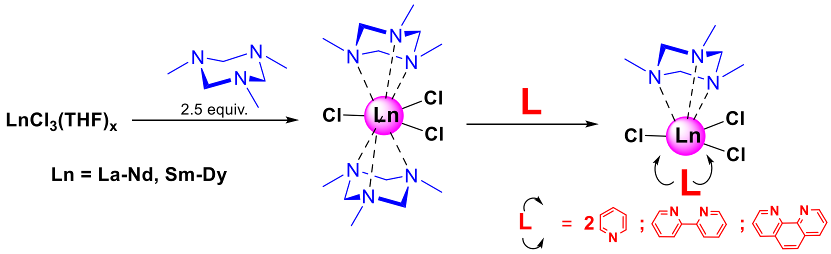
Tridentate N-heterocyclic ligands1,3,5-trimethyltriazacyclohexane (Me$_3$tach) and 1,4,7-trimethyltriazacyclononane (Me$_3$TACN) can be used as auxiliary ligands in the synthesis of different organolanthanides [Cp'LnCl$_2$(Me$_3$TACN)], and ([Cp'LnCl$_2$(Me$_3$tachn)] (Cp'=Ph$_2$C$_5$H$_3$, Ph$_3$C$_5$H$_2$, Ph$_4$C$_5$H)[1] and coordination compounds ([LnCl$_3$(Me$_3$tachn)$_2$], [LnCl$_2$(Me$_3$tachn)(thf)(μ-Cl)]$_2$, [LnCl$_2$(Me$_3$tachn)$_2$]$^+$[LnCl$_4$(Me$_3$tachn)]$^-$; [LnCl$_3$(Me$_3$TACN)(thf)].[2]



Different structural types of coordination compounds are stabilized by the use of Me$_3$tach in the design of REE complexes.



The lanthanides at the beginning of the series form complexes [LnCl$_3$(Me$_3$tach)$_2$], or [LnCl$_2$(Me$_3$tach)(thf)(μ-Cl)]$_2$, depending on the reaction stoichiometry; heavier lanthanides form complexes such as [LnCl$_2$(Me$_3$tach)$_2$]$^+$[LnCl$_4$L]$^-$, L=Me$_3$tach. The [LnCl$_3$L$_2$] complexes are extremely soluble in organic solvents, including hydrocarbons, and are characterized by an unusual planar trigonal structure of the {LnCl$_3$} fragment. Pr, Sm, Eu, Tb and Dy complexes luminesce in the visible region.

The talk will describe how the inexpensive and readily available tridentate ligand 1,3,5-trimethyl-1,3,5-triazacyclohexane can be used to open up new possibilities in the organometallic and coordination chemistry of rare earth metals.

lanthanide coordination compounds with Me$_3$tach and Me$_3$TACN will be discussed in the.

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The Pursuit of Exotic Oxidation States in Rare Earth Chemistry

Siddhartha De, Arpan Mondal, Richard A. Layfield*

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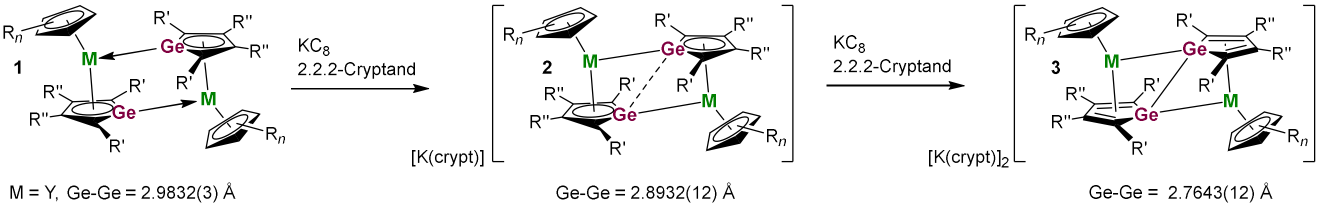
The divalent oxidation state is known for all rare earth elements except promethium. For the ‘classical’ divalent rare earths samarium, europium and ytterbium, molecular compounds have been known for many decades and are now widespread, whereas the ‘non-classical’ divalent oxidation state was established more recently for the other rare earths.[1] Cyclopentadienyl ligands have proven to be important for stabilizing divalent rare earths,[2] with other ligands such bulky amides and aryloxides also being used to good effect.[3]

Recently, we and others have begun using dianionic Group 14 metallole ligands Cp^E (E = Si, Ge, Sn, Pb) with trivalent lanthanides, with a focus on the development of metallocene-like single-molecule magnets (SMMs).[4] Currently, we are interested in exploring the idea that metallole ligands such as germoles can also stabilize divalent rare-earth elements.

Aiming to synthesize a series of divalent rare-earth hetero-metallocenes, reduction of the germole complexes **1** (M = Y, Gd, Dy) was attempted with one and two equivalents of KC_8, producing [**2**][K(crypt)] and [**3**][K(crypt)]$_2$, respectively (Scheme 1).[5] Upon reduction, a striking feature in the structures of **1**-**3** is a significant shortening of the transannular Ge···Ge distance to less than twice the van der Waals radius. Furthermore, whereas **1** and **2** feature butterfly-like $[M_2Ge_2]$ rings, the ring in doubly reduced **3** is perfectly planar.



Scheme 1. Synthesis of [**2**][K(crypt)] and [**3**][K(crypt)]$_2$ (M = Y, Gd, Dy).

The molecular structures of reduced germole complexes **2** and **3** invite the question: *where do the added electrons reside?* Using a combination of magnetic measurements, EPR and UV/vis spectroscopy and computational studies, an unusual non-innocent role for the germole ligand has been identified and will be described in the presentation.

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Photoswitching lanthanoid luminescence with diazocines

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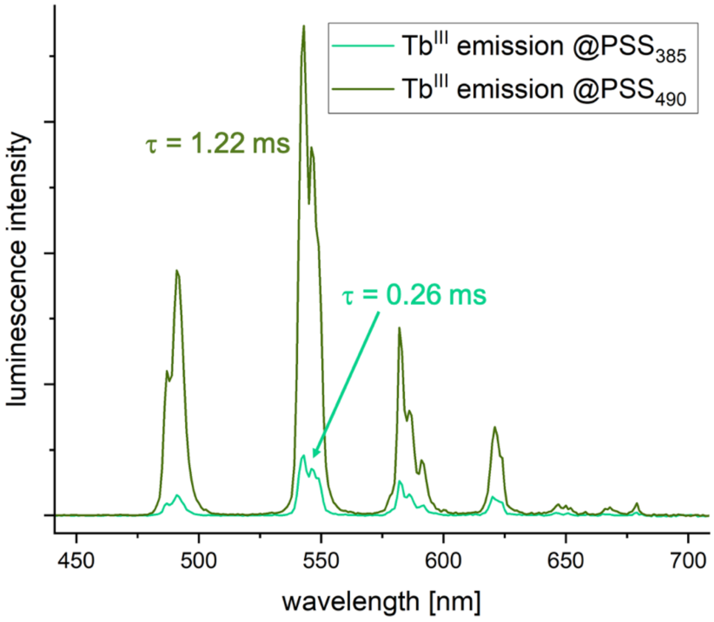
The unique photophysical properties of the lanthanoids make them especially suitable for the construction of stimuli responsive or smart materials. Among these, systems which can be controlled by light are particularly interesting and have a wide potential of applications ranging from bioimaging over anti-counterfeiting to information storage, just to name a few.[1-3]

The pioneering examples of photoswitchable lanthanoid complexes were dithienylethene-based Eu^{III} emitters, and today this is still the predominant motif in the literature, with considerably less examples employing different photoswitches or different lanthanoids.[4] As we were recently able to show, diazocines[5] are an alternative photoswitch scaffold with high potential for this purpose. In simple systems containing unfunctionalised diazocine and dipicolinic acid anions as antenna, we could photoswitch the luminescence intensities of Eu^{III}, Tb^{III} as well as Yb^{III} by up to 87 %. Eu^{III} and Tb^{III} luminescence lifetimes of the more luminescent states remained in the millisecond range, with a switching effect of up to 1 ms (79 %). Photophysical studies at 77 K and with direct excitation of the lanthanoid contributed to an unraveling of the operating mechanisms.



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NIR-NIR Lanthanide Emitting Bioprobes for Invivo Imaging

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What is more needed than a long luminescence lifetime and sharp emission in the infrared spectral range when it comes to *in vivo* imaging? Thanks to the lanthanides that meet these remarkable spectroscopic properties, which make them our subject of interest [1].

Our main concern in this thesis is the synthesis of new bioprobes using ligands incorporating π-conjugated systems that allow an efficient sensitization of excited states of lanthanide ions by one or two-photon processes, aiming to extend these probes to the NIR spectral range corresponding to the biological transparency window and which opens the way to deep imaging of biological tissues (biopsy) and in vivo imaging. π-conjugated systems, based on donor-acceptor moieties, were developed and functionalized on different macrocycles to efficiently sensitize NIR emitters namely Sm, Nd, and Yb, through a process known as “antenna effect”[2]. Complexes are then bioconjugated to a peptide and internalized into the cells or in zebrafish[3]. Interestingly, living cells were nicely stained by the Sm complex, which gave access to a NIR-NIR bio-probe (fig.1).

In the particular case of Nd, it was never possible to achieve a pure two-photon sensitization (2PA) in literature due to the domination of the f-f transitions in the 2P excitation range (700-900 nm). Seeking our goal, and to overcome this issue, we have prepared a set of different red-shifted sensitizing antennae with absorption covering a wide range of the spectrum; recently extended up to 500 nm. This will make it possible to excite its corresponding Nd complex at 1000nm by 2PA for the first time.

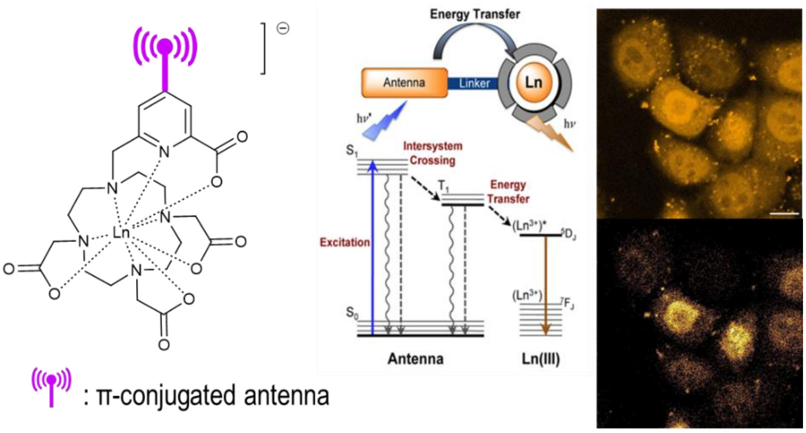

Figure 1. General presentation of the studied complexes (left), Sensitizing effect of the antenna (middle), Bioimage of a cell labelled by Samarium complex (right).

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Non-Radiative Transitions in Lanthanide Photophysics

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In 1963, Kropp and Windsor reported enhanced luminescence from samples of Eu^{3+} and Tb^{3+} in D_2O over samples in H_2O.[1] This effect was attributed to energy transfer to vibrationally excited states of small-atom oscillators. Horrocks and Sudnik realized that this effect could reveal the number of coordinated solvent molecules in solution.[2] Together with the modified Horrocks method formulated by Beeby et al. this remains among the most powerful tool for characterizing lanthanide complexes in solution.[3] In this work, we expand on this approach, using the methodologies of molecular photophysics to reveal the underlying mechanisms of the process. By mapping the excited state dynamics of simple Ln^{3+} complexes, we can quantify the quenching processes to OH and OD oscillators.[4,5] We find that the non-radiative quenching processes are an order of magnitude faster than all other relaxation pathways from the lanthanide excited state. We also study the effect of the OH vibrational oscillator, Ln-OH distance, temperature and dynamic effects.[6,7]

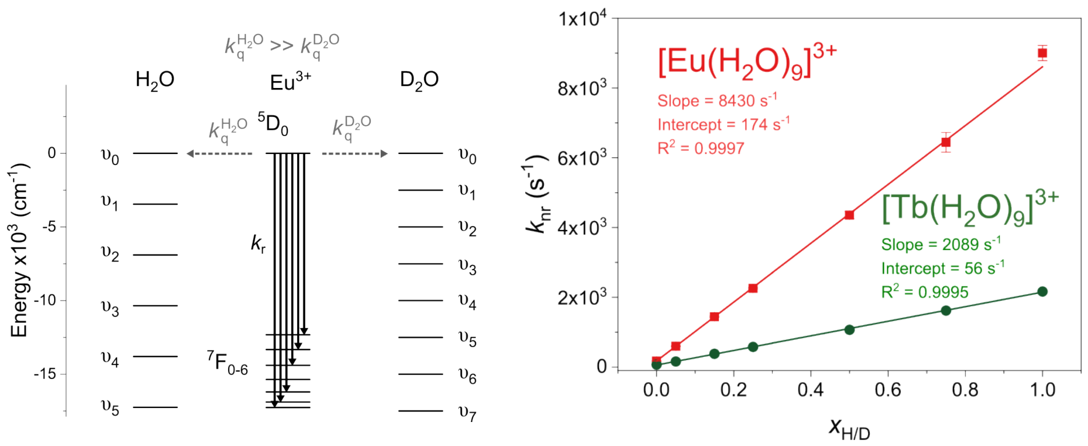

Figure 1. (left) Simplified schematic of the energy levels involved in lanthanide photophysics (right) Rate of non-radiative energy transfer for $[Eu(H_2O)_9]^{3+}$ (red) and $[Tb(H_2O)_9]^{3+}$ (green) in mixtures of protonated and deuterated solvent.

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Determination of actinide central-field covalency with $3d4f$ resonant inelastic X-ray scattering (RIXS)

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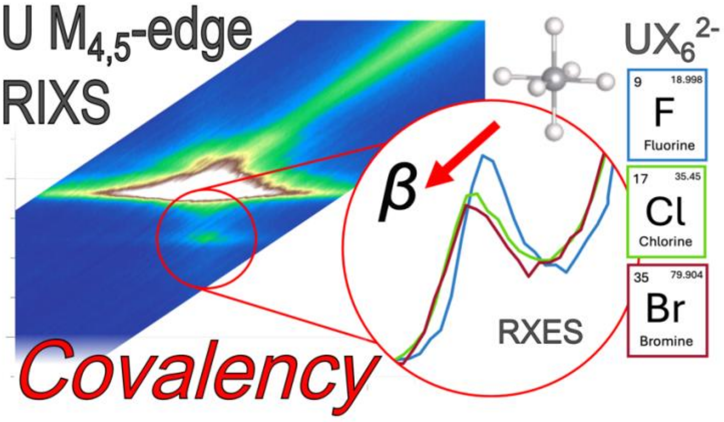
Understanding the nature of actinide-ligand bonding is of paramount importance to the radiochemistry community for both fundamental chemistry and the implications for nuclear fuel processing and radioactive waste clean-up. However, actinide-ligand bonding interactions are complex and notoriously challenging to predict. Our work addresses this challenge by developing new spectroscopic strategies for evaluating actinide-ligand bonding, using resonant inelastic X-ray scattering (RIXS) techniques.

We present a systematic investigation of uranium(IV) hexahalides, $[UX_6]^{-2}$, where X=F, Cl, Br, highlighting the sensitivities of several RIXS techniques to specific aspects of uranium electronic structure and bonding. Specifically, new insights from $M_{4,5}$-edge *3d4f* RIXS are presented, demonstrating the technique as a probe of uranium(IV)-ligand bond covalency. Measurements are supported by *ab initio* calculations and interpreted using ligand field multiplet theory.

The presented techniques are predicted to be universal to actinide and ligand element identity, actinide oxidation state, and actinide coordination symmetry. Consequently, these methods are expected to contribute widely to actinide analytical chemistry and material characterisation.



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Lanthanide vertices in main group clusters

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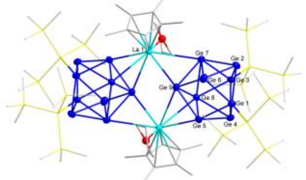
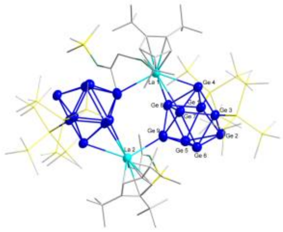
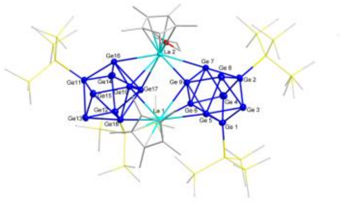
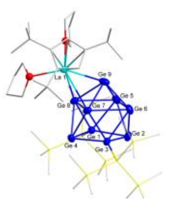
Over the past decades, a great progress was achieved in the coordination chemistry of f-elements. The rare earths molecular compounds with heavy p-block elements have recently gained significant attention. While the solid-state structural chemistry of rare earth tetrelides was being extensively studied, the coordination chemistry of f-elements with heavy tetrels has been fast asleep so far. Recently, we have shown the di-substituted dianionic metalloid germanium cluster $[Ge_9Hyp_2]^{2-}$ (Hyp = $Si(SiMe_3)_3$) with incomplete shielding of the cluster core readily forms complexes with divalent lanthanides of the common formulae $[(thf)_5Ln(Ge_9Hyp_2)]$ (Ln = Eu, Sm).[1] In contrast, lanthanide triiodides LnI_3 (Ln = Eu, Sm, Yb) reacted with $[Ge_9(Hyp)_2]^{2-}$ resulting in the one-electron oxidation and subsequent enlargement of the cluster core to Ge_{18} ones.[2]

Using cyclopentadienyl lanthanum complexes with lower oxidation ability than LaI3 we expected higher stability of lanthanum coordination environment. Indeed, we succeeded in the isolation of four lanthanum complexes with coordinated di-silylated metalloid germanium cluster $[Ge_9(Hyp)_2]^{2-}$: $[Cp^*La(thf)(\eta^{2,3}\text{-}Ge_9(Hyp)_2)]_2$ (**1**), $[Cp^{ttt}La(NCCH_2C(Me)NSiMe_3)(\eta^{1,3}\text{-}Ge_9(Hyp)_2)]_2$ (**2**), $[Cp^*La(thf)(\eta^{2,3}\text{-}Ge_9(Hyp)_2)][Cp^*La(\eta^{2,3}\text{-}Ge_9(Hyp)_2)]$ (**3**) and $[Cp^{ttt}La(thf)_2(\eta^{3}\text{-}Ge_9(Hyp)_2)]$ (**4**) (Cp = Cp* - pentamethylcyclopentadienyl and Cp^{ttt} – 1,2,4-tri(tert-butyl)cyclopentadienyl). Thus, we have significantly expanding the range of trivalent rare earth complexes with very rare Ln(III)-Ge bonds.[3]

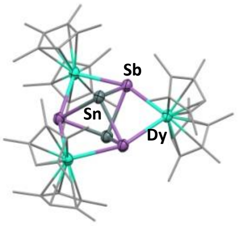


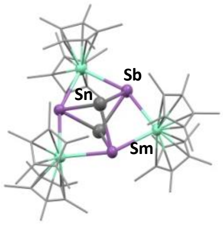






A number of new clusters with Ln-Sb *exo*-bonds $[K(2.2.2\text{-crypt})]_2[Sn_2Sb_3(LnCp^{\#}_2)_3]$ (Ln = Dy, Tb, $Cp^{\#}$ = C_5Me_4H) has been prepared by the reaction of Zintl salt $[K(2.2.2\text{-crypt})]_2[Sn_2Sb_2]$ with $Cp^{\#}_3Ln$ in o-diflourobenzene and crystallized by layering with toluene. Dy compound reveals single magnet molecule properties. Analogous samarium complex $[K(2.2.2\text{-crypt})]_2[Sn_2Sb_3(SmCp^*_2)_3]$ (Cp^* = C_5Me_5) with bulkier Cp* ligand has been obtained in the reaction of $[K(2.2.2\text{-crypt})]_2[Sn_2Sb_2]$ with samarocene $Cp^*_2Sm(THF)_2$ by the similar work-up procedure.





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Relating Electronic Structure with molecular structure of Neodymium(III) complexes

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Neodymium(III) is a near-infra red emissive and magnetic ion, which has found use in various high-technology applications. Yet, accurate predictions of the luminescence and magnetic properties of neodymium(III) based on the coordination environment remain to be done. Difficulties of measuring neodymium(III) in solution include the high multiplicity of electronic transitions and typical low quantum yields. This can be overcome with good instrumentation where high-resolution luminescence spectroscopy allows the crystal field of neodymium(III) to be unambiguously resolved in solution, taking into account the relative thermal populations in the relevant multiplets.[1,2] Using *ab initio* calculations, such as CASSCF, we are able to reproduce well the observed energy splitting in single crystals where the structure is known.[3] By combining these methods, we attempt to establish structure-property relationships for neodymium(III). We use this to model the structure of the aqua ion as shown in Figure 1 and to relate the electronic structure with the point group symmetry that dictates the crystal field splitting.[3,4]

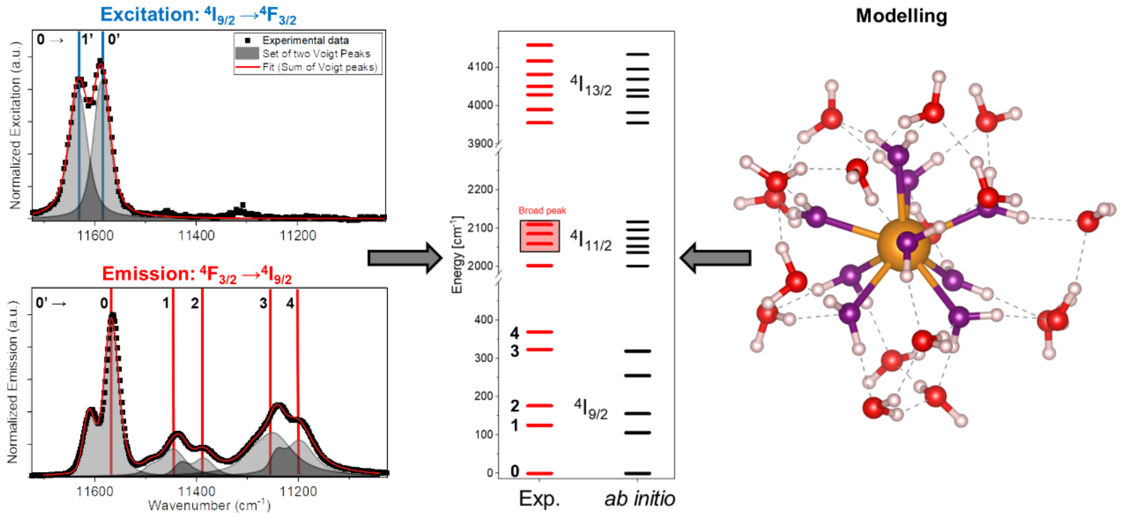

Figure 1. The electronic structure of Neodymium(III) in water is resolved using combined excitation and emission spectroscopy (left) and modelled through *ab initio* calculations and geometry optimizations (right). The observed and modelled electronic structure is then compared (middle).

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Low-coordinate lanthanide complexes with bulky silylphosphide ligands

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Lanthanide (Ln) ions are hard Lewis acids, and prefer to interact with hard Lewis bases; this is evidenced by the rich coordination chemistry found for ligands containing oxygen and nitrogen donor atoms.[1] Conversely, there is a paucity of literature on Ln complexes which contain ligands that incorporate donor atoms from the second row of the periodic table, for example, sulfur or phosphorus.[1]

One ligand that has been intrinsic to the development of Ln coordination chemistry is bis(trimethylsilyl)amide, $\{N(SiMe_3)_2\}$, which has supported fascinating advances for over half a century since the disclosure of the synthesis of the landmark trigonal pyramidal complexes $[Ln\{N(SiMe_3)_2\}_3]$.[2,3] The chemistry of the softer heavy pnictogen analogue bis(trimethylsilyl)phosphide, $\{P(SiMe_3)_2\}$, is far less developed for the Ln. Only a handful of structurally characterised examples of Ln complexes containing this phosphide ligand have been reported previously, namely $[Y\{P(SiMe_3)_2\}_2\{\mu\text{-}P(SiMe_3)_2\}]_2$[4], $[Ln\{P(SiMe_3)_2\}_3(THF)_2]$ (Ln = Nd, Tm) [5,6] and $[Sm\{P(SiMe_3)_2\}\{\mu\text{-}P(SiMe_3)_2\}_3Sm(THF)_3]$.[7]

Here, we expand upon the Ln chemistry of $\{P(SiMe_3)_2\}$ through the synthesis of a series of complexes, $[Ln\{P(SiMe_3)_2\}_3(THF)_2]$ (Ln = La, Ce, Pr, Nd, Sm) (**1-Ln**). Solution state $^{31}P\{^1H\}$ NMR spectroscopy reveals large chemical shifts whereas the geometries of the phosphorus centres can be observed from solid-state ^{31}P NMR MAS spectroscopy.

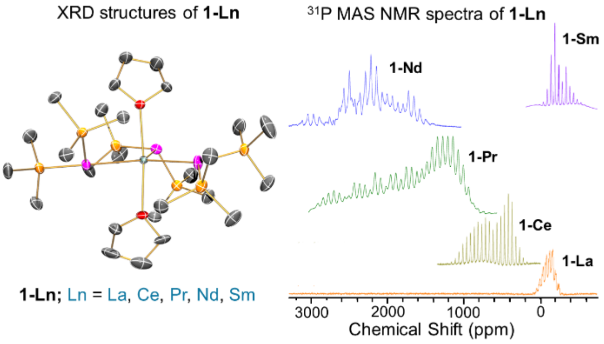

Figure 1. SC-XRD structures of **1-Ln** (left) and ^{31}P NMR MAS spectra of **1-Ln** (right).

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Rare Earth Diaza-diborolyl Complexes

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Substituted cyclopentadienyl (Cp^R; $\{C_5R_5\}$) ligands have been used extensively in rare earth chemistry, where they provide steric and electronic stabilization through formally occupying multiple coordination sites and balancing the charge of the highly Lewis acidic metal centers. These ligands have supported high-performance rare earth single molecule magnets (SMMs),[1] catalysts[2] and previously unattainable divalent rare earth complexes.[3]

By adapting literature procedures,[4] we have prepared a diaza-diborolyl ligand, $\{^t\mathrm{BuCH_2C(BMe)_2(N^iPr)_2}\}$, an isoelectronic analogue of Cp^R with more localized electron distributions and lower rigidity. We have used this ligand to prepare homoleptic and heteroleptic Y borohydride complexes *via* salt metathesis methods. Reduction of such complexes proceed by N-N bond cleavage to form a trianionic ligand, whilst hydride abstraction reactions give cationic complexes with predominantly axial ligand fields (Figure 1). All complexes were characterized by multinuclear NMR and ATR-IR spectroscopy, elemental analysis, single crystal XRD and DFT calculations. We have recently expanded the chemistry of these ligands to La and U complexes.

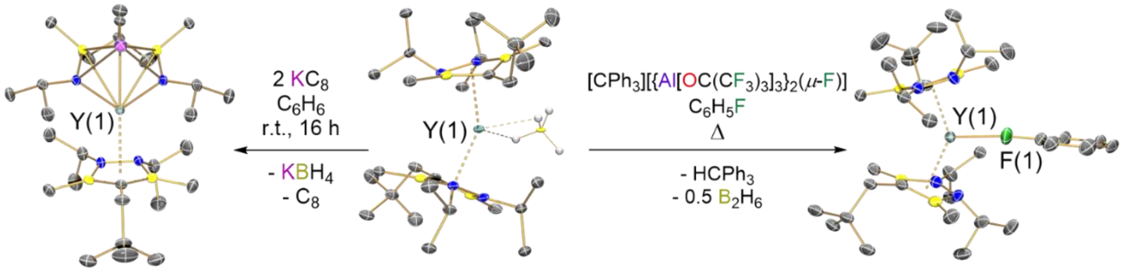

Figure 1. Synthesis of yttrium(III) diaza-diborolyl complexes.

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Rare-earth-metal complexes bearing group 13 heterobenzene ligand

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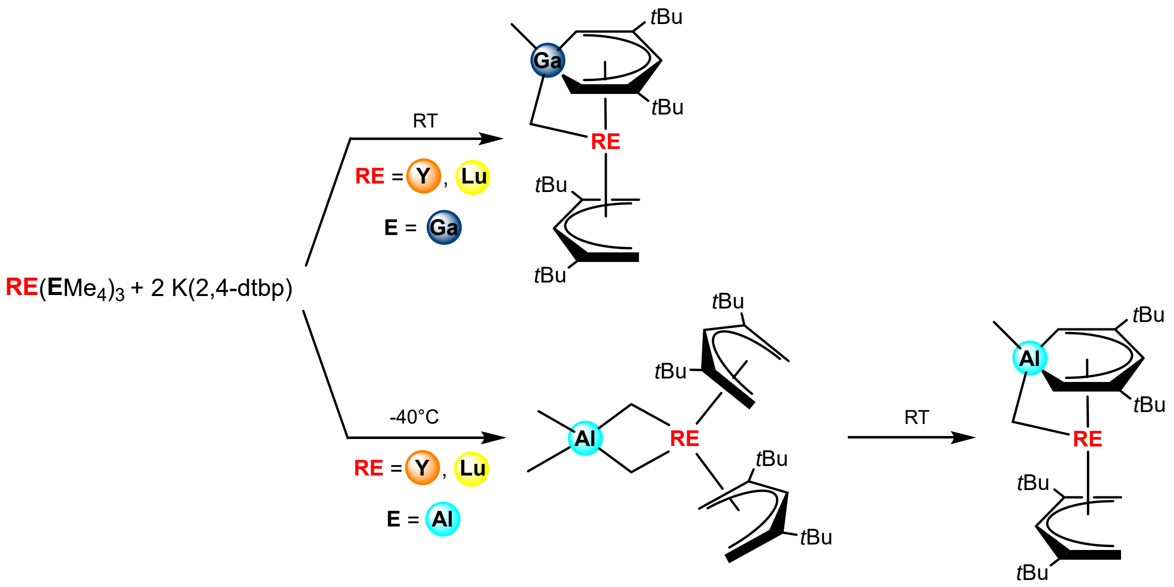
Following the synthesis of the first anionic aluminabenzene in 2014 by Yamashita et al. [1] and the synthesis of transition-metal complexes bearing it, [2] the goal of designing new rare-earth-metal complexes supported by an aluminabenzene ligand became very attractive. To achieve this goal, our group investigated the reactivity of homoleptic rare-earth-metal tetramethylaluminates toward potassium pentadienides. The resulting half-open sandwich complexes can react further to form the desired aluminabenzene complexes. [3] These complexes have shown unprecedented reactivities such as single-component catalyst behavior in 1,3-diene polymerization. Herein new complexes including the ones obtained with gallium instead of aluminum will be presented.



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Towards Rare-Earth-Transition Metal Complexes for Application in Hydrofunctionalisation Catalysis

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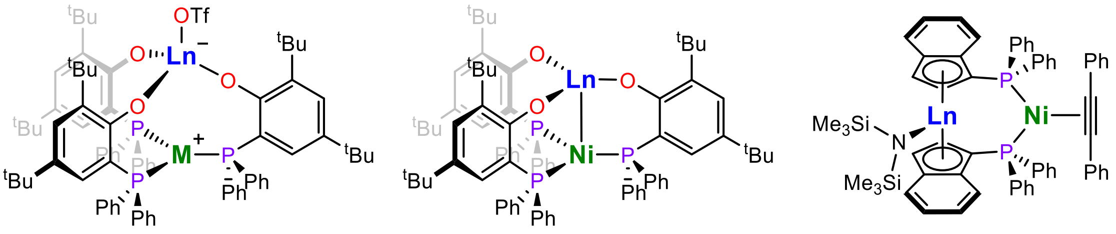
The chemistry of complexes featuring both early and late transition metals provided insight into aspects such as metal-metal interaction and cooperative reactivity. In contrast to the early transition metals, the elements of the f-block have received significantly less attention. Previous examples were reported by the groups of Kempe and Roesky exploring aspects such as intermetallic bonding.[1,2] Only recently, Lu and co-workers demonstrated the application of rare-earth-transition metal complexes in hydrogenation catalysis.[3]

In this contribution, our work on heterobimetallic rare-earth-late transition metal complexes based of supporting phosphinophenolate and -indenyl ligands will be present (Figure 1).[4,5] For the latter systems, we recently demonstrated its utility to catalyse hydroamination reactions.[4] Expanding this chemistry to heterobimetallic systems, we investigated complexes featuring late transition metals such as nickel or palladium. As part of this work, we also investigated the reactivity of these rare-earth-group 10 metal complexes in hydroamination and alkyne oligomerisation catalysis.



M = Cu, Ag; Ln = La, Sm, Yb, Y

Ln = La, Sm

Figure 1. Selected examples of heterometallic rare-earth-transition metal complexes.

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Synthesis and Structure of a Mg(0)-Yb(II) Complex

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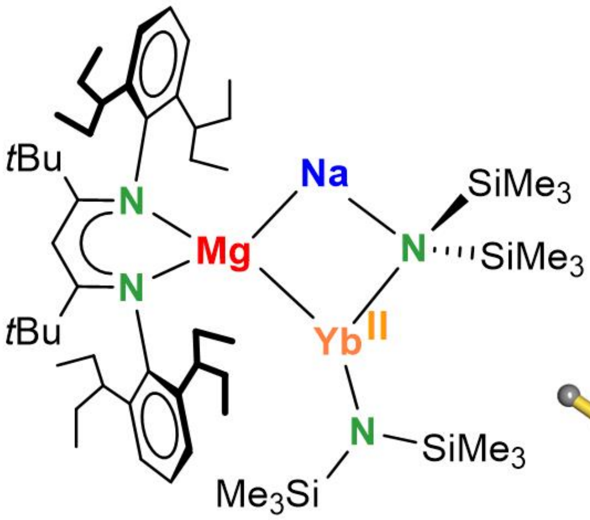
Use of superbulky β-diketiminate ligands has led to some remarkable breakthroughs in alkaline-earth metal chemistry, among which N_2 activation at Ca [1] and the isolation of first Mg(0) complexes [2].

Herein, we discuss the formation of a Mg(0)-Yb(II) complex [3]. Its crystal structure shows the first evidence for s-block metal-lanthanide bonding. We discuss syntheses, structures and DFT-analyses.



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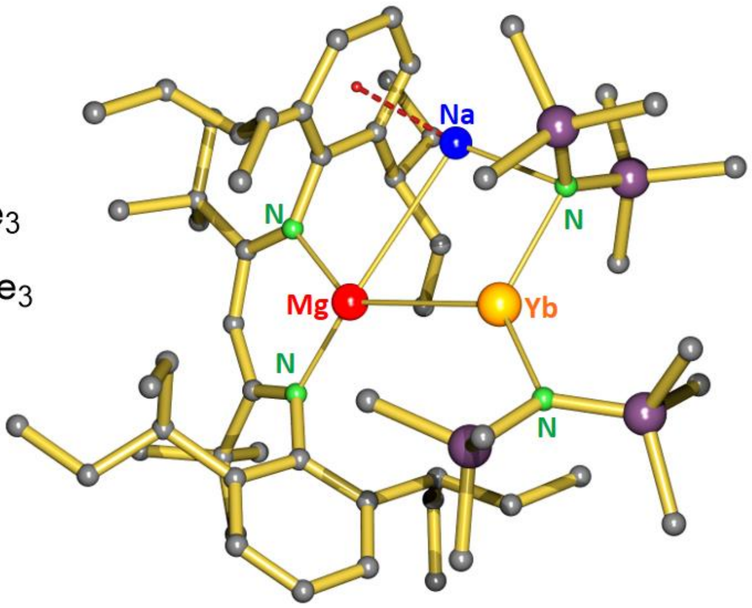

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Using ionic liquid to generate anhydrous lanthanide acetate complexes

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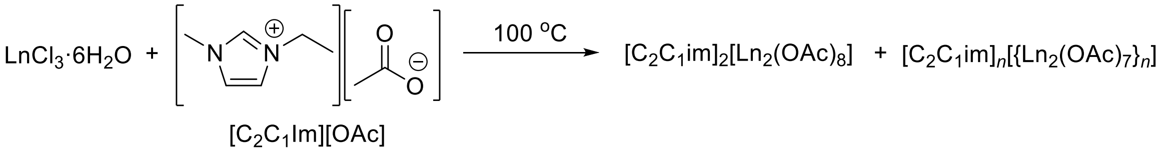
The generation of anhydrous lanthanide acetate complexes is always a challenge. The procedure usually involves anaerobic atmosphere [1] and removing potential water molecules from stable complexes requires an important amount of energy.

Ionic Liquids (ILs) are low melting salts (melting point below 100 °C) and are a class of compounds known for their interesting properties like low-vapor pressure and high thermal stability. [2]

As the access to anhydrous lanthanide complexes has been limited because of their high affinity for oxygen, we have been exploring the use of ILs to dehydrate metallic salts. With 1-ethyl-3-methylimidazolium acetate $[C_2C_1Im][OAc]$ as reagent and medium, we were able to obtain anhydrous compounds from hydrated lanthanide chloride salts ($LnCl_3·6H_2O$, with (Ln = Pr, Nd, Sm-Lu) in ambient atmosphere. [3] This combination can generate two different complexes, a dimer and a polymer (Scheme 1). The formation of the final product is mainly driven by the size of the metal center as well as the ratio Ln/IL.



Scheme 1. General procedure to synthesize the two anhydrous lanthanide complexes (Ln = Pr, Nd, Sm-Lu).

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Molten Salts and Ionic Liquids for f-Element Chemistry

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The differentiation between molten salts and ionic liquids appears to be somewhat arbitrary. When speaking about molten salts it is typically referred to salts with a melting point way above 100 °C, typically composed of inorganic ions. In contrast, the term ionic liquids is used to address molten salts that are liquid at room temperature and below. These at a minimum contain one, if not two, organic ions. In the context of f-element chemistry both classes, molten salts and ionic liquids have their merits, in particular as reaction media.

The employment of simple metal halide molten salts as fluxes allow the synthesis of f-element compounds, in particular intermetallic phases at temperatures way below the melting points of the elements. Because of this, phases can be realized that are not thermodynamically stable. Even for simple binary systems, new phases can be found that have not been reported before.

The use of ionic liquids allow to further decrease the reaction temperatures and allow the use of organic components as reaction partners, which, because of decomposition, is not possible in molten salts. Compared to reaction in traditional solvents, employing the ionic liquid with its organic component both, as the solvent and reaction partner, removes the competition of traditional solvent molecules about coordination to the f-element.

Thus, employing molten salts and ionic liquids as reaction media allow for the synthesis of new compounds, unattainable through traditional synthesis – be it high temperature solid state synthesis or wet chemistry.

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Towards linear lanthanide single-molecule magnets

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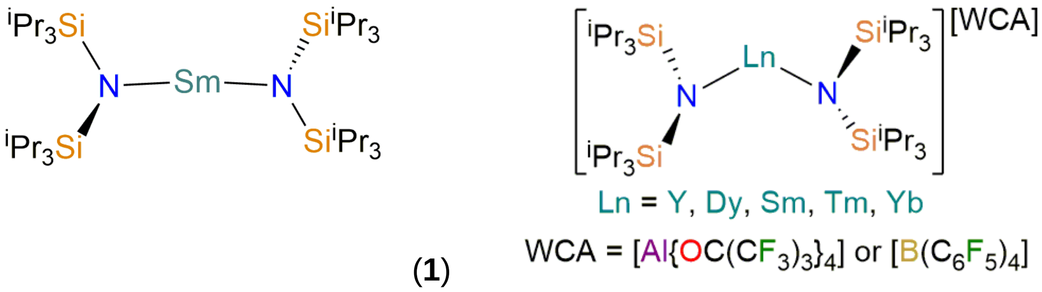
Linear dysprosium and terbium single-molecule magnets (SMMs) should provide the largest energy barriers to magnetic reversal (U_{eff}) and the highest hysteresis temperatures (T_{H}).[1] In 2015 we reported the first near-linear lanthanide (Ln) complex [Sm{N(SiMe$_3$)$_2$}$_2$] (**1**), and predicted that a linear Dy(III) analogue could exhibit a record U_{eff} of *ca*. 2600 K.[2] In the interim we have reported the bent Ln(III) complexes [Ln{N(SiMe$_3$)$_2$}$_2$][WCA] (**2-Ln**; Ln = Sm, Tm, Yb, WCA = [B(C$_6$F$_5$)$_4$]; Ln = Y, Dy, WCA = [Al{OC(CF$_3$)$_3$}$_4$]);[3,4] the Dy(III) analogue showed a lower than predicted U_{eff} = 950 ± 30 K, due to a combination of the bent N–Dy–N angle (128.7(2)°) and the flexible Dy coordination sphere facilitating magnetic relaxation. Here we report efforts to synthesise Dy bis-amide complexes with N–Dy–N angles closer to linearity, in order to provide two-coordinate Ln SMMs with U_{eff} and T_{H} values that rival those containing isolated dysprosocenium cations.[5,6]



(**1**) (**2-Ln**)

Fig. 1. Lanthanide complexes **1** and **2-Ln**.

Acknowledgments: We thank the European Research Council (StG-851504 and CoG-816268), the EPSRC (EP/R002605X/1, EP/P001386/1, EP/S033181/1 and EP/T011289/1), the Royal Society (URF191320), the EPSRC UK National Electron Paramagnetic Resonance Service, and the University of Manchester Computational Shared Facility.

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Circularly Polarized Luminescence of Curium and Americium molecular complexes.

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Circularly polarized luminescence (CPL) is the preferential emission of right- or left-handed circularly polarized light. Because of the core-like nature of 4f orbitals, the split between energy levels of 4f-elements is larger through spin-orbit coupling than through crystal field splitting. In 4f-elements, each luminescent transition between spin-orbit coupling term levels is associated with a specific transition type, resulting in different relative CPL strengths. More importantly, CPL spectroscopy allows for better distinction of the individual components resulting from crystal field splitting, though these transitions' selection rules are not well understood.

We will show that by employing appropriate ligands, well-resolved CPL spectra of a trans-plutonium elements (Am and Cm) can be observed. More importantly, the quality of the data allowed for the deconvolution of the energy levels providing the first experimental mapping of the fundamental electronic structure of a Cm(III) coordination complex in solution.

f-elements in solution, do we care?

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Coming from fluorescence spectroscopy and a tradition where knowing the speciation in solution is a pre-requisite [1-2], lanthanide solution chemistry is interesting. We can—to some extend—agree on an oxidation state for lanthanides ions in water and polar solvents, but argue ion pairing, coordination numbers, and sometimes size. If we spend years studying a system, as in the case of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetracarboxylate (DOTA) ligand, we are fairly certain about the **constitution** of the lanthanide complexes formed. For the [Ln.DOTA]$^-$ complexes it is the **conformations** that become tricky. The DOTA complexes exist in four forms, two sets of enantiomers, each with a specific set of properties. This we understand, but any variation on the ligand scaffold introduces additional complexity and new properties [3]. A complexity that often has made crystalline systems the favorite subject of study, but I will here present evidence (Fig. 1) that our tools are so evolved that we should be able to start looking at solutions. That does not answer the question in the title, but I will claim that we are able to care.

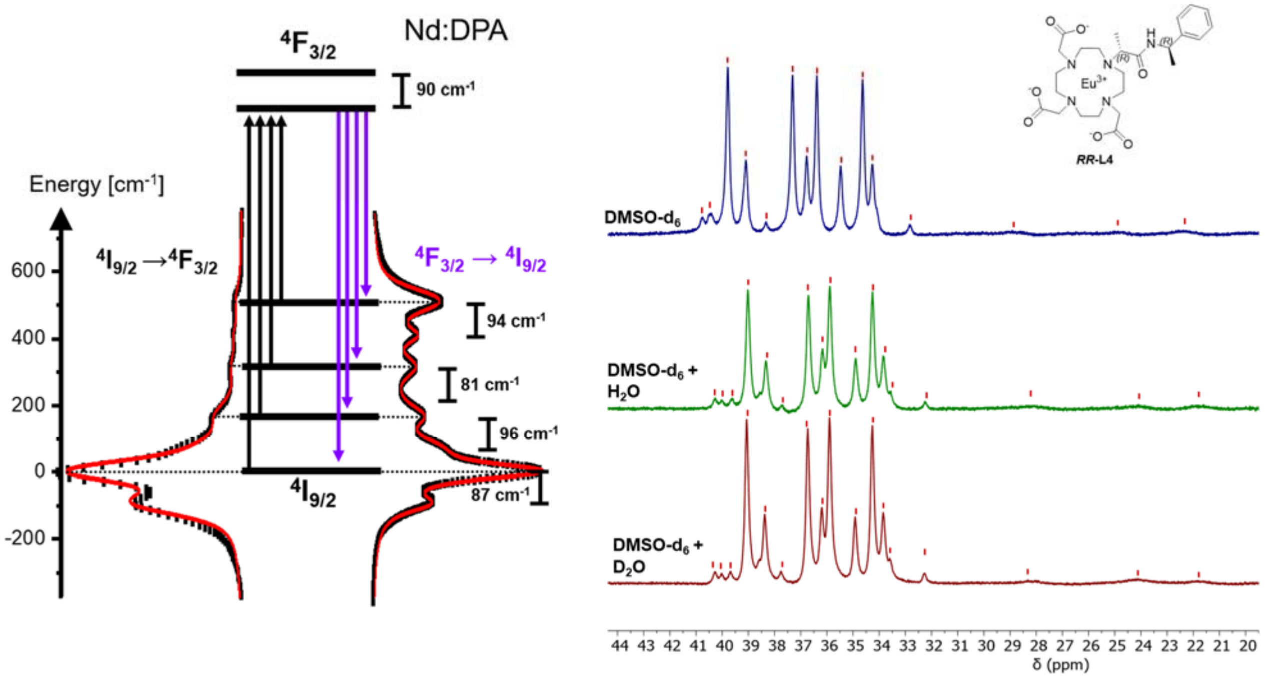

Figure 1. Left: Neodymium(III) emission and excitation spectra recorded in solution and resolved using the Bolzmann populations in the involved multiplets. Right: ^{1}H NMR of a Eu.DOTA-monoamide complex with additional chiral elements showing much more thatn the expected four resonances from the cSAP form of the complex.

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Multidecker Sandwich Compounds

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Lanthanide triple-decker complexes were reported first in the 1970ies. While $[\mathrm{Ce_2(COT)_3}]$ was initially reported in 1976,[1] its characterization using single-crystal X-ray diffraction remained elusive. This changed when Edelmann and coworkers obtained the linear sandwich complex $[\mathrm{Nd_2(COT'')_3}]$ (COT'' = 1,4-$(\mathrm{Me_3Si})_2\mathrm{C_8H_6}^{2-}$).[2] This discovery opened up a way of creating analogous triple-decker complexes with other lanthanides,[3] and also lead to the discovery of other triple-decker complexes ligated by other rings.[4]

Herein, three different types of new multi decker complexes are reported. First, the homoleptic, anionic multidecker compounds of the type $[\mathrm{K\{Ln^{III}(\eta^8\text{-}Cot^{TIPS})_2\}}]_n$ are shown (Figure 1, **A**).[5] Depending on the solvent used for crystallization and the ionic radii of the lanthanide cations, the compounds form three different categories of one-dimensional heterobimetallic coordination polymers in the solid state. Second, the first structurally characterized organometallic multi-decker sandwich complexes featuring a cycloheptatrienyl ring (Cht, $\mathrm{C_7H_7}^{3-}$) in the coordination sphere are presented (Figure 1, **B**).[6] These compounds are the first examples of rare earth triple-decker complexes not bridged by a Cot-derivative, based on purely carbon ligands. The magnetic properties of the respective $\mathrm{Er^{III}}$ congeners were investigated in detail. Third, we showcase the first lanthanide triple-decker compounds featuring a heterocycle (9,10-diborataanthracene) in the coordination sphere (Figure 1, **C**).[7] They show a strong antiferromagnetic interaction of the lanthanide ions.

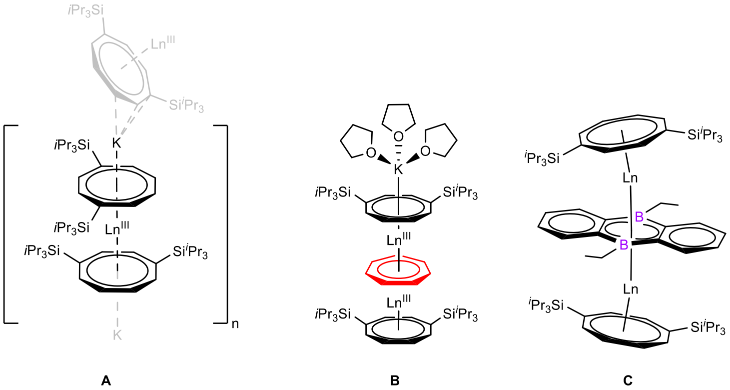

Figure 1: New multidecker sandwich compounds of the lanthanides.

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Rare Earth doped Borosulfates – Candidates for Quantum cutting?

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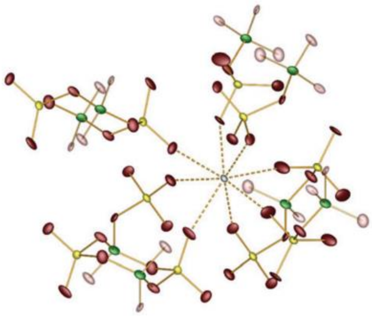
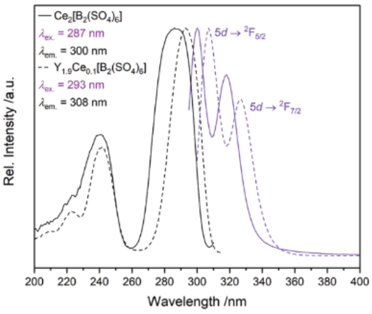
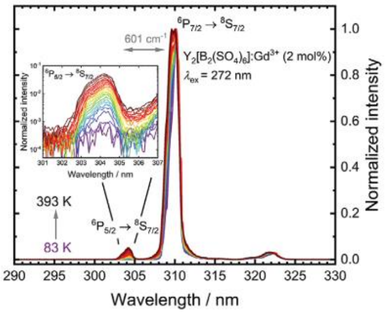
The research of our group primarily focuses on silicate-analogous materials with possible applications in several fields of research. These materials typically consist of tetrahedral building units such as those found in borates, phosphates, or tungstates. Borosulfates combine borate and sulfate tetrahedra to build up 0 to 3-dimensional anionic structures which classifies them as silicate-analogous materials [1]. This relatively new compound class has recently gained interest due to its great structural variability and vast possible application spectrum, i. e. in non-linear optics as SHG material [2], as ion conductors for solid state batteries [3] or in optical applications as Boltzmann thermometers [4] used in biothermal imaging (see figure below). Borosulfates are known to exhibit a weakly coordinating environment as demonstrated in a Tanabe-Sugano analysis based on reflectance spectra of α-$Co_4[B_2O(SO_4)_6]$ and α-$Ni_4[B_2O(SO_4)_6]$ which revealed relatively small Racah parameter B and ligand field splitting Δ in comparison to their respective sulfates [5].







In this contribution, we focus on $R_2[B(SO_4)_2]_4$ (R = La…Lu) [6] the so far only literature known rare earth borosulfates as well as $RX[B(SO_4)_2]_4$ (R = La…Lu; X = NH_4…) [7], a new structure containing rare earth elements. Herein, we elucidate their crystal structures and compare their thermal properties. Eventually, a detailed optical analysis of the trivalent cation (Gd^{3+}, Eu^{3+}, Ce^{3+}, Pr^{3+}) doped compounds provides new insights into the properties of borosulfates and their possible fields of application.

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In situ investigations on H/O exchange reactions in yttrium hydride oxide YHO

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Recently, rare-earth heteroanionic hydrides, especially hydride oxides, have received increasing attention for their optical properties as thin film materials.[1] Many of their representatives exhibit photochromism in thin films, meaning they reversibly change color upon illumination by UV and/or visible light.[2] Oxygen-rich yttrium hydride oxide thin films are of particular interest due to their extraordinary air stability and color-neutral photochromic effect under moderate illumination intensities, making them promising candidates for applications such as smart windows.[3]

We have developed a synthetic procedure to produce bulk samples of orthorhombic YHO, which crystallizes in a distorted ordering variant of the CaF_2-structure type, known as the anti-LiMgN structure type.[4] During our investigation of this substance's air stability through *in situ* X-ray and neutron diffraction experiments, we observed that its decomposition to yttrium sesquioxide (Y_2O_3) proceeds via an intermediate phase with a different crystal structure (**Fig. 1**). We hypothesize that this intermediate phase, occurring between YHO and Y_2O_3, is an oxygen-rich yttrium hydride oxide $Y(H_{1-2x}O_x)O$, which could resemble the photochromic phase observed in thin films. This phase can be isolated as a single phase, and its oxygen content can be modified by quenching samples after different annealing times in air.

In this contribution, we present the results of *in situ* reaction tracking using X-ray and neutron diffraction, the structural identification of the intermediate phase, and investigations into the photochromism of these substances.

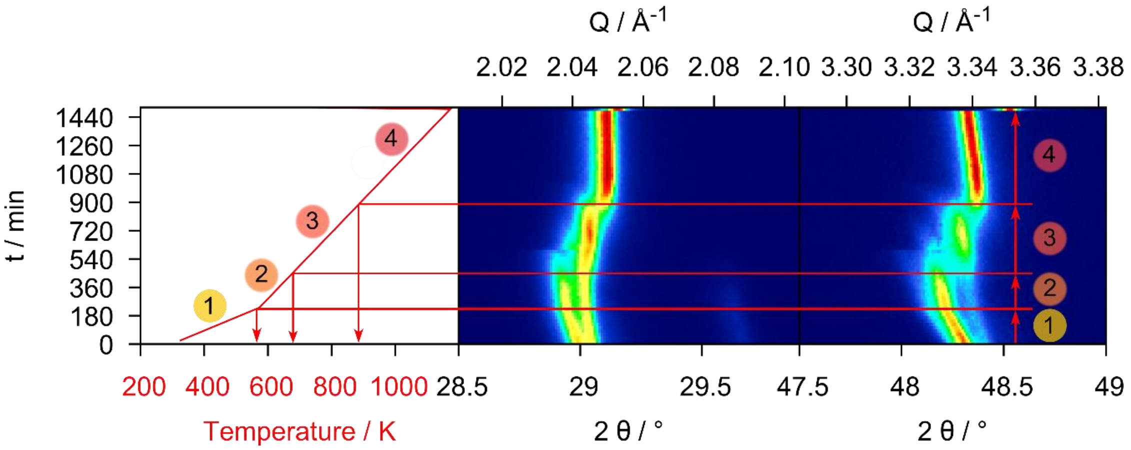

Fig. 1. False-color plot (red: high intensity, blue: low intensity) of the *in situ* X-ray diffraction experiment observing the decomposition of orthorhombic YHO in air (λ: Cu-$K_{\bar{\alpha}}$, 21 min per measurement) showing only two small angular sections of the measured diffraction patterns. The formation of an intermediate phase (step 3) that can clearly be distinguished from orthorhombic YHO (steps 1 and 2) and bixbyite-type Y_2O_3 (step 4) can be observed.

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Putting the F in Phosphorus: Lanthanide Chemistry with Anilidophosphine Ligands

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Despite being well established in the chemistry of (early) transition metals e.g., stabilizing highly reactive group III[1] and IV[2] metal complexes, anilidophosphine ligands with a PN(P) coordination mode have been mostly neglected with the f-elements, especially the lanthanides.[3] This is peculiarly surprising, since the first lanthanide phosphinidene complex, isolated over a decade ago,[4] was stabilized by such a pincer-type PNP ligand, highlighting their enormous potential in f-element chemistry. Similarly, the transient existence of a rare uranium(IV) nitride complex supported by an anilidophosphine ligand has been proven recently.[3f]

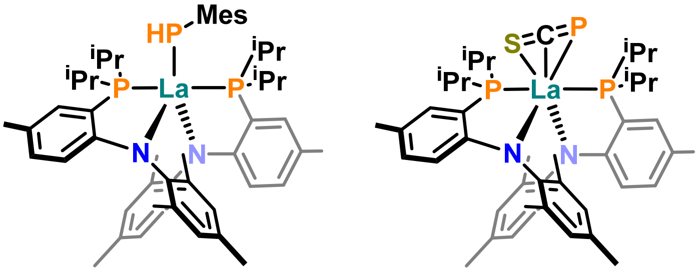

Figure 1: Primary phoshanido and 2-Phosphaethynthiolato complexes supported by anilidophosphine ligands. (Mes = 2,4,6-trimethyhphenyl)

Here, the use of bidentate, monoanionic anilidophosphine ligands (PN ligands)[5a] for the synthesis of heteroleptic lanthanide(III) complexes of the general formula **La(PN)$_2$X** (X = anionic co-ligand) are evaluated with special emphasis on the reactivity of primary phosphanido complexes (Figure 1, left).[5b] Insertion chemistry into the La-P bond will be discussed,[5c,d] and the propensity of the PN ligand framework to stabilize terminal lanthanum phosphinidene complexes will be evaluated.[5e,f]

Furthermore, we will present unprecedented η^3-coordination modes heavy cyanate ions, namely of the $[SCP]^-$ and the $[SCAs]^-$ anions (Figure 1, right) and their subsequent activation chemistry. [5g,h]

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New rare earth iminophosphoranomethanide complexes: synthesis, characterisation and applications

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Iminophosphoranomethanide ligands of the type $\{(R–N=P(Ph)_2)_2CH\}^-$ (^{R}BIPM-H, R = trimethylsilyl, *iso*-propyl, cyclohexyl, aryl) have been used extensively to prepare rare earth (RE) and lanthanide (Ln) methanide complexes (Figure 1),[1] These compounds have been investigated for their reactivity,[2] and have also been employed as precursors towards the stabilisation of alkylidene complexes.[3,4] In this work, we develop further the chemistry of non-symmetric the iminophosphoranomethanide $\{Me_3SiN=P(Ph)_2CHSiMe_3\}^-$ (^{TMS}NPC-H) originally developed by Lappert and co-workers and expand its synthesis and characterisation of alkali metal salts to sodium and potassium. Furthermore we report on the preparation of alkaline earth and Ln(II) *bis*-methanide complexes, and trivalent RE(III) *tris*-methanide complexes, together with the detailed magnetic characterisation of Eu(II) complex [Eu(^{TMS}NPC-H)$_2$] (Figure 1). We also investigate the applications of our new methanide complexes as protonolysis reagents for the synthesis of RE amide and aryloxide complexes.

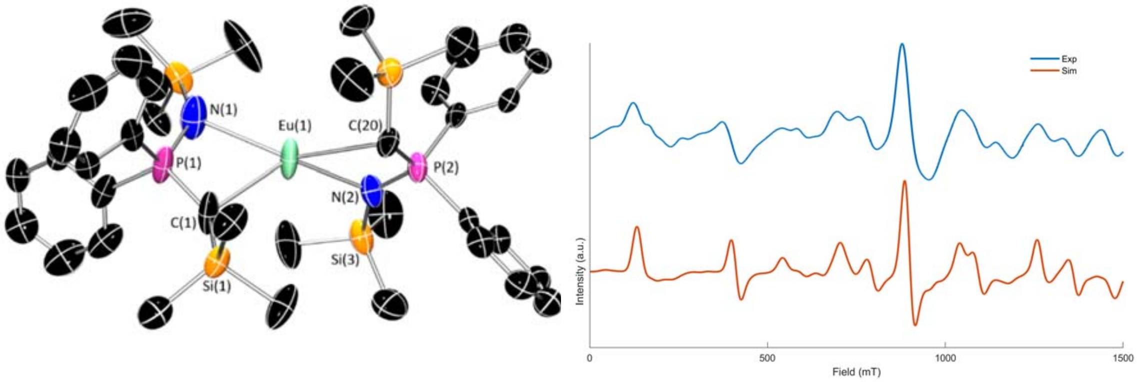

Figure 1: X-ray structure of [Eu(^{TMS}NPC-H)$_2$] and its solid-state Q-band EPR spectrum.

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Donor-free samarium silylamides

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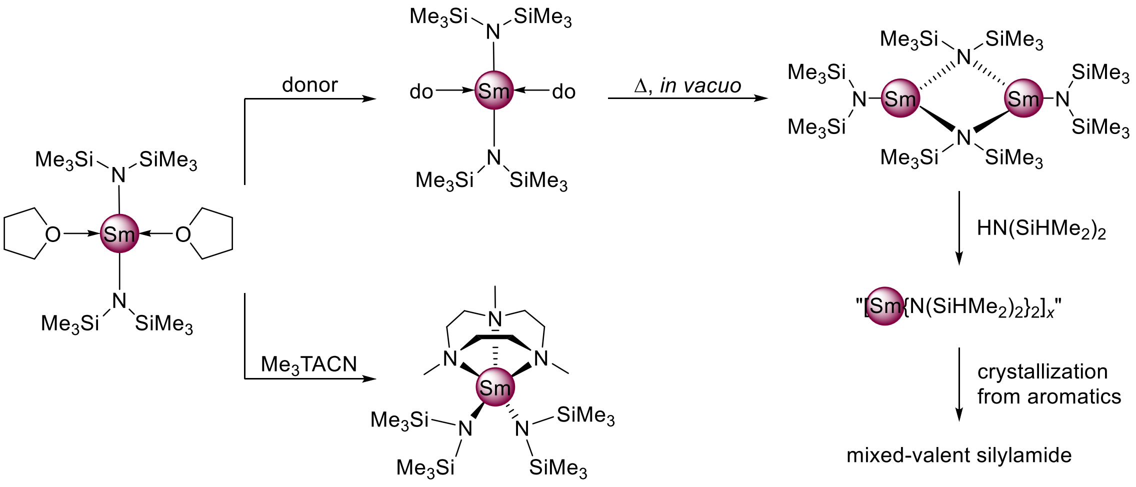
Rare-earth-metal alkyls are widely applied in catalysis[1] and organic synthesis.[2] Rare-earth-metal amides and in particular silylamides are useful precursors displaying expedient stability and solubility.[3] Divalent rare-earth-metal silylamides are routinely obtained as solvated complexes and employed as such, *e.g.*, $Sm[N(SiMe_3)_2]_2(THF)_2$.[4] To the best of our knowledge, monomeric $Ln[N(Si^iPr_3)_2]_2$ bearing super bulky ligands is the only homoleptic donor-free silylamide investigated in detail for the bigger traditional divalent rare-earth metals samarium and europium.[5]

A new strategy has been developed to elucidate the influence of donor molecules toward the reactivity of rare-earth-metal silylamides. We report on the synthesis and characterization of several samarium silylamides with ethereal and *N*-nitrogen donor ligands as well as donor-free complexes. Especially samarium silylamides were investigated by X-ray structure analysis and NMR spectroscopy. Exemplarily, an extensive NMR study on donor free $[Sm\{N(SiMe_3)_2\}_2]_2$ has been conducted.



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Phosphinoaryloxide Rare Earth Complexes for Frustrated Lewis Pair Chemistry

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Since the ground-breaking research by Stephan *et al.* in 2006,[1] Frustrated Lewis Pair (FLP) chemistry has been a rapidly developing area of research. This is due to the potential economic and environmental benefits of using cheap and abundant p-block elements in small molecule activation and catalysis. There has been a lot of interest in exploiting the Lewis acidity of metal cations for developing novel FLP systems.[2] In this respect, rare earth (RE) cations display high Lewis acidity. However, examples of FLP-type reactivity with these metals remain scarce.[3–5] Wass and co-workers exploited the Lewis acidity of Group 4 metals combined with the use of bulky phosphinoaryloxide ligands to develop FLP-type reactivity.[6,7] Group 4 cations Ti^{4+}, Zr^{4+} and Hf^{4+} are isoelectronic to RE^{3+} (RE = Sc, Y and La) cations, thus providing us the inspiration to develop analogous systems that could be intriguing candidates for metal-based FLP activity. In this work, we present the synthesis and characterisation of a family of novel RE^{3+} complexes bearing phosphinoaryloxide ligands, as well as the investigation of their reactivity with H_2, CO and CO_2.

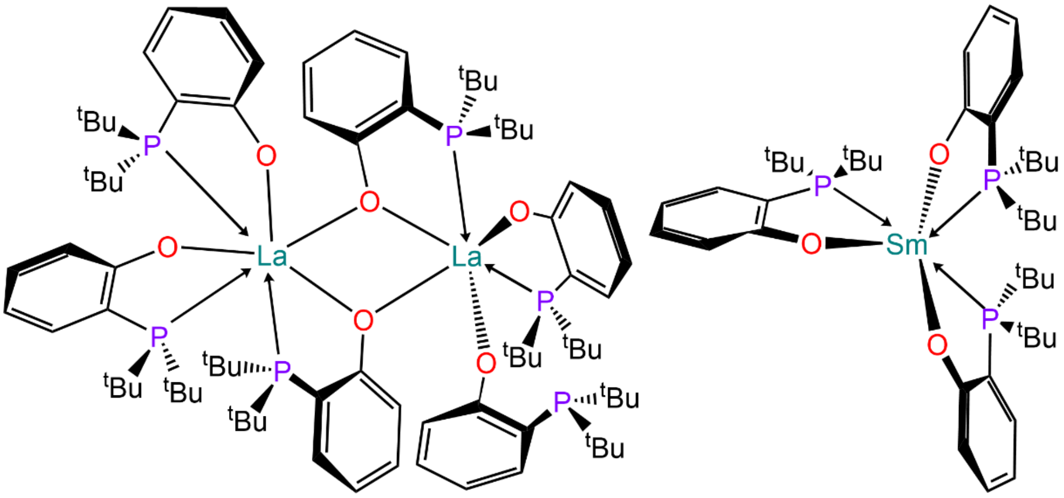

Figure 1 Selected Examples of RE Complexes Synthesised

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Halides as Electrolytes for All-Solid-State Batteries

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Ternary halides of the rare-earth elements (R = Sc, Y, La-Lu), of alkali- and pseudo-alkali-metals (A = Li-Cs, Ag, NH_4, In, Tl, …) and the triad X = Cl, Br, I, have been synthesized at great length decades ago [1, 2], their crystal structures determined as well as some of their properties (luminescence, magnetism, ionic conductivity). The formula type A_3RX_6 appears most frequently, and all crystal structures contain isolated $[RX_6]^{3-}$ octahedra with the A^+ cations in appropriate coordination polyhedra, the smaller ones, A = Li, Na, Ag, predominantly also in an octahedral environment.

The crystal structures may be derived mostly from closest packings of halide and, for the larger A's, spheres and/or as derivatives of simple binary trihalides, such as $AlCl_3$ or $FeCl_3$. In these, for the formula A_3RX_6, there are six octahedral and 12 tetrahedral holes of which one is occupied by R^{3+} and three by A^+ where under-occupancy of some interstices is possible. This leads to high A^+-cation conductivity, especially for A = Li, Na, Ag, well known since the 1990's [2].

Recently, the engineering of all solid-state batteries, ASSB's, led to a resurrection of $A_3[RX_6]$ type compounds. Although somewhat difficult to prepare, for thermodynamic reasons and for their moisture sensitivity, the iodides, $Li_3[RI_6]$, should be the most interesting as the interstices in the hexagonal or cubic closest packed iodide structures are the biggest and the packing the "softest" (most polarizable), thus Li^+-ion conductivity should be the "fastest" at the lowest temperatures. This is indeed the case.

$Li_3[YI_6]$ crystallizes with a cubic closest-packed iodide lattice ($C2/m$, $Z = 2$) with the Li^+ ions disordered over three crystallographically distinct positions [3]. There are two other phases frequently observed of which one is richer and the other poorer in Li^+ content. They may even be better ionic conductors.

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Poster Presentations

P01 M. Tomar, A. Thapper, K. E. Borbas: Exploring chromophore-Ln(III) Interaction to Improve Photocatalytic Efficiency

P02 C. Foster, D. Sneddon, L. Hacker, E. Hammond, S. J. Conway, S. Faulkner: Activatable lanthanide complexes for luminescence and MRI

P03 V. Wessels, N. S. Kaur, S. Kügle, H. A. Höppe: Sulfatotungstates – Promising Candidates as Antenna Phosphors?

P04 E. C. J. Gießelmann, S. Engel, G. Kickelbick, O. Janka: Synthesis and oxidation of intermetallic aluminum compounds

P05 S. Engel, O. Janka: The rare earth platinides series $\mathit{RE}\mathrm{Al}_5\mathrm{Pt}_3$ and $\mathit{RE}_2\mathrm{Al}_{16}\mathrm{Pt}_9$

P06 P. Preisenberger, C. Maichle-Mössmer, R. Anwander: Reactivity of Ytterbium and Calcium pyrazolate complexes towards CO_2

P07 J. Emerson-King, C. Clayton, A. Adel a Babtain, S. Sarfraz, G. F.S. Whitehead, D. P. Mills: Synthesis and reactivity of low-coordinate rare-earth silylamide complexes

P08 K. Huang, M. P. Walter: Synthesis of Open Base-free Metallocenes with Divalent Rare-earth and Alkaline-earth Metals

P09 O. F. Fellner, P. Sagar, E. Moreno-Pineda, A. Sunil, R. Herchel, W. Wernsdorfer, I. Nemec: Towards a Toroidal Moment via Carboxylate Ligand Exchange

P10 G. Buchner, P. Ettlinger, H. A. Höppe: Silver-Rare-Earth-Double-Sulphate-Hydrates $\mathrm{Ag}\mathit{Ln}(\mathrm{SO}_4)_2\cdot\mathrm{H}_2\mathrm{O}$ (Ln = La – Nd, Sm – Gd)

P11 J. Locher, L. Vondung: Lanthanide Complexes with Bis-Phosphine Ligands

P12 P. Wetzel, D. C. Burghardt, C. Maichle-Mössmer, R. Anwander: Gallium outperforms aluminum in rare-earth-metal-based isoprene polymerization

P13 K. K. Wolff, L. H. Tjeng, M. Jansen: 3d-5d double perovskites containing rare earth metals

P14 C. Odenwald, C. Maichle-Mössmer, R. Anwander: Sandwich and Half-Sandwich Lanthanum Methyl Complexes

P15 H. Redmill, A. Brookfield, G. F. S. Whitehead, E. J. L McInnes, D. P Mills: Solvent-free Rare Earth Bis(trimethylsilyl)phosphide Complexes

P16 J. Kohl-Chandramohan, M. R. Schweikert, T. Junginger, I. Hartenbach, Marie-Louise Lemloh: Bioaccumulation and excretion of rare earth-containing particles in the single-celled eukaryote Tetrahymena

P17 R. Risken, E. Kreidt: DOTA-based photoswitchable ligands for lanthanoids

P18 K. Mamonov, M. C. Wied, T. J. Sørensen: Effect of charge on oxyanion sensing in Eu(III)-based nanooptodes

P19 M. C. Wied, K. Mamonov, T. J. Sørensen: Preparation of a europium(III)-based nanooptode for bicarbonate sensing by nanoparticle surface post-complexation

P20 L. Y. Dorsch, T. Hansen, H. Kohlmann: Investigating the hydrogenation of Zintl phases EuTt (Tt = Si, Ge, Sn)

P21 C. Schwab, E. Kreidt: Azobenzene Cryptates as Photoswitchable Ligands

P22 N. Winterholler, E. Kreidt: Diazocines as building blocks in lanthanoid coordination compounds

P23 A. Babtain, D. Willcox, D. P. Mills: Expanding Lanthanide Chemistry Using Redox-Active Di(Imino)Pyridine Ligands

P24 R. E. MacKenzie, C. A. P. Goodwin: Valence Electron Configurational Isomers – f-Block Elements Acting Like d-Block Elements?

P25 K. Engel, Th. Schleid: From $RbEu[AsS_4]$ to $Rb_4Eu[AsS_4]_2$: Synthesis and Characterization

P26 B. Knies, I. Hartenbach: The Neodymium Tantalate $NdTaO_4$ in the M-Fergusonite Structure Type

P27 C. A. von Randow, G. Thiele: The Quest of a Samaride – The First Isolated Lanthanide Anion

P28 R. J. C. Locke, A. Erden, Th. Schleid: $Pr_3OI[AsO_3]_2$: The First Oxide Iodide Oxoarsenate of the Rare-Earth Metals

P29 Y. Rechkemmer, J. Fischer, R. Marx, M. Dörfel, P. Neugebauer, M. Gysler, J. van Slageren: Crystal Field Splittings in Molecular Lanthanide Tetra-Carbonates

P30 V. Babizhetskyy, Yu. Tyvanchuk, V. Smetana, A.-V. Mudring: Crystal and electronic structure of the ternary silicides $RFe_{1-x}Si_2$ (R = Gd, Tb, Er, Tm, Yb)

Exploring chromophore-Ln(III) Interaction to Improve Photocatalytic Efficiency

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Lanthanide (Ln) coordination compounds have applications in areas as diverse as renewable energy generation and medical imaging. Most Ln(III) ions are lumiescent.[1] Ln(III) luminescence is commonly sensitized by a light-harvesting antenna in close proximity to the metal ion.[2] Upon antenna excitation, both Ln(III) luminescence and Ln(II) can be produced. If the excited state of the antenna is a strong reductant, electron transfer to the reducible Ln(III) centers (e.g. Ln = Eu, Sm, Yb) is possible.[3] The transiently formed Ln(II) species has been harnessed in organic synthesis, and the photochemical generation of Ln(II) from Ln(III) is the basis of catalytic Ln(II)-mediated reduction reactions. This photocatalytic approach offers the potential to replace stoichiometric reductions and photosensitizers based on precious metals. This opens up new avenues for more sustainable and environmentally friendly synthetic strategies in organic chemistry.

Many organic chromophores are strong reductants in their excited states. Eu(III) is the most reducible (E_{red} = –0.35 V vs NHE) of the Ln(III) ions.[4] Therefore, we expected that Eu(II) could be generated from Eu(III) via PeT using relatively mildly reducing donors, i.e. those with excited states in the visible. The identification of chromophores that can generate Ln(II) even upon excitation with long wavelength-light would greatly expand the scope of the current methodology and would allow for catalytic applications using sunlight.[5]

We present the results of an investigation of intermolecular PeT from a broad variety of commercially available or readily synthesized chromophores to Eu(III). We evaluate the interactions between the chromophores and Eu(III) in the ground state using a range of spectroscopic and electrochemical methods, and explore the utility of the chromophores in organic synthesis.

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Activatable lanthanide complexes for luminescence and MRI

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MRI imaging of soft tissues using contrast agents has considerable potential if they can be selectively activated under certain conditions. Hypoxia (typically <2% oxygen) is characteristic of solid tumours and hypoxia-activated prodrugs and profluorophores are being researched to develop molecules which can be selectively activated in cancerous tissues.[1] The use of lanthanide-based complexes instead of organic fluorophores for imaging is advantageous due to their long-lived luminescence in optical imaging (europium and terbium) and their use for MRI (gadolinium), allowing for non-invasive imaging. This project aims to develop novel lanthanide complexes to be used as MRI contrast agents which are selectively activated under hypoxia to enable more detailed imaging, by attaching hypoxia-activatable groups to known MRI contrast agents. Under activation, the hypoxia-activated lanthanide complex will undergo a symmetry change (evident in the ^{1}H NMR spectra, Figure 1) and release the known MRI contrast agent GdDOTA, causing a change in T_1, therefore changing image contrast selectively in cancerous tissues.

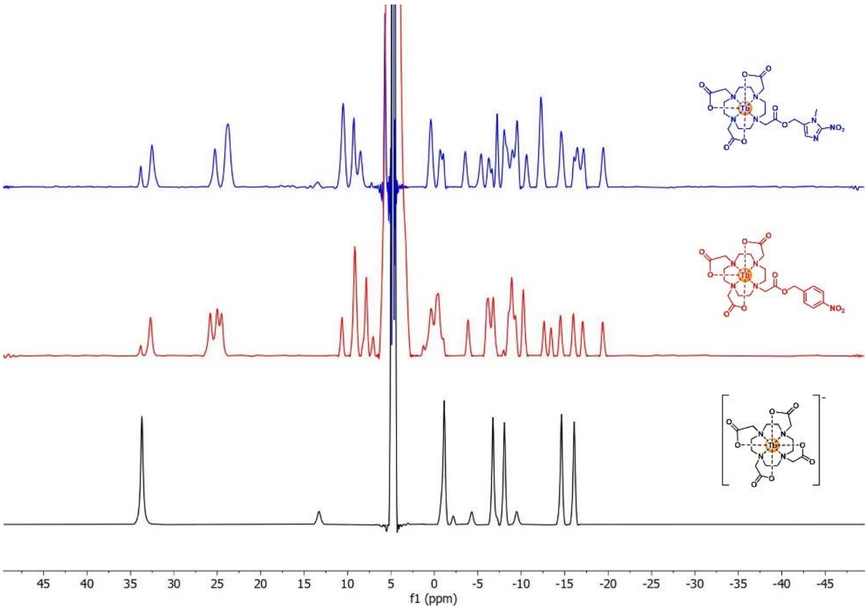

Figure 1: The stacked paramagnetic ^{1}H NMR spectrum of TbDOTA (black) in comparison to the synthesised activatable lanthanide complexes TbNB (red) and TbNI (blue).

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Sulfatotungstates –
Promising Candidates as Antenna Phosphors?

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Our research focuses on the investigation of new silicate-analogous materials with interesting optical properties as promising phosphor materials. Such materials contain tetrahedral building units as a structural motif, including compounds such as sulfates, phosphates, and borates. Sulfatotungstates constitute a rather new host structure material. In addition to $[SO_4]^{2-}$ units, they are capable of forming $[WO_6]^{6-}$, $[WO_5]^{4-}$ and $[WO_4]^{2-}$ moieties which classifies them also as silicate-analogous materials. Tungstate moieties are known for their ability to act as antenna, enabling energy transfer towards an activator, such as a rare-earth element, thereby enhancing its *f*-*f* transitions. In addition to acting as an antenna, sulfatotungstates may also feature weak coordination behaviour in their anionic host structure, which makes them promising candidates as host structure materials for rare-earth elements. To date, only two different host structures have been found, namely $M_8[W_2O_4(SO_4)_6]$ (M = K, Rb) and $R_2[W_2O_3(SO_4)_6]$ (R = Sm, Eu, Gd, Ho), with only the crystal structures having been determined [1-3]. In this contribution, we not only present two new host structures with new metal cations as counter balancing ions but also elucidate the optical properties of sulfatotungstates for the first time [4,5].

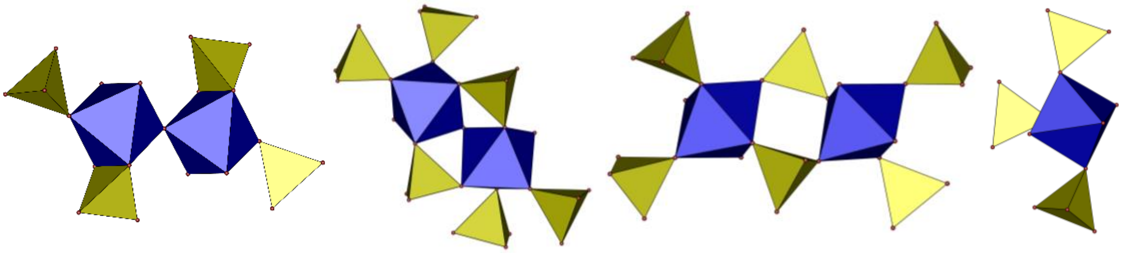

Figure 1: Host structures of the investigated sulfatotungstates; tungstate octahedra (blue), sulfate tetrahedra (yellow).

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Synthesis and oxidation of intermetallic aluminum compounds

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Within this work binary and ternary intermetallic aluminum compounds containing rare earth metals are synthesized and investigated. Besides the classical investigation methods (X-ray diffraction on powder and single crystal), the synthesized compounds can be investigated by e.g. Raman spectroscopy as well as X-ray photoelectron spectroscopy (XPS).[1]

The diamagnetic compounds formed primarily with Sc, Y, Lu, La and if divalent Yb can be additionally investigated by using ^{27}Al or ^{45}Sc MAS solid-state magnetic resonance spectroscopy (NMR).[2] Beside the validation of the crystal structure (number of crystallographic sites correlates with the number of signals), NMR spectroscopic investigations enable statements about structural features like local distortions or the formation of solid solutions. In addition, the interpretation of the chemical shift allows an assertion about the electron transfer in these materials. Raman spectroscopy provides insights to force constants of lattice vibrations, which can be useful for quantum chemical calculations. The analysis of the electronic structure and the bonding situation is performed by band structure calculations on the DFT level. With the help of these, Bader charge analyses can be performed in addition to the determination of the band structures and the interpretation of interatomic interactions with respect to their bonding character. These also allow an estimation of electron transfer in these compounds. Real space analyses (ELF) can also be used to illustrate the bonding situation.[1, 3]

Another central aspect of the research is the targeted oxidation (sulfidation, nitridation etc.) of the synthesized intermetallic compounds. This may offer the possibility of obtaining novel oxides (sulfides, nitrides etc.) that are hardly or not accessible by direct reaction of the oxides. For the case of the rare earth elements for which multiple oxidation states are known, e.g. Eu$^{2+/3+}$ and Yb$^{2+/3+}$, the question arises which oxidations states are obtained for different synthetic strategies.[4, 5]

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The rare earth platinides series $RE\mathrm{Al}_5\mathrm{Pt}_3$ and $RE_2\mathrm{Al}_{16}\mathrm{Pt}_9$

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Rare earth containing intermetallic materials exhibit a wide range of application fields, starting from everyday used objects, like e.g. $\mathrm{Nd}_2\mathrm{Fe}_{14}\mathrm{B}$ as permanent hard magnets or specialized steels in the field of construction and in tools, to superconductors like $\mathrm{Nb}_3\mathrm{Sn}$ compounds used in medical and analytical equipment. Aluminum intermetallics have additionally a plethora of uses, e.g. $\mathrm{Ti}_3\mathrm{Al}$ as high temperature and $\mathrm{Ni}_3\mathrm{Al}$ as a super alloy, which exhibit a high resistance to extreme temperatures, oxygen or acids.[1]

Many rare earth intermetallics have unpaired f-electrons, giving rise to highly interesting physical properties like the superconductivity, magnetic ordering and heavy fermion behavior, in which Ce, Eu and Yb occupy a special place. Due to their two available valencies of $\mathrm{Ce}^{3+/4+}$, $\mathrm{Eu}^{2+/3+}$ and $\mathrm{Yb}^{2+/3+}$ major changes in their magnetic properties can occur. The ternary *RE*-Al-metallide $\mathrm{Eu}_2\mathrm{Al}_{15}\mathrm{Pt}_6$ exhibit a first order valence transition from divalent to trivalent below 45 K. This behavior can be influenced by substituting Al with Ga, even a small amount of Ga substitution leads to a shift of the Eu valence to the divalent oxidation state and an antiferromagnetic ordering as found in the pure Ga compound. The influence of the valence change can also be obtained by substituting Pt with Ir, Pd and Au, whereas Au substitution prevents a valence transition, Ir induces a higher transition temperature of 52 K compared to the pure compound.[2-4]

The two series $RE_2\mathrm{Al}_{16}\mathrm{Pt}_9$ and $RE\mathrm{Al}_5\mathrm{Pt}_3$ will be presented in the poster, which have been investigated by X-ray crystallography alongside quantum chemical calculations, giving insight into the bonding situation and oxidation state of the $\mathrm{YAl}_5\mathrm{Pt}_3$. XPS as well as a ^{27}Al MAS NMR have been conducted to gain a deeper insight into the electronic structures. Additionally the magnetic properties of the Y, Ce-Nd & Gd-Ho compounds were investigated.[5,6]

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Reactivity of Ytterbium and Calcium pyrazolate complexes towards CO_2

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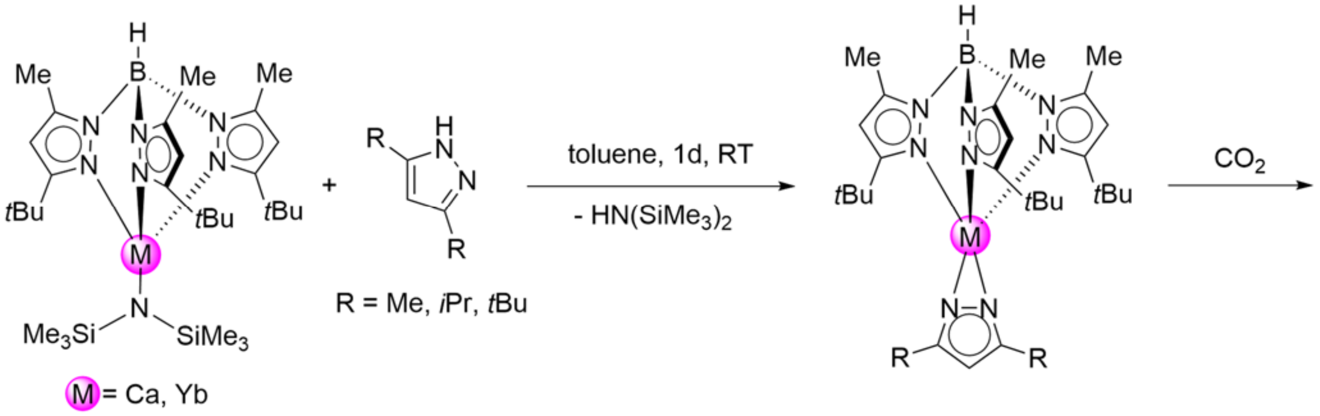
In the search for new carbon-capture methods, our group has recently started to investigate the reactivity of metal pyrazolates towards CO_2. Both magnesium and cerium complexes have been shown to insert CO_2 at room temperate and promote the reverse reaction at slightly elevated temperatures.[1–3] In addition to simple CO_2 insertion, these complexes also engage in catalytic reactions, being able to selectively convert propylene oxide into the respective cyclic carbonate. While a mechanism for this catalysis has been proposed, many aspects remain unclear.[1,3] The bulky trispyrazolylborat “scorpionate” Ligand assist in studying this mechanism, as it limits the amount of reactive sites to one per metal while significantly affecting the solubility behaviour

. Herein, a number of complexes with calcium and ytterbium are presented along with preliminary CO_2 reactivities.



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Synthesis and reactivity of low-coordinate rare-earth silylamide complexes

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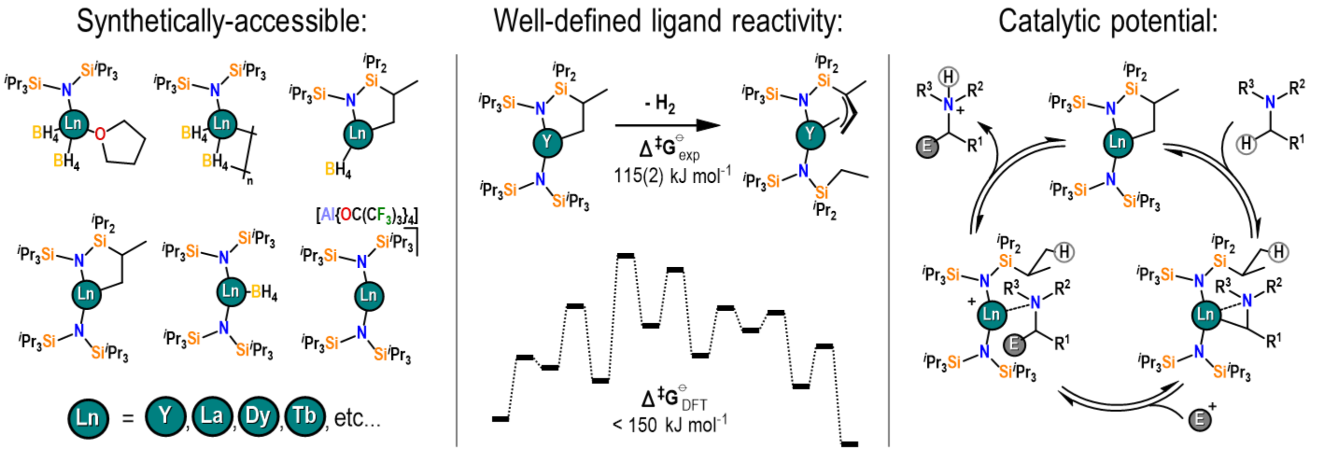
The use of bulky silylamide ligands in general, and $\{N(Si^iPr_3)_2\}$ in particular, has proved a highly successful strategy for synthesizing low-coordinate rare-earth complexes with precise geometries.[1] Expanding on earlier work, including the synthesis of $[Ln^{III}\{N(Si^iPr_3)_2\}_2][B(C_6F_5)_4]$ (Ln = Sm, Tm, Yb), and their divalent precursors $[Ln^{II}\{N(Si^iPr_3)_2\}_2]$ (Ln = Sm, Eu, Tm, Yb),[2-4] we have now developed methodologies that allow access to a wide variety of trivalent rare-earth complexes with one or two $\{N(Si^iPr_3)_2\}$ ligands, from commonly used starting materials. These include the long-targeted $[Dy^{III}\{N(Si^iPr_3)_2\}_2]^+$ cation,[5] and other closely related systems.[6]

We have found that in many cases trivalent rare-earth $\{N(Si^iPr_3)_2\}$ complexes, and their derivatives, tend to be only thermodynamically metastable; possessing a propensity to enact C-C, C-H, and H-H bond cleavage reactions under mild conditions. In previous work we succeeded in mitigating this side-reactivity to enable the preparation of our synthetic targets. In this contribution we describe our complementary efforts to further understand this chemistry from a precise mechanistic standpoint, in the context of our ongoing work seeking to leverage this reactivity to enact useful chemical transformations on small-molecule chemical feedstocks.



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Synthesis of Open Base-free Metallocenes with Divalent Rare-earth and Alkaline-earth Metals

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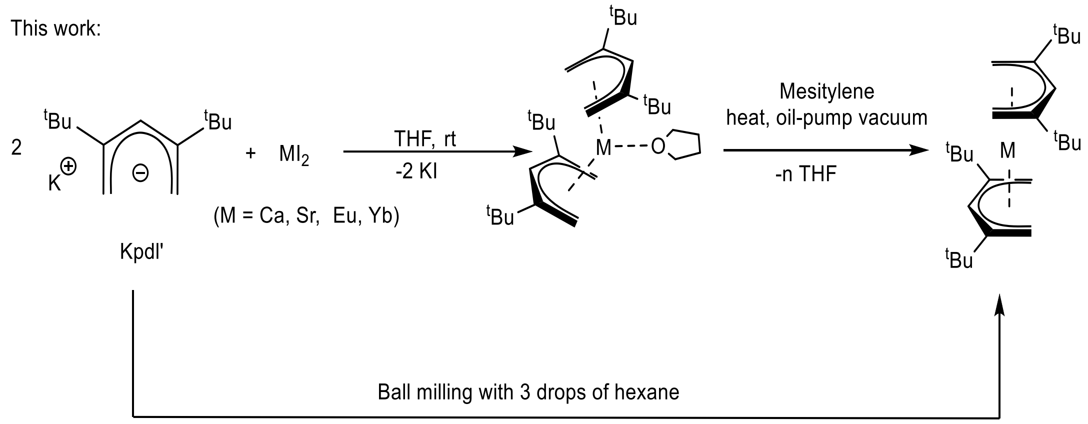
In contrast to the flourishing coordination chemistry of the cyclopentadienyl ligand, the related pentadienyl system has been neglected for many years. This is surprising considering that the first metal pentadienyl complexes have been prepared more than 40 years ago,[1] and the pentadienyl ligands adopt an intermediate position between the cyclopentadienyl and allyl ligands.

Over last decade our group has systematically explored the sterically encumbered pentadienyl ligand pdl' (pdl' = $2,4\text{-}^t\text{Bu}_2\text{C}_5\text{H}_5$) and its coordination chemistry towards heavy-alkaline earth metals such as Ca, Sr and Ba[2] as well as trivalent rare-earth metals.[3] For the latter series the reaction products can be categorized as (a) salt-metathesis, (b) metal reduction-ligand oxidation and (c) deprotonation reactions.[3]

In this work, the synthesis of base-free open-metallocenes $[(\eta^5\text{-pdl'})_2\text{M}]$ of the heavy alkaline-earth metals (M = Ca, Sr) and rare earth metals (M = Yb, Eu) are studied by salt-metathesis between MI_2 and Kpdl' with post-synthetic modification under oil pump vacuum ($1.0 * 10^{-3}$ mbar) and heat.[4] Instead of the tedious process in solution, solid-phase reactions mediated by ball milling provides an attractive synthetic alternative. The application of wet ball milling in the synthesis of base-free metallocenes highlights its simplicity, rapidity and high yields.



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Towards a Toroidal Moment via Carboxylate Ligand Exchange

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We present a series of six wheel-like hexanuclear Dy(III) coordination compounds with the general formula [$Dy_6(H_3bis\text{-}tris)_6(carboxylate)_6$] (carboxylate = 4-Chlorobenzoic, 4-Bromobenzoic, 4-Iodobenzoic, 4-formylbenzoic, Pivalic and Trifluoroacetic acid). The structures of these complexes were obtained by monocrystal X-ray diffraction, and their purity confirmed via X-ray powder diffraction. Subsequently, the complexes were further characterized by theoretical (DFT, CASSCF) and magneto-chemical (SQUID, micro-SQUID) methods.

Our study builds upon the foundation laid by the previously reported complex [$Dy_6(H_3bis\text{-}tris)_6(benzoate)_6$]. Analysis of its DC magnetic data suggested a diamagnetic ground state with a toroidal magnetic moment. Motivated by this observation, we sought to explore the potential for modulating the toroidal magnetic moment by varying the carboxylic ligands. We observed a significant difference in both structural and magnetic features between derivatives of acetic and benzoic acid.

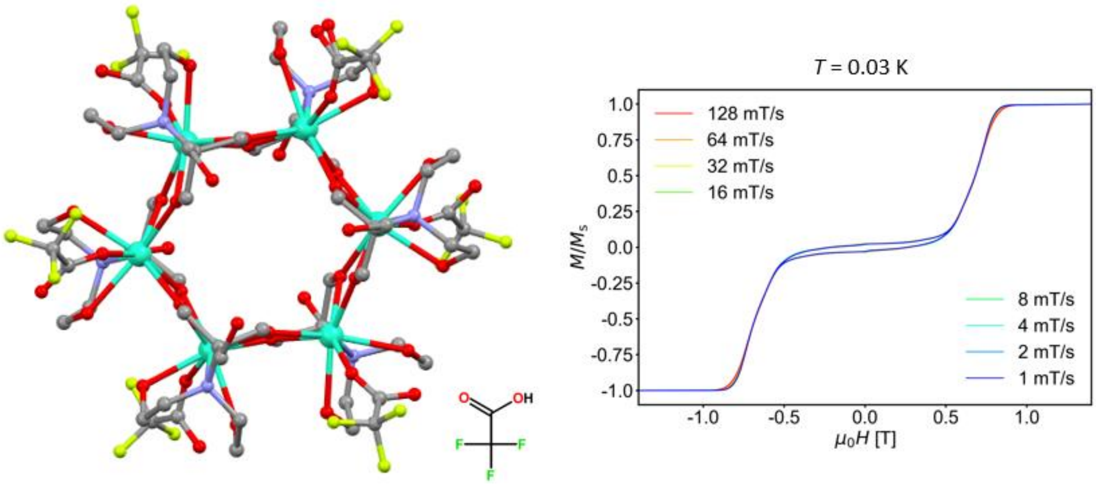

Fig. 1. Structure of [$Dy_6(H_3bis\text{-}tris)_6(Trifluoroacetate)_6$] (left) and its single-crystal magnetisation *M* vs applied field measurement with different field sweep rates at *T* = 0.03 K (right). Legend: Dy (light blue), O (red), N (blue), C (grey), F (yellow), H atoms were omitted for the clarity.

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Silver-Rare-Earth-Double-Sulphate-Hydrates Ag*Ln*$(SO_4)_2 \cdot H_2O$ (*Ln* = La – Nd, Sm – Gd)

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Silicate-analogous materials comprise a vast range of quickly emerging compounds with potentially interesting optical properties e.g. nonlinear optics. The basic building unit of these representatives are tetrahedra with the composition TO_4. These compounds include, for example, borates (*T* = B) as well as sulphates (*T* = S) and even combinations of these like borosulphates with *T* = B, S [1]. To enhance their possible application as new phosphor materials some of them can be doped or even synthesised with various rare-earth elements. Whereas quite a number of rare-earth-double-sulphates $ALn(SO_4)_2 \cdot H_2O$ (e.g. *A* = K) [2] were characterised quite well, most of $AgLn(SO_4)_2 \cdot H_2O$ have not been completely analysed so far. In 1992, Jordanovska and Shiftar synthesised $AgLn(SO_4)_2 \cdot H_2O$ (*Ln* = La – Nd, Sm – Gd), but no detailed crystal structure determination was given [3], while in contrast Audebrand et al. have published almost only this for $AgCe(SO_4)_2 \cdot H_2O$ in 1998 [4]. Only in 2021 Denisenko et al. characterised $AgEu(SO_4)_2 \cdot H_2O$ in more detail [5]. Our research group has also investigated this group of silver-rare-earth-double-sulphate-hydrates in recent years. This contribution focuses on two different synthesis methods of single crystals, the detailed crystal structure determination of the latest synthesised compounds $AgNd(SO_4)_2 \cdot H_2O$ and $AgSm(SO_4)_2 \cdot H_2O$ (**Fig. 1** *left*) as well as the silver-rare-earth-double-sulphates' optical behaviour (**Fig.1** *right*), dehydration ability (exemplary) and suitability as nonlinear optical materials as SHG materials.

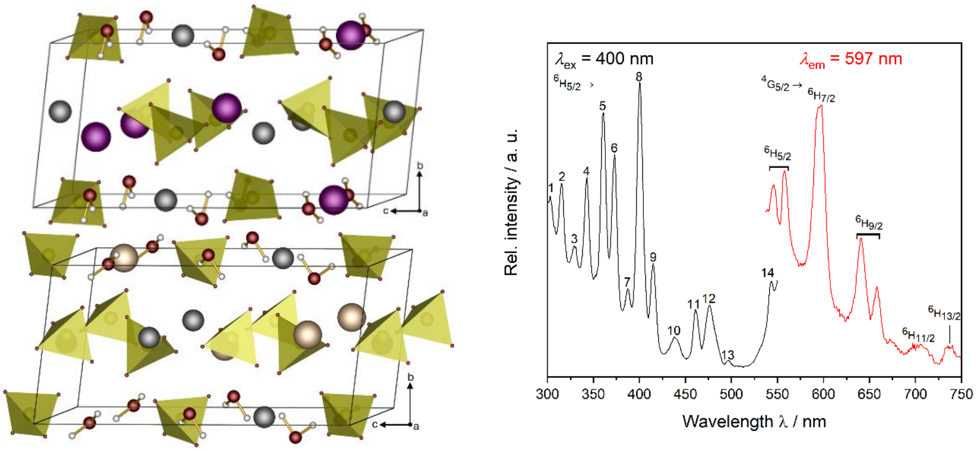

Fig. 1: *left*: unit cell of $AgNd(SO_4)_2 \cdot H_2O$ (top) & $AgSm(SO_4)_2 \cdot H_2O$ (bottom); sulphate-tetrahedra yellow, silver grey, samarium orange, neodymium purple, oxygen red and hydrogen white; *right*: Fluorescence spectrum of $AgSm(SO_4)_2 \cdot H_2O$.

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Lanthanide Complexes with Bis-Phosphine Ligands

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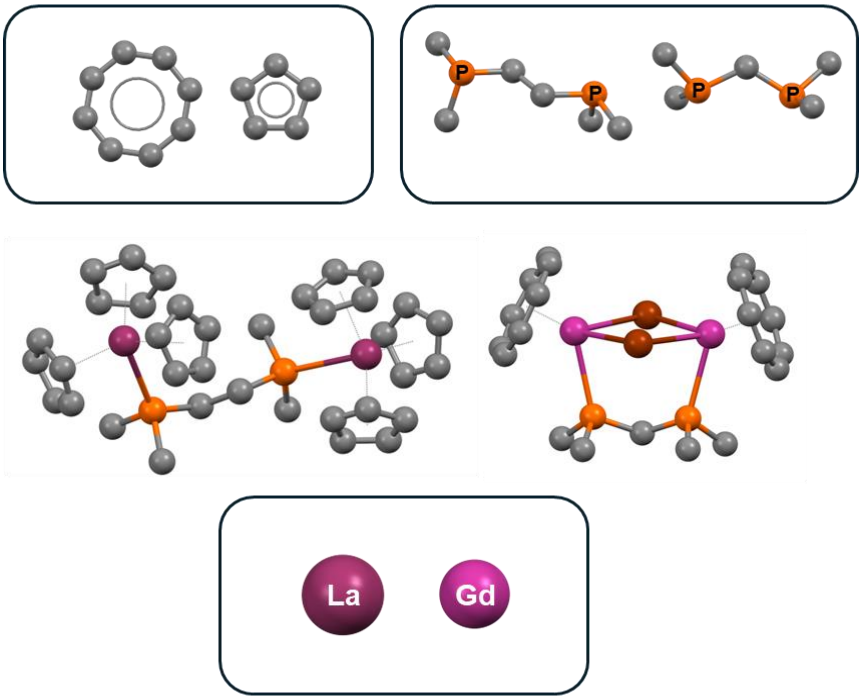
The use of neutral phosphine ligands is well established in transition metal chemistry, for example in catalysts.[1] For lanthanides however there are only eleven structurally characterized complexes with neutral tertiary phosphine ligands reported.[2] The lanthanide phosphine bonding in these examples was hardly investigated further.[3] Therefore, we set out to explore the coordination chemistry and lanthanide phosphorus bonding of this ligand class. As supporting ligands, the cyclooctatetraene dianion (COT^{2-}) and cyclopentadiene (Cp^{-}) were chosen, due to their established use in lanthanide organometallic chemistry.[4] Recently four new erbium COT phosphine complexes were reported, showing the feasibility of this approach.[5]

In our work, two bis-phosphine ligands with varying linkers were used to investigate the influence of the alkyl backbone, as well as of the ancillary ligands and metal ion size on the binding mode.

With this approach we obtained the first lanthanum complex with non-chelating neutral bis-phosphine, as well as the first three structurally characterized gadolinium complexes with neutral phosphines. The magnetic properties of the dimeric gadolinium complexes were characterized using SQUID magnetometry.



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Gallium outperforms aluminum in rare-earth-metal-based isoprene polymerization

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Polyisoprene is a material with a broad portfolio of industrial applications, such as for the fabrication of tires, industrial seals and conveyor belts.[1] In theory, the polymerization of isoprene can give access to eight distinct polymers (*cis*-1,4-; *trans*-1,4-; s/i/a-1,2- and s/i/a-3,4-polyisoprene), with *cis*-1,4-polyisoprene being the most-demanded in terms of application potential. Catalyst design mainly involves rare-earth metals as active sites, which were shown to produce the *cis*-1,4-isomer with >98% selectivity.[2] Structure-reactivity analysis of molecular catalyst precursors has mainly contemplated the variation of ancillary ligands, while industrially applied Mischkatalysatoren draw upon empirically developed mixtures of inexpensive neodymium carboxylates and organoaluminium cocatalysts.

It was revealed that such multinary mixtures form the active species via Nd–Al bimetallic alkyl intermediates like $Nd(AlR_4)_3$.[3] Here we wish to elucidate the occurrence of any intrinsic "aluminum effect" by comparing the polymerization performance of rare-earth-metal tetramethylaluminate complexes $Ln(AlMe_4)_3$ with that of the gallium congeners $Ln(GaMe_4)_3$.[4] Various precatalyst–cocatalyst combinations have been investigated, revealing a significant increase in selectivity for the gallium derivatives.[5]

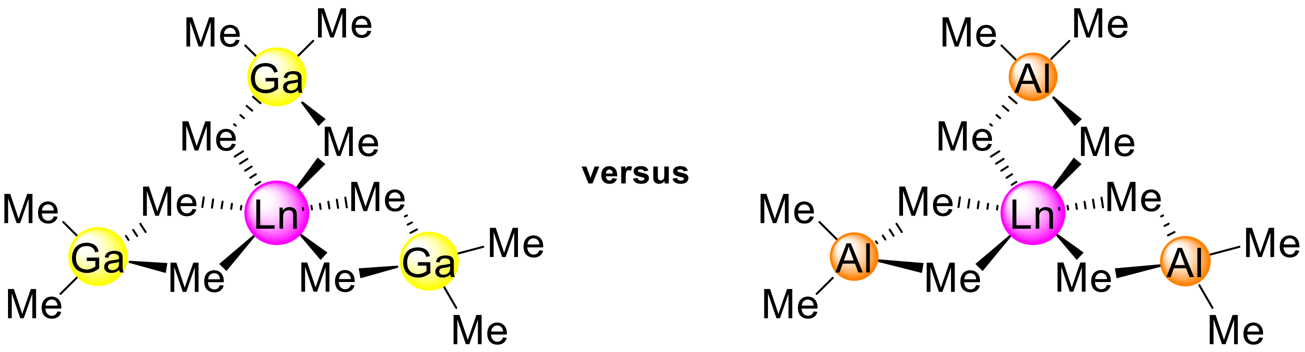

Figure: Discrete heterobimetallic precatalysts used for isoprene polymerization (Ln = La, Y, Nd).

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3d-5d double perovskites containing rare earth metals

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Double perovskites with the general formula $A_2BB'O_6$ (A = alkaline earth or rare earth metal, B = 3d transition metal, B' = 4d or 5d transition metal) with an ordered rock-salt-like arrangement of corner-sharing alternating BO_6 and $B'O_6$ units are functional materials and have been extensively studied. They are suitable for many applications, especially new magnets. For instance, Sr_2FeMoO_6 is a half-metallic ferromagnet (T_C = 415 K) showing colossal magnetoresistance [1], and Sr_2CrOsO_6 [2] exhibits ferrimagnetic ordering up to very high temperatures (T_C = 725 K).

There are several representatives of double perovskites of the type A_2BIrO_6 (B = trivalent metal) containing Iridium in the formal oxidation state +5. Due to strong spin-orbit coupling the $5d^4$ configuration of iridium is assumed to lead to a nonmagnetic ground state as realized in $NaIrO_3$ [3]. The report about long-range magnetic order in Sr_2YIrO_6 [4] at low temperatures raised some questions about this picture [5, 6]. Composition $SrLaBB'O_6$ gives the possibility to combine divalent transition metal ions with Ir^{5+}. By this approach, $SrLaNiIrO_6$ [7, 8] and $SrLaCuIrO_6$ [9] have been synthesized. The first compound crystallizes monoclinic, whereas the latter presents higher tetragonal symmetry with significant Jahn-Teller distortion in the coordination sphere of the $3d^9$ ion Cu^{2+}. Magnetic and electronic properties of both compounds were investigated.

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Sandwich and Half-Sandwich Lanthanum Methyl Complexes

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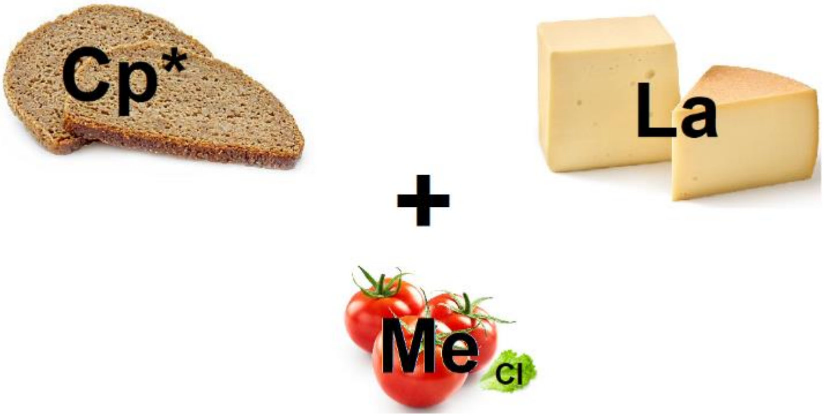
The stabilizing effect of the cyclopentadienyl (Cp) ligand has been known for over 70 years.[1] Since then many organometallic complexes were described with either the plain Cp or the substituted (Cp^R) ligand. In 1986, the sandwich lanthanide chloride and methyl complexes were described.[2] Only the praseodymium complex was crystallized back then and the same structure presumed for all lanthanides.

Rare-earth-metal complexes bearing the pentamethylcyclopentadienyl ligand (Cp*) have triggered myriad applications in homogeneous catalysis including small molecule activation and polymerization. Half-sandwich methyl complexes display crucial components and were effectively employed as monomeric tetramethylaluminates $[Cp^*Ln(AlMe_4)_2]$ or trimeric $[Cp^*Ln(\mu\text{-}Me)_2]_3$.[3] Investigations into the active species of such polymerization reactions suggest the formation of bridging methylidenes before activation with the cocatalyst.[4]

Similar but even larger aggregates with lanthanides have been described for scandium halides. Variations of the substituents of the Cp ring emerged in tetramers of the corresponding chlorides and iodides.[5,6] Unsurprisingly, the larger lanthanum forms cluster-type structures like $[Cp'La(\mu\text{-}X)_2]_{12}$ ($Cp' = C_5H_4SiMe_3$; X = Br, I).[7]

In this work we wanted to get further insights in the reactivity of the sandwich and half-sandwich methyl complexes of the larger lanthanides, especially lanthanum as it is the largest one. Even though some complexes of lanthanum with Cp* ligands are already known the simple lanthanocene methyl complex has been suggested previously,[2] but could not yet be crystallized just like the half-sandwich Cp* lanthanum dimethyl complex.



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Solvent-free Rare Earth Bis(trimethylsilyl)phosphide Complexes

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Rare Earth (RE) heavy pnictide chemistry is immature compared to that of N-donor ligands due to the preference of hard Lewis acid RE ions to bond with hard Lewis base donor atoms.[1,2] For example, bis(trimethylsilyl)amide, $\{N(SiMe_3)_2\}$, has supported many advances in RE chemistry,[3] but the chemistry of bis(trimethylsilyl)phosphide, $\{P(SiMe_3)_2\}$, is still in its infancy.[2] In recent years our group and collaborators have used a combination of ^{31}P NMR and EPR spectroscopy, and DFT and *ab initio* calculations, to probe the electronic structures of solvated RE silylphosphide complexes.[4–6]

In previous work Westerhausen reported the synthesis of the dimeric solvent-free Y(III) $\{P(SiMe_3)_2\}$ complex $[Y\{P(SiMe_3)_2\}_2\{\mu\text{-}P(SiMe_3)_2\}]_2$ (**1-Y**) by the protonolysis reaction of $[Y\{CH(SiMe_3)_2\}_3]$ with 3 eq. $HP(SiMe_3)_2$ in toluene.[7] Here we expand this series *via* modified protocols to synthesise the structurally analogous complexes $[RE\{P(SiMe_3)_2\}_2\{\mu\text{-}P(SiMe_3)_2\}]_2$ (**1-RE**) (RE = Gd, Dy, Er) (Fig. 1). Further, we find that the 'ate' complexes $[RE\{P(SiMe_3)_2\}_2\{\mu\text{-}P(SiMe_3)_2\}_2K]_\infty$ (**2-RE**; Y, Gd, Dy, Er) are straightforwardly synthesised by the reaction of **1-RE** with 2 eq. $KP(SiMe_3)_2$. Here we report characterisation data for **1-RE** and **2-RE**.

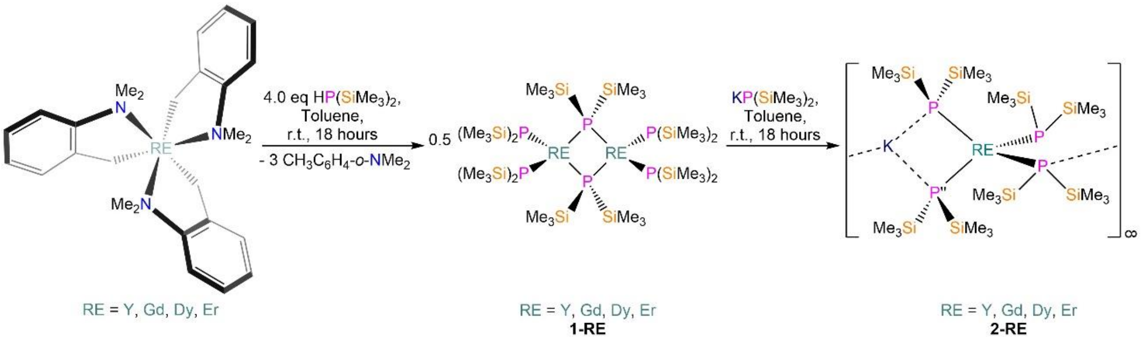

Fig. 1. Synthesis of $[RE\{\mu\text{-}P(SiMe_3)_2\}\{P(SiMe_3)_2\}_2]_2$ (RE = Y, Gd, Dy, Er; **1-RE**),[7] and $[RE\{P(SiMe_3)_2\}\{\mu\text{-}P(SiMe_3)_2\}_3K]_\infty$ (**2-RE**) (RE = Y, Sm, Gd, Dy, Er; **2-RE**).

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Bioaccumulation and excretion of rare earth-containing particles in the single-celled eukaryote *Tetrahymena*

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Understanding how organisms deal with critical elements in their environment is becoming increasingly important with the growing use of high-tech materials. The single-celled **eukaryote ciliate species *Tetrahymena*** can tolerate high concentrations of toxic heavy metals and it is known to have developed several detoxification strategies – in particular the intracellular bioaccumulation and transformation of dissolved heavy metals in their environment into solid intracellular metal-containing particles with subsequent excretion of the particles into the surrounding media [1].

In our research, we investigated the process of tolerance, cellular uptake and bioaccumulation of several rare earth elements (**La, Ce, Sm, Eu, Gd, Dy**) in the ciliate species *Tetrahymena* using cell culture, light and electron microscopy (SEM-EDX) and analytical methods (ICP-OES). Exposition of the cells with dissolved rare earth elements in their organic growth medium results in the uptake of the ions and an intracellular bioaccumulation with the formation of uniformly sized biogenic rare earth element-containing particles. The particles consist of a metal-organic material (for example: Gd, C, O, P, Na, Mg, K, and Ca [1]), are amorphous and have a uniform size of about 3 µm in diameter. It is possible to separate the particles from working solution. With this cellular process, for example, 53% of dissolved Gd from the organic growth medium can be removed within 72 h [1].

Cellular bioaccumulation pathways are a promising approach for finding new bio-inspired strategies for recycling or remediation. Furthermore, the study of bio-composite materials, such as these rare earth-containing particles, is of interest for novel applications in medicine, chemistry or materials science [2].

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DOTA-based photoswitchable ligands for lanthanoids

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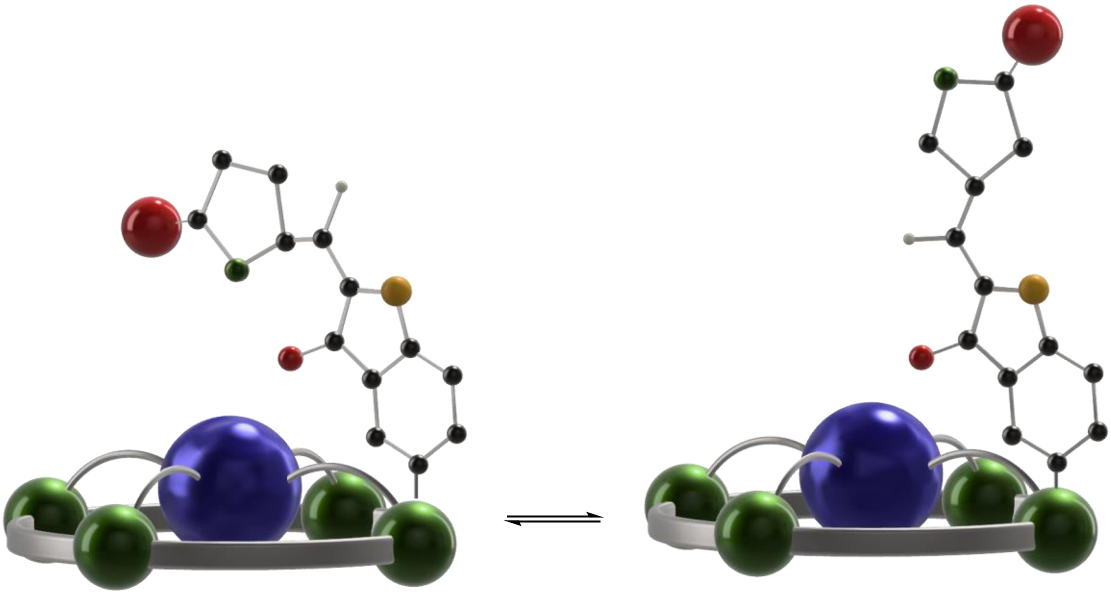
Particularly in the biomedical context, incorporation of lanthanoids is a powerful strategy to utilize their unique properties. While the lanthanoid provides the core functionality, the ligand can support or modify the lanthanoid-centered properties and ensure compatibility with the specific application. [1,2] For example, for the realisation of europium-based emitters an organic antenna for indirect sensitization is required [3] and gadolinium-based contrast agents for MRI have to be extremely stable against decomposition and yet leave a coordination site vacant for water molecules to coordinate.[1] Those ligand-centered properties can in principle be manipulated with a large amplitude structural rearrangement of the ligand. This would, for example, pave the way to photoswitchable gadolinium-based contrast agents for MRI. Hemithioindigo is a photoswitchable building block which is a suitable candidate for the realisation of such types of ligands.[4]



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Effect of charge on oxyanion sensing in Eu(III)-based nanooptodes

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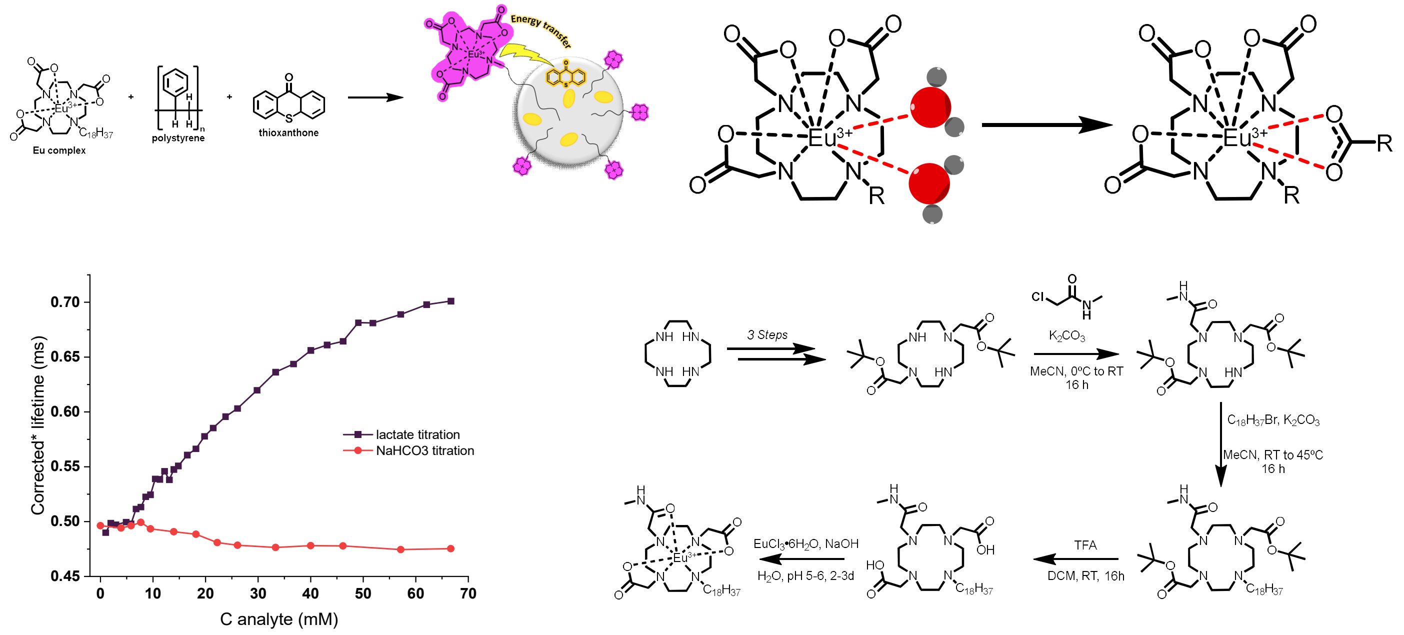
Lanthanide complexes have garnered significant attention of the academic community as promising sensing agents over the past 3 decades.[1] Europium and terbium, in particular, possess inherent properties such as long luminescence lifetimes and sharp emission spectra, making them remarkably useful for assays in biological media.[2] Lanthanide complexes with 7-dentate polyaza macrocyclic ligands have been reported to selectively bind chelating oxyanions by displacing two inner sphere water molecules.[3] However, many complexes and ternary complexes with analytes suffer from poor solubility and aggregation in aqueous solutions, which poses a major issue for biological measurements.[4] Previous work conducted by our group demonstrated that Eu(III)·DO3A complexes could be successfully attached to the surface of polystyrene nanoparticles, while retaining the ability to quantitatively detect oxyanions in solution.[5] Furthermore, the developed protocol allowed for the incorporation of antenna dyes into the PS nanoparticles, resulting in a significant increase in luminescence intensity.[5] In this study, our objective is to investigate the effect of the complex charge on binding of oxyanions and behavior of the whole nanoparticle system.



Top left: synthesis of nanooptodes; Top right: binding of chelation oxyanions;
Bottom left: responce to lactate and carbonate titrations; Bottom right: synthetic pathway

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Preparation of a europium(III)-based nanooptode for bicarbonate sensing by nanoparticle surface post-complexation

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In the realm of sensing, responsive lanthanide complexes have been of great interest due to sharp emission peaks, large Stokes shifts, and long excited state lifetimes.[1] Due to low molar absorptivity an antenna chromophore has to be included for an efficient signal to be obtained.[2] Recently, a europium(III)-based nanooptode was developed by Wang et al., by loading polystyrene nanoparticles with thioxanthone (antenna) and coating the surface with a Eu·DO3A complex, which has shown promise for sensing purposes.[3] However, the progress from laboratory experiments to an industrial setting is a slow process, due to challenges concerning robust materials and preparation protocols.

Here, we expand on this work and present a method for preparation of a nanooptode for bicarbonate sensing, by post-complexation on the nanoparticle surface. Following the protocol developed by Wang et al., nanoparticles loaded with an antenna chromophore (thioxanthone) and coated with a DO3A ligand were synthesized by a sonification microemulsion method. Following the nanoparticle synthesis, DO3A was complexed with different lanthanides (Eu^{3+}, Pr^{3+}). The success of the complexation process was determined by time-gated emission spectroscopy measurements before and after complexation, and the results were compared to similarly synthesized nanoparticles where the antenna chromophore was omitted.

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Investigating the hydrogenation of Zintl phases Eu*Tt* (*Tt* = Si, Ge, Sn)

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Zintl phases display a wide range of structure and boding motifs upon hydrogenation and several of the phases *MTt* (*M* = Ca, Sr, Ba; *Tt* = Si, Ge, Sn) were already reported to reversibly take up hydrogen.[1]
The CrB type structure (space group no. 63, *Cmcm*) features planes of edge sharing *M* tetrahedra with rows of polyanionic “zig-zag”-chains in between. Upon hydrogenation, the tetrahedral sides are filled with hydride ions, oxidating the chains and leading to a decrease in bond length. These hydrides can be classified as “interstitial hydrides”, whereas the hydrogenation beyond fully occupied tetrahedra leads to so called “polyanionic hydrides”. [2] They feature tilted chains, with new *Tt*-*Tt*-bonds in between and are terminated by covalently bound hydrogen. The maximal hydrogen uptake rises alongside the cation size as increasing inter chain distances favor the termination with hydrogen (e.g.: $CaSiH_{4/3-x}$, $SrSiH_{5/3-x}$, $BaSiH_{2-x}$). The contrary can be observed for heavier anions.[1] Given the almost identical ionic radii between Eu^{2+} and Sr^{2+}, one would expect the three phases Eu*Tt* (*Tt* = Si, Ge) to behave similarly to the known $SrSiH_{5/3-x}$[2] and $SrGeH_{4/3-x}$[1]. However, only one report of $EuSiH_{1.8}$ was published so far, with the hydrogen content being determined via carrier hot gas extraction.[2]
Eu*Tt* (*Tt* = Si, Ge, Sn) were synthesized by induction heating, hydrogenated in autoclaves and analyzed with powder X-Ray diffraction and Rietveld refinement. An *in situ* neutron powder diffraction experiment was carried out on the hydrogenation behavior of EuGe, where multiple hydrides as well as reversibility between the phases could be observed.

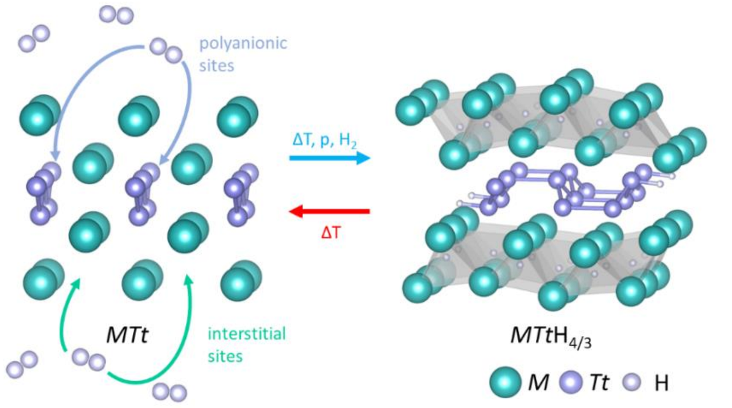

Figure 1: Structural features of CrB-type *MTt* and the ternary hydride $MTtH_{4/3}$.

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Azobenzene Cryptates as Photoswitchable Ligands

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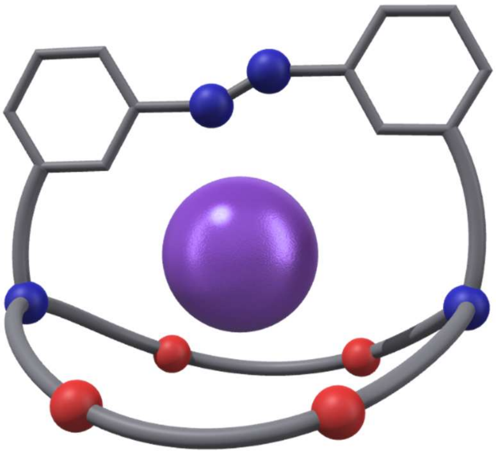
Due to their highly preorganized cavity, macrobicyclic cryptands form complexes of very high stability and exhibit excellent ion selectivity. Variation of size, donor atoms and rigidity of the building blocks connected by the bridge heads allows to fine tune their properties. Applications include ion extraction, phase transfer catalysis and the use as ligand for luminescent lanthanoid complexes.[1,2]

A particularly interesting variant of cryptates results from the incorporation of photoswitchable building blocks. By that, the properties of the cryptates become dynamically controllable, paving the way for more elaborate applications. This requires fine tuning of the overall rigidity of the scaffold in both switching states and righteous choice of complementary building blocks.[3,4]



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Diazocines as building blocks in lanthanoid coordination compounds

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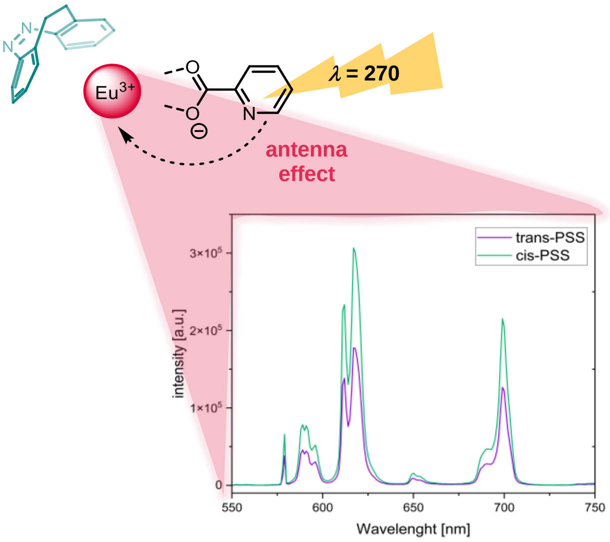
Ligand field effects in lanthanoid coordination compounds are small, yet decisive for some of the most fascinating properties of the lanthanoids. Most important examples include their magnetic properties and their ability to emit circularly polarised light[1] (CPL, “enantioenriched” light). Most ligands for lanthanoids, including the archetypical DOTA scaffold, provide a highly dynamic coordination environment. This hinders understanding and design of these important properties.

Diazocines are promising photoswitches for the modulation of lanthanoid luminescence in terms of luminescence intensity and lifetimes in the visible as well as the NIR.[2] Upon irradiation with light, diazocines perform a moderate yet distinct change of their geometry.[3] This is promising as tool for the manipulation of the delicate interplay of rigidity and flexibility in lanthanoid coordination compounds - in situ and with an excellent spatiotemporal resolution. By incorporation of diazocines into ligand scaffold for lanthanoids we explore their potential for an optimised photoswitching of lanthanoid luminescence and more elaborate phenomena.



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Expanding Lanthanide Chemistry Using Redox-Active Di(Imino)Pyridine Ligands.

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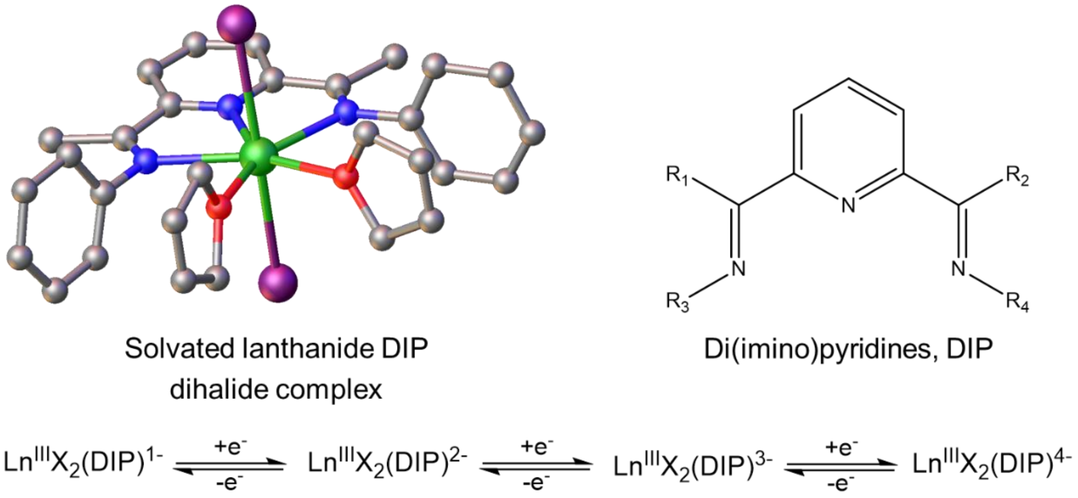
Lanthanides (Ln) have a strong predisposition to adopt the +3 formal oxidation state,[1] which tends to limit their redox chemistry in comparison to d-transition metals. However, using redox-active ligands such as di(imino)pyridines (DIP), which can store as many as four electrons within their delocalized orbitals,[2] can greatly expand Ln redox chemistry by diverting electron-transfer processes from the metal centers to the ligands.[3] The predominantly ionic bonding regimes of Ln ions minimizes their influence on the electronic properties of ligands,[1] and the simplicity of synthesizing DIP ligands[4] streamlines the design of novel complexes exhibiting unique reactivity profiles. Precise tuning and optimization of reactivity can be achieved by modification of the Ln ion and co-ligands, as well as functionalization of the DIP backbone. We are currently investigating the potential of Ln DIP complexes in mediating stoichiometric and catalytic redox-driven organic transformations. Here we report the synthesis and characterization of a structurally analogous series of Ln DIP dihalide complexes, [Ln(DIP)(I)$_2$(THF)$_2$] (Fig. 1), which vary by Ln ion and DIP substituents, using simple synthetic protocols.


Solvated lanthanide DIP dihalide complex

Di(imino)pyridines, DIP

$$Ln^{III}X_2(DIP)^{1-} \xrightleftharpoons[-e^-]{+e^-} Ln^{III}X_2(DIP)^{2-} \xrightleftharpoons[-e^-]{+e^-} Ln^{III}X_2(DIP)^{3-} \xrightleftharpoons[-e^-]{+e^-} Ln^{III}X_2(DIP)^{4-}$$

Fig. 1. Crystal structure of [Sm(DIP)(I)$_2$(THF)$_2$] and predicted redox processes.

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Valence Electron Configurational Isomers – f-Block Elements Acting Like d-Block Elements?

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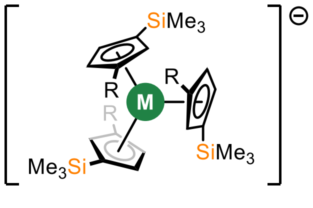
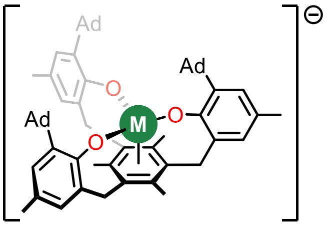
Rare-earth elements often exhibit limited redox chemistry and are dominated by the trivalent (3+) oxidation state. While the 2+ oxidation state is known in non-aqueous molecular systems for several of the rare-earth elements (Sm^{2+}, Eu^{2+}, and Yb^{2+}) for over 40 years,[1] it has only been in the last two decades that molecular examples have been realized for the rest of the rare-earth elements (save radioactive Pm).[2] Recent works have demonstrated the use of sterically demanding ligands capable of forming metal-arene π-interactions as a strategy for stabilizing low valent rare-earth and actinide complexes with varying degrees of metal or ligand contributions to their highest occupied molecular orbitals.[3-5]

We recently reported the use of bulky *meta*-terphenyl anilido ligands that enforce a *pseudo bis*-arene environment around the metal.[6] This has led to the isolation of several room temperature stable formally divalent rare-earth complexes which we have characterized by SQUID magnetometry, and UV-Vis-NIR and EPR spectroscopies, as well as computational methods. Analysis of their structures (**C**) reveal distortion of one or both coordinating arene rings that occur due to M-arene δ-bonding interactions, with differences in the electronic structure arising between the solid and solution state. We will also present our results extending this work to synthesize the entire rare-earth series (save Pm) and exploring the chemical reactivity, redox properties, and electronic structure of these systems.



Y, La–Lu (not Pm), U; R = H
La–Nd, Th, U–Pu; R = $SiMe_3$

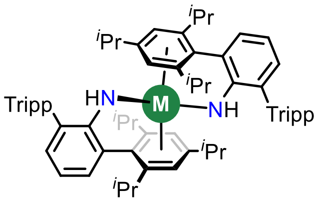
A



U, Y, La, Ce, Pr, Sm,
Yb, Nd, Gd, Dy, Er

B

Tripp = C_6H_2-2,4,6-^{i}Pr



Sc, Y, La, Sm,
Eu, Tm, Yb + others

C: This Work

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From RbEu[AsS_4] to Rb_4Eu[AsS_4]$_2$: Synthesis and Characterization

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Alkali-metal polysulfide-flux syntheses have already been used several times in the past for the successful synthesis of quaternary europium(II) thiophosphates and arsenates, such as KEu[PnS_4] or A_4Eu[PnS_4]$_2$ (A = Na or K and Pn = P or As) [1-3]. Nevertheless, RbEu[AsS_4] and Rb_4Eu[AsS_4]$_2$ are the first formula-analogous compounds with a larger alkali metal that will be presented here.

Red single crystals of RbEu[AsS_4] were synthesized by using Eu:Rb_2S_3:As_2S_3:S mixtures in a molar ratio of 1:1:1:6, which were heated up to 500 °C for 4 days. It crystallizes orthorhombically in the space group *Pnma* with $a = 1729.53(9)$ pm, $b = 679.18(4)$ pm, $c = 670.46(4)$ pm and $Z = 4$. The crystal structure is characterized by isolated [AsS_4]$^{3-}$ tetrahedra, whose sulfur edges form europium-centered bicapped trigonal prims with d(Eu–S) = 299 – 310 pm for the six shorter distances and d(Eu–S') = 354 pm for the caps. These [EuS_8]$^{14-}$ polyhedra are thus edge-linked forming infinite layers parallel to the (100) plane, separated by Rb^+ cations in eightfold sulfur coordination.
In an attempt to synthesize phase-pure RbEu[AsS_4], the molar ratio of the reactants was changed to 2:1:1:2, resulting in the formation of orange single crystals of Rb_4Eu[AsS_4]$_2$ as a second phase. Rb_4Eu[AsS_4]$_2$ crystallizes in the orthorhombic space group *Ibam* with $a = 913.46(5)$ pm, $b = 1873.08(11)$ pm, $c = 1010.23(6)$ pm for $Z = 4$. The crystal structure is again built of isolated [AsS_4]$^{3-}$ tetrahedra, whose edges coordinate the Eu^{2+} cations forming twisted tetragonal prims [EuS_8]$^{14-}$ (d(Eu–S) = 314 – 319 pm). In contrast to RbEu[AsS_4], not all edges of the [AsS_4]$^{3-}$ tetrahedra are involved in the europium-centered sulfur polyhedra. This results in the formation of infinite chains of edge-connected [EuS_8]$^{14-}$ polyhedra along the [001] direction with bridging [AsS_4]$^{3-}$ units pointing S1 thorns between the chains. Due to these dangling S1-ligands, channels along [100] and [001] arise, in which the Rb^+ cations reside, coordinated by 6+2 and 8 sulfur atoms.

RbEu[AsS_4] and Rb_4Eu[AsS_4]$_2$ were both characterized by single-crystal Raman spectroscopy to confirm the presence of tetrahedral [AsS_4]$^{3-}$ units. Both show typical symmetric stretching modes at 388 cm^{-1} and 391 cm^{-1}, respectively, and asymmetric stretching modes split into several bands at slightly higher wavenumbers (432 – 472 cm^{-1}), while the deformation vibrations occur at 150 – 240 cm^{-1}.

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The Neodymium Tantalate $NdTaO_4$ in the *M-Fergusonite* Structure Type

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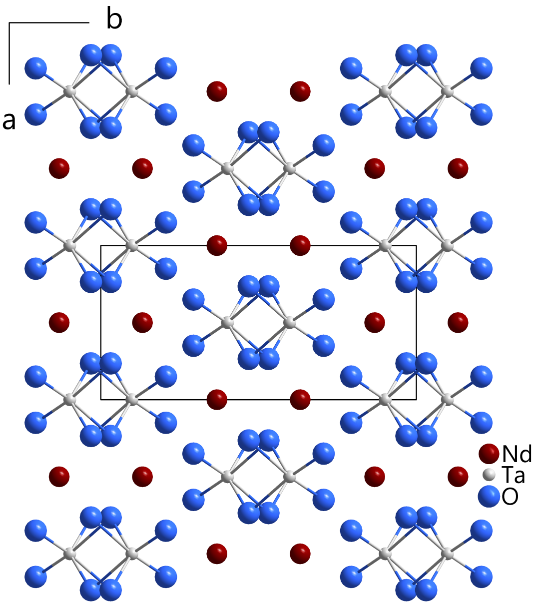
An unsuccessful attempt of the solid state synthesis to yield sodium neodymium chloride tantalate $NaNd_3Cl_3[TaO_6]$ led to the formation of neodymium tantalate $NdTaO_4$ in the *M-fergusonite* structure type [1]. It crystallises in the monoclinic space group $C2/c$ (a = 713.88(6) pm, b = 1123.34(9) pm, c = 511.47(4) pm, β = 129.791(3)°) with four formula units per unit cell. $NdTaO_4$ shows polymorphism, since it is previously reported to crystallise in the $LaTaO_4$ structure type ($P2_1/c$) [2], in the *M'-fergusonite* [3] and the *T-fergusonite* structure types ($I4_1/a$, similar to *scheelite* structure type) [4].

The Nd^{3+} cations are coordinated in the shapes of distorted tetragonal antiprisms by eight oxygen anions. The $[TaO_6]^-$ anions represent strongly distorted octahedra [5] which form strands by sharing common edges according to $^{1}_{\infty}\{[\mathrm{TaO}^{k}_{4/2}\mathrm{O}^{t}_{2/1}]^{-}\}$. These strands are roughly arranged according to a hexagonal rod packing with the neodymium cations residing in between (see figure).



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The Quest of a Samaride – The First Isolated Lanthanide Anion

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A charge of +III has been long demonstrated as the most stable oxidation state throughout the lanthanides, alongside occurrence of +II, +IV or even +V for some of the elements.[1] Well-established oxidation states of elements remain under review constantly as the boundaries of known reactivities and bonding situations are probed and expanded continuously. Due to the reducing nature of the lanthanides, historically, their monovalent cations have not been easily accessible, however, Ln(I) (Ln = La, Pr, Tb, Tm, Yb) species were isolated with the help of boride clusters.[2] A transient samarium(I) complex was recently reported in the mechanism of a Sm(I)/Sm(III) redox couple towards the four-electron reduction of benzene by a samarium(II) alkyl.[3] The synthesis of bis(η-arene) complexes provides access to lanthanides in the oxidation state zero. Stretching the oxidation state even further, lanthanide anions have been studied by means of theoretical calculations, as well as determined experimentally as transient species using low-energy electron collisions from a caesium sputter source combined with accelerator mass spectrometry.[4] Accessing lanthanide compounds in low oxidation states will vastly expand the chemistry of these elements posing as even stronger reducing agents and will potentially advance their technological applications.

We hereby propose research on the topic of monovalent lanthanide anions, with particular focus on isolation of a samarium(−I) species, a *samaride*. To this end, we propose a synthetic approach *via* electride solutions in liquid ammonia at temperatures ≤ -60 °C. The formation and highly reducing properties of solvated electrons upon dissolution of certain metals in liquid ammonia has been known since the early 20th century.[5] Adding a sequestering agent, such as a crown ether or cryptand, results in the complexation of the oxidised metal cation, hindering the recombination of the cation and the electron, effectively increasing the reduction potential of the reaction mixture.

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$Pr_3OI[AsO_3]_2$: The First Oxide Iodide Oxoarsenate of the Rare-Earth Metals

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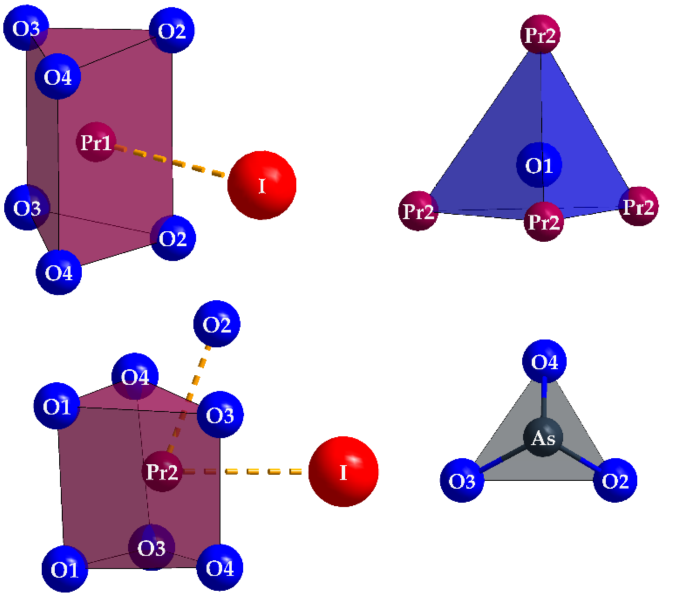
In analogy to the *non*-centrosymmetric $Ln_3OX[AsO_3]_2$ representatives (Ln = Ce – Nd, Sm – Dy; X = Cl and Br)[1–4], the isostructural iodide $Pr_3OI[AsO_3]_2$ was obtained in synthetic experiments with Pr, PrI_3, As_2O_3 with CsI as flux by means of a partial metallothermic reduction at 850 °C. The green, needle-shaped crystals could be recovered phase-pure after removal of the resulting monolithic arsenic crystal. $Pr_3OI[AsO_3]_2$ crystallizes in the tetragonal space group $P4_2nm$ with the lattice parameters a = 1289.13(9) pm, c = 559.24(5) pm and c/a = 0.434 for Z = 4 (CSD-2306280). The crystal structure contains two positions for the Pr^{3+} cations, only one for I^- and As^{3+} as well as four O^{2-}-anion sites. $(Pr1)^{3+}$ is surrounded sixfold by O^{2-} anions forming trigonal prisms, which are capped by an I^- anion each ($[(Pr1)O_6I]^{10-}$), whereas $(Pr2)^{3+}$ has also one I^-, but seven O^{2-} anions as coordination sphere resulting in bicapped trigonal prisms $[(Pr2)O_7I]^{12-}$ (Figure 1). These $[(Pr2)O_7I]^{12-}$ polyhedra are stacked alternatingly along [001] to form columns and edge-linked with $[(Pr1)O_6I]^{10-}$ polyhedra, which alternate with each other and form rings parallel to the (001) plane. The *non*-bonding electron pairs at the ψ^1-tetrahedral $[AsO_3]^{3-}$ anions point into cavities, which run along [001] (Figure 2), as do the chains of *trans*-edge shared $[(O1)Pr_4]^{10+}$ tetrahedra.



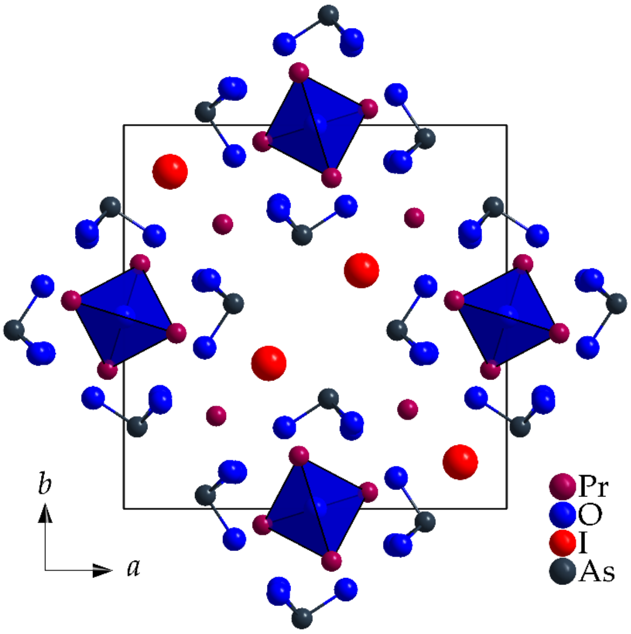


Figure 1. Capped and bicapped trigonal prisms $[(Pr1)O_6I]^{10-}$ and $[(Pr2)O_7I]^{12-}$ (*left*) as well as $[OPr_4]^{10+}$ tetrahedron and ψ^1-tetrahedral $[AsO_3]^{3-}$ anion (*right*) in the crystal structure of $Pr_3OI[AsO_3]_2$.

Figure 2. View at the tetragonal crystal structure of $Pr_3OI[AsO_3]_2$ along [001].

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Crystal Field Splittings in Molecular Lanthanide Tetra-Carbonates

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In recent years, the interest in f-elements within molecular nanomagnets has increased enormously [1]. Their high magnetic moments and anisotropy often lead to slow relaxation of the magnetisation, an essential property for possible applications like novel data storage devices. The magnetic properties of the compounds are linked to their electronic structure, which can be probed by several experimental methods, including magnetic circular dichroism (MCD) spectroscopy. MCD spectroscopy combined with electronic absorption spectroscopy is an outstanding technique for studying the excited state as well as the ground state properties at the same time.

High-resolution MCD and absorption spectroscopy at low temperatures enabled us to directly observe the crystal field splittings of the excited states of several f-element based nanomagnets. These excited state splittings were then used for the determination of the corresponding crystal field parameters which in turn yield information about the electronic ground state.

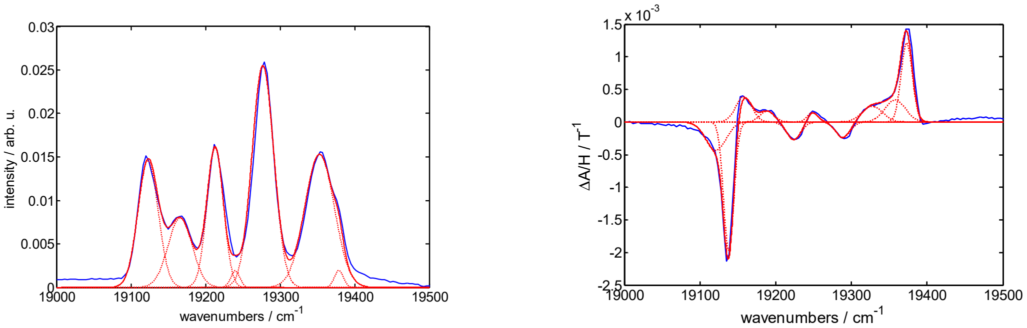

Figure 1: Solid state electronic absorption and MCD spectra of molecular Erbium Carbonate at 2 K. The spectra show the transition to the $^2H_{11/2}$ state.

Special attention was paid to molecular tetra-carbonates of Erbium and Dysprosium [2], which both show field-induced single ion magnet behaviour. In combination with a range of further experimental techniques including magnetometry, far infrared spectroscopy and electron paramagnetic resonance, an in-depth investigation of the electronic structure was performed.[3]

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Crystal and electronic structure of the ternary silicides $R\mathrm{Fe}_{1-x}\mathrm{Si}_2$ (R = Gd, Tb, Er, Tm, Yb)

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A range of ternary compounds $RT_{1-x}\mathrm{Si}_2$ (R – rare earth, T – transition element) have been reported for the last decades. Their crystal structures are characterized by the stacking of BaAl_4 and AlB_2 slabs. The light rare earth manganese $R\mathrm{Mn}_{1-x}\mathrm{Si}_2$ (R = La-Sm) and iron silicides $R\mathrm{Fe}_{1-x}\mathrm{Si}_2$ (R = La-Nd, Gd-Lu) are known to crystallize in the LaMnSi_2-type structure, a structure closely related to that of CeNiSi_2-type structure, and characterized by site exchange between transition-metal and main-group elements within the BaAl_4 block; while the stoichiometric $R\mathrm{FeSi}_2$ (R = Nd, Sm, Gd, Tb) crystallize in the NdRuSi_2-type structure ([1, 2] and refereces therein).

The crystal structure of new ternary silicide $\mathrm{YbFe}_{1-x}\mathrm{Si}_2$, $x = 0.52(1)$ has been determined from X-ray single crystal data. Intensity data were collected at room temperature using the Bruker D8 Quest diffractometer equipped with Mo-anode X-ray tube and Photon CCD detector. From the EDX analysis of the annealed sample $\mathrm{Yb}_3\mathrm{FeSi}_6$ the composition $\mathrm{Yb}_{29.7(3)}\mathrm{Fe}_{12.3(3)}\mathrm{Si}_{58.0(3)}$ was deduced, being in good accordance with the results obtained from the crystal structure refinement. $\mathrm{YbFe}_{1-x}\mathrm{Si}_2$ crystallizes in the CeNiSi_2 structure type, orthorhombic space group *Cmcm*, Pearson symbol *oC*16, $a = 3.9916(4)$, $b = 15.4314(18)$, $c = 3.8780(4)$ Å, $R1=0.027$ ($wR_2=0.059$ for 273 reflections with $I_o \geq 2\sigma(I_o)$). In the crystal structure of $\mathrm{YbFe}_{1-x}\mathrm{Si}_2$ all atoms are in Wyckoff positions 4(c) – 0 y 1/4: Yb ($y = 0.39780(3)$, $U_{\mathrm{eq}} = 0.0050(1)$ Å^2), Fe ($y = 0.1951(2)$, $U_{\mathrm{eq}} = 0.0263(7)$ Å^2), Si1 ($y = 0.0481(2)$, $U_{\mathrm{eq}} = 0.008(1)$ Å^2), Si2 ($y = 0.7506(2)$, $U_{\mathrm{eq}} = 0.021(1)$ Å^2). The refined Fe site occupancy is $G = 0.52(1)$. The structure contains zigzag chains of Si1 and planar nets of Si2 atoms. The latter show shortened interatomic distances to Fe atoms. According to the powder XRD data and EDXS analysis of alloys homogenized at 1070 K the homogeneity ranges of $R\mathrm{Fe}_{1-x}\mathrm{Si}_2$ (R=Gd→Lu) were refined. Formation of the stoichiometric compound GdFeSi_2 (NdRuSi_2 -type structure) was also confirmed in course of our studies at 1070 K.

Zintl concept can be applied for an ordered variant $R\mathrm{Fe}_{0.5}\mathrm{Si}_2$ the which results in formal oxidation states $R^{3+}(\mathrm{Fe}^{2+})_{0.5}\mathrm{Si}(1)^{1-}\mathrm{Si}(2)^{3-}$. The electronic structure of this variant $\mathrm{GdFe}_{0.5}\mathrm{Si}_2$ was analyzed using the tight-binding LMTO method.

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