

Program

Oral Contributions

The Conference Room is on Deck 8 of M/S Mariella.

Contributions are listed, with a few exceptions, in alphabetical order of the cities of the affiliations of the presenting author.

Swedish Time + 1 hour = **Finnish Time**

| Thursday, May 30, 2019 | | Swedish Time |
|------------------------|---|-----------------------|
| 14:15 | Check-In at Viking Line Terminal, Stockholm, Sweden | |
| 15:00 | Welcome: Anja-Verena Mudring | Stockholm, S |
| 15:10 | Rhett Kempe | Bayreuth, D |
| 15:30 | Anne E. V. Gorden | Auburn, AL, USA |
| 15:50 | Julie E. Niklas | |
| 15:55 | Karl W. Krämer | Bern, CH |
| 16:10 | Julia-Maria Hübner | Dresden, D |
| 16:20 | Eteri Svanidze | |
| 16:40 | Selvan Demir | East Lansing, MI, USA |
| 17:00 | Alessia Provino | Genoa, I |
| 17:20 | Joy H. Farnaby | Glasgow, GB |
| 17:35 | Samuel J. Horsewill | |
| 17:45 | Bradley Wilson | |
| 18:00 | Nathalie Kunkel | Göttingen, D |
| 18:15 | Chimednorov Otgonbayar | Halle/S., D |
| 18:30 | Michael T. Gamer | Karlsruhe, D |
| 18:35 | Luca Münzfeld | |
| 18:40 | Peter W. Roesky | |
| 19:30 | Dinner | |
| 20:30 | Robin Rogers | Stockholm, S |
| 20:50 | Terraе Rarae Award 2019 | |

| Friday, May 31, 2019 Finnish Time | | |
|--|---------------------------------------|-----------------|
| 7:30-8:45 | Breakfast | |
| 8:40 | Helene Obel Bøch Andersen | København, DK |
| 8:45 | Elena Del Giorgio | |
| 8:50 | Nicolaj Kofod | |
| 8:55 | Patrick R. Nawrocki | |
| 9:00 | Aida Raauf, Köln, D | Köln, D |
| 9:10 | Oleg N. Antzutkin | Luleå, SE |
| 9:30 | Frank T. Edelmann | Magdeburg, D |
| 9:35 | David P. Mills | Manchester, GB |
| 9:55 | Benjamin L. L. Réant | |
| 10:00 | Glen B. Deacon | Melbourne, AUS |
| 10:15 | Peter J. Junk | Townsville, AUS |
| 10:30 | Guillaume Bousrez | Stockholm, SE |
| 10:50 | Yury Belousov | Moscow, RUS |
| 11:00 | Ilya Taydakov | |
| 11:15 | Dmitrii Roitershtein | |
| 11:35 | Lena J. Daumann | München, D |
| 12:00-15:00 | Free Time in Helsinki, Finland | |

Swedish Time + 1 hour = **Finnish Time**

| Friday, May 31, 2019 | | | Finnish Time |
|----------------------|-------|-----------------------|-----------------------|
| | 15:00 | Svetlana V. Eliseeva | Orléans, F |
| | 15:15 | Stéphane Petoud | |
| | 15:35 | Nathaniel Rosi | Pittsburgh, PA, USA |
| | 15:50 | Eric Schelter | Philadelphia, PA, USA |
| | 16:15 | Florian Jaroschik | Reims, F |
| | 16:30 | Katharina V. Dorn | Stockholm, D |
| | 16:35 | Sebastian Kunkel | Stuttgart, D |
| | 16:40 | Felix C. Goerigk | |
| | 16:50 | Beate M. Schulz | |
| | 17:00 | Ingo Hartenbach | |
| | 17:15 | Reiner Anwander | Tübingen, D |
| | 17:30 | Dennis A. Buschmann | |
| | 17:35 | Alexandros Mortis | |
| | 17:40 | Vadim G. Kessler | Uppsala, S |
| | 17:55 | Gulaim A. Seisenbaeva | |
| | 18:10 | Gunnar Westin | |
| | 18:40 | Magdalena Sobota | Wroclaw, PL |
| | 19:00 | Joanna Cybinska | |
| | 20:00 | Dinner | |
| 21:00-21:45 | | Brando Adranno | Stockholm, S |
| | | Chris Celandia | |
| | | Olivier Renier | |
| | | Volodymyr Smetana | |
| | | Siméon Ponou | |
| | | Alexander Ovchinnikov | |
| | 21:45 | Holger Kohlmann | Leipzig, D |
| | 22:00 | The End | |

| Saturday, June 1, 2019 Swedish Time | | |
|---|--------------------------------|--|
| 7:00-9:45 | Breakfast | |
| 10:00 | Arrival at Stockholm, Sweden | |
| 10:15 | Bus Ride to Ytterby | |
| | Ytterby Gruva and Leisure Time | |
| 13:30 | Bus Ride back to Stockholm | |
| 15:00 | End of Conference | |

Bayreuth, Germany

Anorganische Chemie II - Catalyst Design, University of Bayreuth, 95444 Bayreuth, Germany

- **Rhett Kempe**: Bimetallic Complexes and Catalyst Systems Combining Rare Earth Elements and Transition Metals

Auburn, Alabama, USA

Department of Chemistry and Biochemistry, Auburn University, Auburn, AL, 36849, USA

- **Emily E. Hardy, Ethan A. Hiti, Julie E. Niklas, Kevin M. Wyss, John D. Gorden, Anne E.V. Gorden**: Tunable emission in naphthylsalophen dinuclear lanthanide(III) sandwich complexes
- **Julie E. Niklas, Katherine M. Hunter, Byron H. Farnum, John D. Gorden, Anne E.V. Gorden**: Tetradentate α -diimine ligands for redox-active *f*-element complexes

Bern, Switzerland

University of Bern, Department for Chemistry and Biochemistry, Freiestrasse 3, CH-3102 Bern, Switzerland

- **Daniel Biner, Karl W. Krämer**: Slow Er^{3+} Spin Relaxation in $\text{Cs}_3\text{Er}_2\text{Br}_9$

Dresden, Germany

Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany

- **Julia-Maria Hübner, Matej Bobnar, Lev Akselrud, Yurii Prots, Yuri Grin, Ulrich Schwarz**: Lutetium Trigermanide LuGe_3 : High-Pressure Synthesis, Chemical Bonding and Superconductivity
- **Eteri Svanidze, A. Amon, Yu. Prots, M. Avdeev, A. Leithe-Jasper, Yu. Grin**: Crystal structure and physical properties of the novel complex intermetallic compounds $\text{R}_8\text{Pt}_{32}\text{Be}_{66}$ ($\text{R} = \text{Y}, \text{La-Nd}, \text{Sm-Lu}$)

East Lansing, MI, USA

Department of Chemistry, Michigan State University, 578 S Shaw Lane, East Lansing, MI, 48824, USA

- **Selvan Demir**: Giant Coercivity and Magnetic Blocking in Radical-Bridged Lanthanide Single-Molecule Magnets

Genoa, Italy

Department of Chemistry, University of Genova, Genova, Italy

- **Alessia Provino, Pietro Manfrinetti**: The structurally related $\text{Gd}_5\text{Pt}_2\text{In}_4$ and $\text{Gd}_{11}\text{Pd}_4\text{In}_9$ compounds

Glasgow, United Kingdom

School of Chemistry, University of Glasgow, University Avenue, Glasgow, G12 8QQ, UK

- **Joy H. Farnaby, James R. Hickson, Samuel J. Horsewill, Bradley Wilson, Christopher Bamforth, Dulcie Phipps, Jake McGuire, Claire Wilson, Stephen Sproules: Modular Synthesis of Rare Earth-Transition Metal Complexes Utilizing a Redox-Active Ligand**
- **Samuel J. Horsewill, J. R. Hickson, D. Phipps, J. McGuire, S. Sproules, C. Wilson, J. H. Farnaby: The Lanthanide Co-ordination Chemistry of the Redox-Active Ligand 1,10-phenanthroline-5,6-dione**
- **Bradley Wilson, Jake McGuire, James McAllister, Haralampos N. Miras, Claire Wilson, Stephen Sproules, Joy H. Farnaby: Molecular and electronic structure of the dithiooxalato radical ligand stabilised by rare earth coordination**

Göttingen, Germany — München, Germany

Institute of Inorganic Chemistry, Georg-August-Universität Göttingen, Tammannstraße 4, 37077 Göttingen, Germany

- **Thomas Wylezich, Alexander Mutschke, Nathalie Kunkel: Optical properties of rare earth doped mixed anionic hydrides and borohydrides**

Halle, Germany

Martin-Luther-University – Mineralogy/Geochemistry – Von Seckendorff-Platz 3, 06120 Halle, Germany, chimednorov.otgonbayar@geo.uni-halle.de

- **Chimednorov Otgonbayar, H. Pölmann: Synthesis and characterization of alkaline earth – rare earth – borates $\text{Me}_3\text{REE}_2(\text{BO}_3)_4$**

Karlsruhe, Germany

Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Engesserstraße 15, D-76131 Karlsruhe, Germany

- **Peter W. Roesky: Molecular Lanthanide Zintl-Phases**
- **Thomas Simler, Thomas J. Feuerstein, Ravi Yadav, Michael T. Gamer and Peter W. Roesky: Access to Divalent lanthanide NHC complexes by redox-transmetallation from silver and CO_2 insertion reactions**
- **Christoph Schoo, Luca Münzfeld, Sebastian Bestgen, Alexander Egeberg, Jasmin Seibert, Svetlana Klementyeva, Claus Feldmann, Sergey N. Konchenko, Peter W. Roesky: Samarium Polypnicogenides derived from highly activated nanoscale Arsenic and Antimony**

Stockholm, Sweden — Tuscaloosa, Alabama, USA

Department of Materials and Environmental Chemistry (MMK), Stockholm University, Svante Arrhenius väg 16 C, 106 91 Stockholm, Sweden

- **Robin D. Rogers: Dehydrating f-Element Salt Hydrates with Ionic Liquids and Using the Anhydrous Salts as Labile Intermediates for Bench top N-Donor Chemistry**

København, Denmark

Nano-Science Center and Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 København Ø, Copenhagen, Denmark

- **Helene Obel Bøch Andersen, Alan M. Kenwright, Thomas Just Sørensen: Solution State Structure of Amide Appended LnDO3A Complexes with Slow Amide Bond Rotation**
- **Elena Del Giorgio, Thomas Just Sørensen: Towards a responsive Lanthanide complex for ROS sensing**
- **Nicolaj Kofod, Riikka Arppe-Tabbara, Thomas Just Sørensen: Electronic Energy Levels of Dysprosium(III) in Solution**
- **Patrick R. Nawrocki, Nikolaj Kofod, Kirsten M. Ø. Jensen, Thomas Just Sørensen: Direct Determination of Solution Structure of Europium(III) Dipicolinate Complexes**

Köln, Germany

Inorganic Chemistry, Department of Chemistry, Universität zu Köln, Greinstraße 6, 50939 Köln (Cologne), Germany

- **Aida Raauf, Mark D. Straub, Jennifer Leduc, Michael Frank, Trevor D. Lohrey, Stefan G. Minasian, Sanjay Mathur, John Arnold: Chemical Vapor Deposition of Phase-Pure Uranium Dioxide Thin Films from Uranium(IV) Amidate Precursors**

Luleå, Sweden

Chemistry of Interfaces, Luleå University of Technology, SE-97187 Luleå, Sweden; Department of Chemistry, KTH Royal Institute of Technology, SE-10044, Stockholm, Sweden; Engineering Sciences & Mathematics, Luleå University of Technology, SE-97187 Luleå, Sweden; NMR Research Unit, Faculty of Science, University of Oulu, P.O. 3000, 90014 Oulu, Finland; Department of Physics, Warwick University, Coventry, CV4 7AL, United Kingdom

- **Vasanth Gowda, Anna-Carin Larsson, Sven Öberg, Megha Mohan, Ville-Veikko Telkki, Perttu Lantto, Juha Vaara, Oleg N. Antzutkin: Structure of Dialkyldithiocarbamate-Phenanthroline and Carboxylato-Rare-Earth Complexes by Solid-State NMR, X-ray Crystallography and First-Principles Calculations**

Magdeburg, Germany — Edmonton, Alberta, Canada

Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, 39106 Magdeburg, Germany
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

- **Marcel Kühling, Phil Liebing, Josef Takats, Felix Engelhardt, Liane Hilfert, Sabine Busse, Frank T. Edelmann: Deliberate synthesis and structural characterization of a scorpionate-supported cerium(III) pentasulfide complex**

Manchester, United Kingdom

School of Chemistry, The University of Manchester, Manchester, M13 9PL, U.K.

- **Hannah M. Nicholas, Michele Vonci, Conrad A. P. Goodwin, Song Wei Loo, Siobhan R. Murphy, Daniel Cassim, Richard E. P. Winpenny, Eric J. L. McInnes, Nicholas F. Chilton, David P. Mills: Electronic Structures of Bent, Formally Two-Coordinate Lanthanide(III) Cations**
- **Benjamin L. L. Réant, Stephen T. Liddle, David P. Mills: Synthesis and development of bis-trialkylsilanide lanthanide chemistry**

Melbourne, Victoria & Townsville, Queensland, Australia

School of Chemistry, Monash University, Clayton 3800, Victoria, Australia.

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

- **Glen B. Deacon, Zhifang Guo, Jenny Luu, Victoria Blair, Peter C. Junk:** What are the prospects of using $\text{Ag}(\text{C}_6\text{F}_5)$ or $\text{Bi}(\text{C}_6\text{F}_5)_3$ instead of HgAr_2 reagents in redox transmetallation/ protolysis reactions of free lanthanoid metals?
- **Peter C. Junk, Elius Hossain, Glen B. Deacon:** Synthesis, characterisation and reactivity of halogenoaluminate complexes of rare earths and alkaline earths
- **Guillaume Bousrez, Melissa V. Werrett, Dominique T. Thielemann, Phil C. Andrews, Peter C. Junk:** Synthesis of new heterobimetallic lanthanoid clusters and their luminescence properties

Moscow, Russia

Chemistry Department, Moscow State University, Vavilov Department of Luminescence, P.N. Lebedev Institute of Physics, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science, Leninskiy prospekt, Moscow, 119991, Russia

- **Yury Belousov, Victoria Gontcharenko, Alexey Lunev, Ilya Taydakov:** Mixed metal Ln-MOF for luminescent sensor with ratiometric response
- **Ilya Taydakov, Yuriy Belousov, Mikhail Kiskin, Evgeniya Varaksina:** Lanthanide tris- and tetrakis complexes with 4-(cyclohexanecarbonyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one – an update

A.V. Topchiev Institute of Petrochemical Synthesis, V.A. Kotel'nikov Institute of Radioengineering and Electronics, A.N. Nesmeyanov Institute of Organoelement Compounds, P.N. Lebedev Physical Institute, N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science, Moscow, Russia

- **Dmitrii Roitershtein, Lada Puntus, Konstantin Lyssenko, Ilya Taidakov, Evgenia Varaksina, Mikhail Minyaev, Alexander Vinogradov, Andrei Churakov, Pavel Komarov, Ilya Nifant'ev:** Organolanthanides with aryl-substituted cyclopentadienyl ligands, structural peculiarities and luminescence

München, Germany

Ludwig-Maximilians-Universität München, Department Chemie, Butenandtstr. 5-13, 81377 München and Center for Integrated Protein Science Munich (CIPSM)

- **Lena J. Daumann:** Lanthanides: Biologically relevant

Orléans, France — Pittsburgh, Pennsylvania, USA

Centre de Biophysique Moléculaire, CNRS, Rue Charles Sadron, 45071 Orléans Cedex 2, France; Department of Chemistry, Willard H. Dow Laboratories, University of Michigan, Ann Arbor, Michigan 48109, USA; Centre d'Imagerie du Petit Animal, PHENOMIN-TAAM, 45071 Orléans Cedex 2, France; Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, PA 15218, USA; Institut de Chimie Organique et Analytique (ICOA), UMR7311, University of Orléans, rue de Chartres, 45000 Orléans, France.

Svetlana V. Eliseeva, Jacob C. Lutter, Tu N. Nguyen, Ivana Martinić, Guillaume Collet, Julien Sobilo, Stephanie Lerondel, Vincent L. Pecoraro, Stéphane Petoud : Functional Properties and Applications of Lanthanide(III)-Based Metallacrowns Emitting in the Near-Infrared Range

- **Stéphane Petoud, Svetlana Eliseeva, Guillaume Collet, Ivana Martinic, Jacob C. Lutter, Tu N. Nguyen, Régis Delatouche, Nicolas Chopin, Vincent L. Pecoraro, Franck Suzenet : New Lanthanide Compounds and Perspectives for Near-infrared Optical Imaging: Small Molecules, Macromolecules and MOF Nanomaterials**
- **Nathaniel Rosi, Stephane Petoud, Svetlana Eliseeva, Kristy Gogick, Kiley White, Tianyi Luo, Chong Liu, Alexandra Collette, Patrick Muldoon: Metal-Organic Frameworks as Platform Materials for Creating NIR-Emitting BioAnalytical Probes**

Philadelphia, Pennsylvania, USA

Department of Chemistry, University of Pennsylvania, 231 S. 34 Street, Philadelphia, PA 19104-6323, USA

- **Eric J. Schelter: Separations of Rare Earth Metals: Challenges and Opportunities Using a Molecular Basis**

Reims & Montpellier, France – Townsville & Clayton, Australia

Institut de Chimie Moléculaire de Reims, 51687 Reims, France, Institut Charles Gerhardt de Montpellier, ENSCM, 34296 Montpellier, France, James Cook University, Townsville 4811, Australia, Monash University, Clayton 3800, Australia

- **Florian Jaroschik, Aymeric Delon, Rory P. Kelly, Daisy Daniels, Jun Wang, Gilles Lemerrier, Glen B. Deacon, Peter C. Junk: New synthetic pathways towards bulky highly luminescent divalent europocene complexes**

Stuttgart, Germany

Institute of Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

- **Katharina V. Dorn, B. Blaschkowski, H. Bamberger, J. van Slageren, K. Doll, R. Claus, Y. Matsumoto, H. Takagi, I. Hartenbach: Black current: Structure, characterization and optoelectronic properties of $\text{Ce}_3\text{Cl}_3[\text{MoO}_6]$**
- **Felix C. Goerigk, Thomas Schleid: Halide-Containing Oxidoarsenates(III) of the Rare-Earth Metals**
- **Ingo Hartenbach: f and d in harmony: Halide derivatives of rare-earth metal molybdates and tungstates as promising materials for luminescence applications**
- **Sebastian Kunkel, Rainer Niewa: Synthesis of $\text{Na}_3[\text{R}(\text{NH}_2)_6]$, Intermediates during the Ammonothermal Synthesis of Rare-Earth Metal Nitrides**
- **Beate M. Schulz, Thomas Schleid: The Structural Variety of Rare-Earth Metal Selenidophosphates**

Tübingen, Germany

Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen, 72076 Tübingen, Germany

- **Damir Barisic, Căcilia Maichle-Mössmer, Reiner Anwander: Elusive trimethylscandium**
- **Dennis A. Buschmann, David Schneider, Căcilia Maichle-Mössmer, Reiner Anwander: Effect of Synthesis and Crystallization Technique on the Formation of Organolanthanum Clusters**
- **Alexandros Mortis, Căcilia Maichle-Mössmer, Reiner Anwander: Synthesis and grafting of yttrium neosilyl complexes onto mesoporous silica**

Uppsala, Sweden

Department of Molecular Sciences, BioCenter, Swedish University of Agricultural Sciences, Box 7015, SE-750 07 Uppsala, Sweden

- **Vadim G. Kessler, Robert Pazik, Gulaim A. Seisenbaeva: Soft chemistry approaches to REE doped nanomaterials**
- **Gulaim A. Seisenbaeva, Elizabeth Polido Legaria, Vadim G. Kessler: Nanotechnology for extraction and separation of Rare Earth Elements**

Department of Chemistry-Ångström, Ångström laboratory, Uppsala University, Uppsala, Sweden

- **Gunnar Westin and Sarmad Naim Katea: Ln doped materials by solution processing**

Wroclaw & Szczecin, Poland — Stockholm, Sweden — Lyon, France

University of Wroclaw, Faculty of Chemistry, 50-383 Wroclaw, Poland; Łukasiewicz Research Network – PORT Polish Center for Technology Development, 54-066 Wroclaw, Poland; Department of Optics and Photonics, Faculty of Fundamental Problems of Technology, Wroclaw University of Science and Technology, 50-370 Wroclaw, Poland; Stockholm University, Department of Materials and Environmental Chemistry, 106 91 Stockholm, Sweden, Institut Lumière Matière (ILM), UMR5306 CNRS- Université Claude Bernard Lyon 1, Université de Lyon, 69622 Villeurbanne, France, Université de Lyon, MATEIS, UMR CNRS 5510, INSA-Lyon, 69621 Villeurbanne, West Pomeranian University of Technology, Department of Inorganic and Analytical Chemistry, 71-065 Szczecin

- **Magdalena Sobota, P. Sobota, M. Bieza, M. Guzik, E. Tomaszewicz, Y. Guyot, G. Boulon: Influence of synthesis route and grain size on structural and spectroscopic properties of cubic Nd³⁺-doped Y₆MoO₁₂ nano- and micro-powders as optical materials**
- **Magdalena Sobota, Marcin Sobczyk, Anja-Verena Mudring, Joanna Cybińska: Ionic liquid-assisted facile hydrothermal synthesis of nanocrystalline Nd³⁺-doped BiPO₄ NIR emitting phosphor**
- **Magdalena Sobota, Krzysztof Rola, Maria Zdończyk, Kacper Prokop, Anja-Verena Mudring, Katarzyna Komorowska, Joanna Cybińska: Ionic Liquids for Lanthanides based Nano-particles Synthesis and Photonic Applications**
- **Kacper Prokop, Małgorzata Guzik, Yannick Guyot, Georges Boulon, Joanna Cybińska: Site selective spectroscopy as an efficient tool for structural and spectroscopic studies of Nd³⁺-doped LuPO₄ micro-powders**

Stockholm, Sweden — Köln, Germany

Department of Materials and Environmental Chemistry (MMK), Stockholm University, Svante Arrhenius väg 16 C, 106 91 Stockholm, Sweden

Centre for Analysis and Synthesis CAS, Lund University, Getingevägen 60, Box 124, SE-22100, Lund, Sweden

- **Brando Adranno, Anja-Verena Mudring: Luminescent Rare Earth Ionic Liquids**
- **Chris Celania, Anja-Verena Mudring: Unexpected Phase Stability in Gd-Au-Te Inter-metallics**
- **Alexander Ovchinnikov, Anja-Verena Mudring: Exploratory studies in the RE-Mn-Au systems (RE = rare-earth metal)**
- **Siméon Ponou, Sven Lidin, Anja-Verena Mudring: Targeted Synthesis, Crystal Structures and Chemical Bonding of the Valence Electron rich phases RE₄CuGe₂ (RE = La, Ce, Pr)**
- **Olivier Renier, Guillaume Bousrez, Volodymyr Smetana and Anja-Verena Mudring: [C₄mim][AlCl₄] used as solvent to oxidize lanthanide metals at low temperature**
- **Thomas Bell, Volodymyr Smetana, Anja-Verena Mudring, Gerd H. Meyer: A Hidden Island of Rare Earth Rich Intermetallics**

Leipzig, Germany

Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany

- **Anton Werwein, Holger Kohlmann: Metal-semiconductor transition in hydrides of Laves phases LnMg₂**

Luminescent Rare Earth Ionic Liquids

B. Adranno, G. Bousrez, O. Renier, M. Wilk-Kozubek, D. Pitz, P. S. Campbell, B. Mallick, A. Lackmann, and A.-V. Mudring*

Stockholm University, Svante Arrhenius väg 16C, Stockholm, Sweden
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Physical and chemical properties of ionic liquids (ILs) make them attractive for several research areas. ILs generally feature a low melting point (below 100°C), low vapor pressure, good electrical conductivity. Because of their modular character they offer large design possibilities. An interesting and promising, but less explored, application of ILs is in light emitting devices. About 25% of the energy worldwide is consumed for lighting. Thus, a tremendous contribution to energy saving could be made by improving the energy efficiency of lighting devices. Since the trivalent rare earth cations are well known for their efficient emission, they are great candidates for luminescent ILs especially when coupled with an light absorbing organic moiety acting as a sensitizer for the rare earth cation.

A series of anionic rare earth salicylato-complexes combined with aromatic and non-aromatic cations, which are known to support IL formation, such as diallyldimethylammonium (DADMA), 1-ethyl-3-methylimidazolium (C₂C₁Im) has been synthesized and characterized.

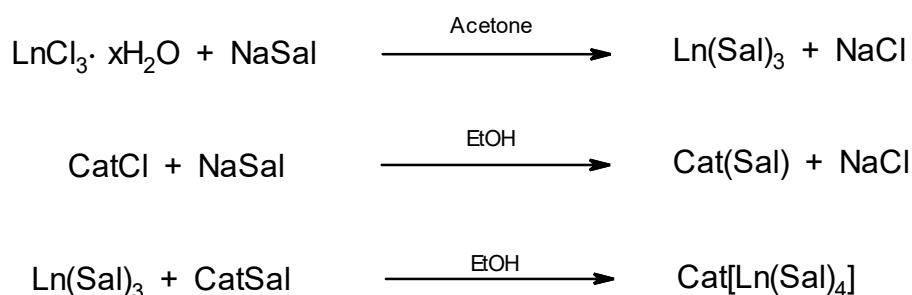


Figure 1. Preparation of (Cat)[Ln(Sal)₄](Cat = diallyldimethylammonium (DADMA), 1-ethyl-3-methylimidazolium (C₂C₁Im), Ln=La, Tb)

Analysis of their photophysical properties show strong green *f-f* emission for all the synthesized Tb compounds. Efficient energy transfer between the salicylate ligand (absorption moiety) and the metal center (emission moiety) could be observed.

Acknowledgement

This work is supported by Energimyndigheten, the Swedish Energy Agency.

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

Helene Obel Bøch Andersen^a, Alan M. Kenwright^b and Thomas Just Sørensen^a

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Kinetically stable DO3A type lanthanide(III) complexes are of great interest due to their applications in bioimaging and as MRI contrast agents.^[1,2] To investigate the inherent chirality of the DO3A ligand we have introduced a chiral amide arm which resolves the many conformations of the complex and illustrates the complicated speciation that must be taken into account when even simple DOTA-like complexes are used in an inherently diastereotopic biological medium.

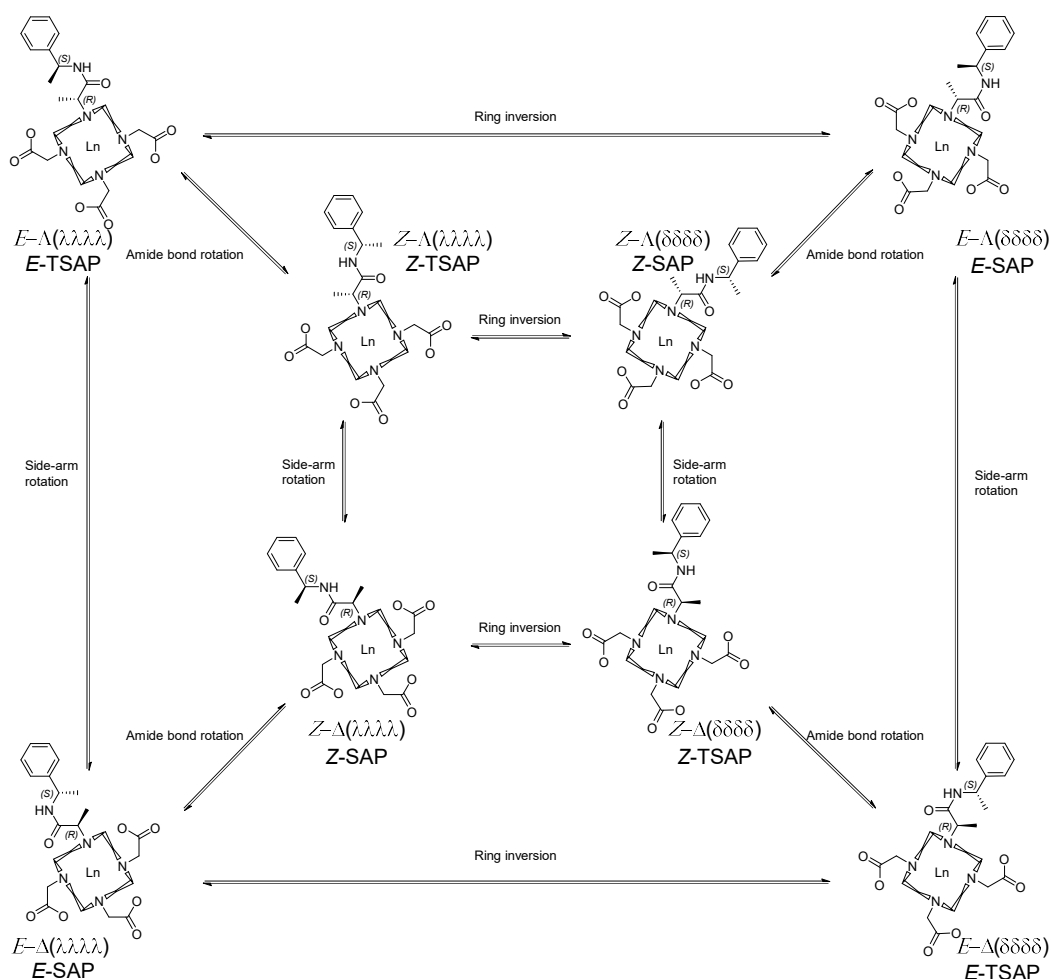


Figure 1. The eight resolved conformations of the complex.

References

- [1] P. Caravan, J. J. Ellison, T. J. McMurry, R. B. Lauffer, *Chemical Reviews*, **1999**, 99, 2293-2352.
- [2] L. G. Nielsen, A. K. R. Junker, T. J. Sørensen, *Dalton Trans.*, **2018**, 47, 10360-10376

Structure of Dialkyldithiocarbamato-Phenanthroline and Carboxylato-Rare-Earth Complexes by Solid-State NMR, X-ray Crystallography and First-Principles Calculations

Vasanth Gowda,^{1,2} Anna-Carin Larsson,¹ Sven Öberg,³ Megha Mohan,⁴ Ville-Veikko Telkki,⁴ Perttu Lantto,⁴ Juha Vaara⁴ and Oleg N. Antzutkin^{1,5}

¹Chemistry of Interfaces, Luleå University of Technology, SE-97187 Luleå, Sweden

²Department of Chemistry, KTH Royal Institute of Technology, SE-10044, Stockholm, Sweden

³Engineering Sciences & Mathematics, Luleå University of Technology, SE-97187 Luleå, Sweden

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A structural analysis method for molecular and electronic structure of rare-earth dialkyldithiocarbamato-phenanthroline complexes $\{[\text{REE}(\text{S}_2\text{CNR}_2)_3\text{PHEN}]\}$ with $\text{R} = \text{C}_2\text{H}_5$ and $\text{PHEN} = 1,10\text{-phenanthroline}\}$ combining solid-state NMR spectroscopy, XRD, and first-principles calculations is presented. A range of X-ray structures with the space group $\text{P2}_1/\text{n}$ of the named REE complexes (but not for yttrium) have been previously reported. In our method, replacing the Nd^{3+} ion with Y^{3+} in the reported crystal structure of $[\text{Nd}(\text{S}_2\text{CNR}_2)_3\text{PHEN}]$ complex generated an approximate 3D structure of the title complex.¹ The structure was then subjected to first-principles quantum chemical geometry optimisation using periodic DFT method and then predicted and experimental powder XRD patterns were compared. Calculated from the optimised 3D-structure NMR chemical shifts were also validated experimentally using solid-state ^{13}C and ^{15}N CP-MAS NMR, showing three structurally different dithiocarbamate groups. The present approach can be further extended to study other rare-earth metal complexes, particularly those having similar but not yet solved crystal structures. In contrary to $[\text{Y}(\text{S}_2\text{CNR}_2)_3\text{PHEN}]$, $[\text{La}(\text{S}_2\text{CNR}_2)_3\text{PHEN}]$ crystallised in the triclinic space group P1 .² Both solid-state ^{13}C and ^{15}N CP-MAS NMR revealed the presence of six structurally different dithiocarbamate groups in the asymmetric unit cell, implying a non-centrosymmetric packing arrangement of molecules and two molecules of the complex in the unit cell (see Figure).² Full assignment of solid-state ^{13}C and ^{15}N CP-MAS NMR spectra as well as analyses of the principal values of the chemical shift tensors were carried out using periodic scalar relativistic DFT modelling. A recently developed methodology for combined density functional theory (DFT) and correlated *ab-initio* computations were applied to investigate the paramagnetic effects on ^1H and ^{13}C NMR chemical shifts (pNMR) of a range of selected $[\text{REE}(\text{S}_2\text{CNR}_2)_3\text{PHEN}]$ complexes, with REE including Nd(III), Eu(III), Er(III), and Yb(III).³ The pNMR data present a unique fingerprint of the paramagnetic centre. The isotropic shifts obtained from these calculations are in good agreement with the experimental results. In addition, La(III) and Nd(III) complexes with malonic acid and 2-benzylpropanedioic acid, which could be used as reagents in froth flotation and separation of different rare-earth elements, were synthesised and studied using solution and solid-state NMR. Analysis of experimental NMR data will be combined with quantum-chemical computational modelling for the named complexes.

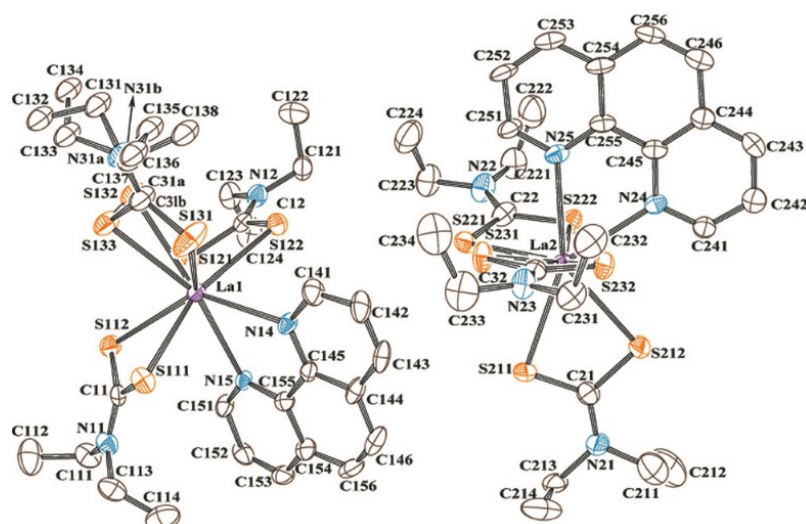


Figure 1. The ORTEP diagram of $[\text{La}\{\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2\}_3\text{C}_{12}\text{N}_2\text{H}_8]$, showing two mononuclear molecules with 50% thermal ellipsoids and the crystallographic atom labelling scheme. H atoms are omitted for clarity.²

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Elusive trimethylscandium

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The scandium neosilyl complex $\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})_2$ was reported by Lappert and Pearce in 1973 [1]. Along with other silylmethyl and (functionalized) benzyl derivatives, such monometallic scandium alkyls emerged as prominent precursors for precatalyst design [2].

As another cornerstone of our efforts toward the further development of rare-earth metal alkyl chemistry we wish to report the synthesis and derivatization of trimethylscandium. The presentation will feature tetramethylaluminate formation/degradation chemistry [3] and the application of heterobimetallic derivatives in isoprene polymerization [4].

Acknowledgements We are grateful to the German Science Foundation for financial support (Grant: AN 238/15-2).

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Mixed metal Ln-MOF for luminescent sensor with ratiometric response

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Complexes $\{Ln(TDA)(H_2O)_2\}$ and $\{NMe_2H_2[Ln(TDA)(HCOO)]\}$ ($Ln=Eu, Gd, Tb$, $H_3TDA=1,2,3$ -Triazole-4,5-dicarboxylic acid) with the MOF structure can be obtained by solvothermal synthesis, depending on the solvent selected. Crystal structures of $\{Eu(TDA)(H_2O)_2\}$ and $\{NMe_2H_2[Ln(TDA)(HCOO)]\}$ ($Ln=Eu, Tb$) were determined by X-ray diffraction. If a mixture of salts of two lanthanides is used in the synthesis, the corresponding mixed metal derivatives can be obtained. Such derivatives of terbium and europium were used as sensory materials, and the ratio of luminescence intensities of terbium and europium transitions served as an analytical signal. The sensory response to traces of water in aprotic solvents and D_2O , as well as with respect to cations, was studied.

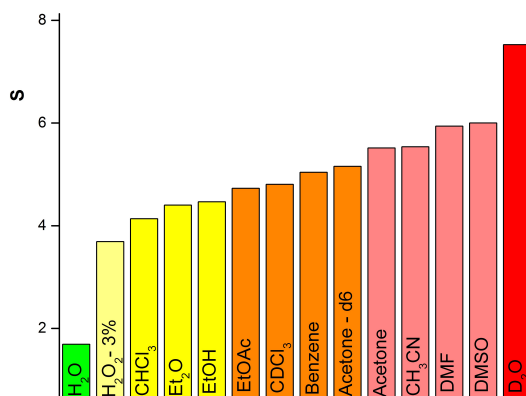


Figure 1. Dependence of S on media for suspension of $\{Eu_{0.1}Tb_{0.9}(TDA)\}$ with different solvents.

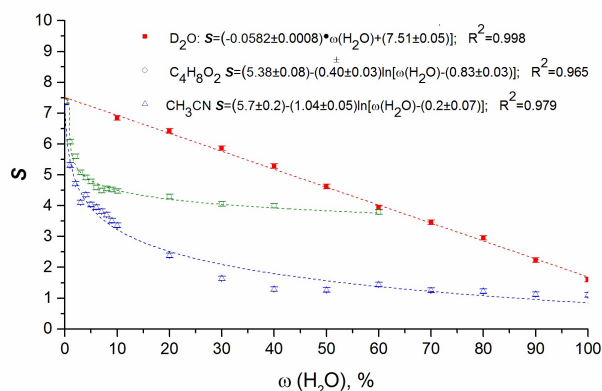


Figure 2. Calibration charts for the H_2O - D_2O (red squares), H_2O -dioxane (green circles) and H_2O - CH_3CN (blue triangles) systems.

Synthesis of new heterobimetallic lanthanoid clusters and their luminescence properties

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The X-ray computed tomography (CT) is a non-invasive method for the visualization of *in vivo* tissue surfaces by means of optical contrast based on tissue-specific X-ray attenuation, and serves therefore as a major imaging modality in clinical radiology.[1] To obtain a good CT attenuation a good contrast agent is necessary. New contrast media based on metal complexes, particular metals have the potential to provide CT attenuation like the rare earth metals (Scandium, Yttrium and Lanthanoids).[2] Complexes with a “cage” structure can provide, once encapsulated, the required stability and solubility.

We report here the synthesis of new mono- and bimetallic lanthanoid cluster compounds (Figure 1). [3] The metal-to metal ratios of pentanuclear clusters were determined by energy dispersive X-ray spectroscopy (EDS). The EDS results show that, for an equal proportion of lanthanide salts introduced, different metal-to-metal ratios are achieved in the clusters. This ratio appears to be dependent on the size and electron density of the metal atoms. Studies realized the best conditions to achieve a 1:1 ratio. A luminescence study of the clusters will be presented and will show the influence of each metal centre.

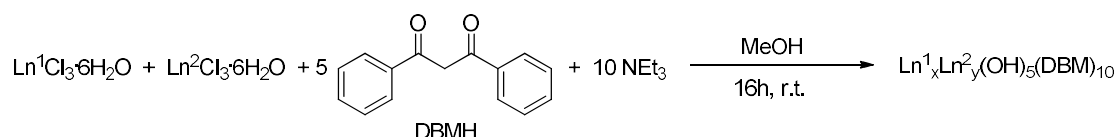


Figure 1.

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Effect of Synthesis and Crystallization Technique on the Formation of Organolanthanum Clusters

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Organorare-earth metal cluster compounds are accessible via diverse synthesis approaches, including the derivatization of rare-earth-metal halides [1] or halogenido for methyl exchange reactions.[2] Cluster compounds display unique structural motifs and can be utilized as model complexes for studying reactivities of heterogeneous catalysts.[3] Due to the highly polarized bonding in rare-earth metal clusters, selective shielding by ancillary ligands is a crucial factor.[4]

Here we wish to report the synthesis of a series of clusters, accessible via halogenido for methyl exchange in lanthanum half-sandwich complex $\text{Cp}^*\text{La}(\text{AlMe}_4)_2$ ($\text{Cp}^* = \text{C}_5\text{H}_4\text{SiMe}_3$). Depending on the halogenido ion size and syntheses/crystallization techniques, homometallic and heterometallic clusters of different nuclearity and distinct structural motifs are obtained.

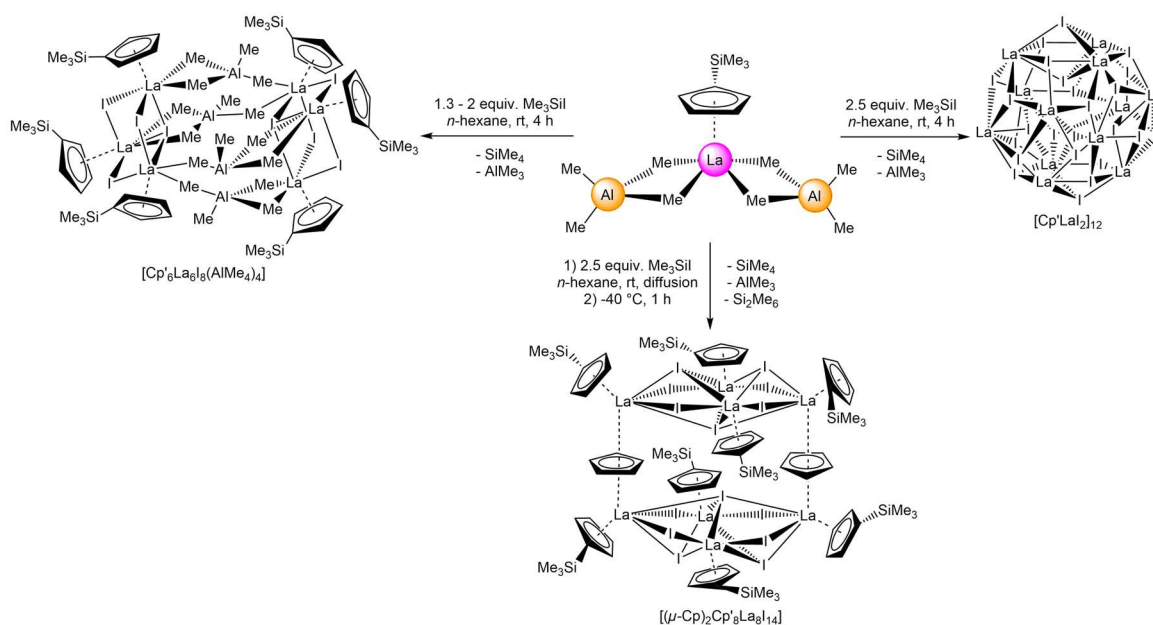


Figure 1. Reactivity of Me_3SiI toward a cyclopentadienyl-stabilized lanthanum bis(tetramethylaluminate) half-sandwich complex, applying different synthesis and crystallization approaches (CpSiMe_3 ligands omitted for clarity for $[\text{Cp}^*\text{LaI}_2]_{12}$).

Acknowledgements We are grateful to the German Science Foundation for financial support (Grant: AN 238/14-2).

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Unexpected Phase Stability in Gd-Au-Te Intermetallics

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To contend with growing industrialization and energy demands across the globe, it is critical to diversify and strengthen our renewable energy sources. Thermoelectric materials allow for the recovery of (“low-quality” waste) heat created during other energy related processes, and therefore, can allow for greener and more efficient energy production. An expanding region of interest for the discovery of new thermoelectric materials is the family of rare earth metal-noble metal tellurides (*R-M-Te*).¹

Specifically, Gd-Au-Te has proven to be a productive field for new compounds with potential for thermoelectric properties. Our exploration within these ternary systems has culminated in the discovery of at least five new compounds, some of which demonstrate unexpected formation of known structure types, completely new structure types, as well as new superstructures. Two compounds that demonstrate surprising formation are $\text{Gd}_7\text{Au}_2\text{Te}_2$ and $\text{Gd}_2\text{Au}_{2.05}\text{Te}_{0.95}$. The former joins a robust family of so-called 7-2-2 structures, but orders into the $\text{Lu}_7\text{Ni}_2\text{Te}_2$ structure type instead of the $\text{Er}_7\text{Au}_2\text{Te}_2$ structure type.^{2,3} The latter compound fits within the large family of U_3Si_2 structure type compounds. While Y_3Au_2 is reported within this family,⁴ a Gd analogue is absent from literature demonstrating an additional example where proper tuning of radii and valence electrons within an intermetallic can stabilize a ternary structure where its binary structure does not exist. These structures and probable explanations for their formations are discussed.

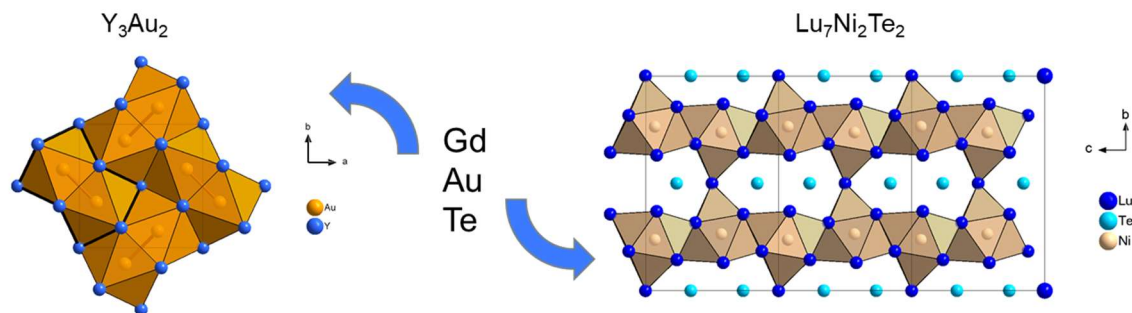


Figure 1. Y_3Au_2 (left) from U_3Si_2 structure type and $\text{Lu}_7\text{Ni}_2\text{Te}_2$ structure type (right).

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Ionic Liquids for Lanthanides based Nanoparticles Synthesis and Photonic Applications

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Progress in development of modern technologies forces the search for new materials that not only meet the application requirements, but are also environmentally friendly. As for functional materials in nano and micro scale the size and shape plays very important role and influences the physicochemical properties, it is crucial to synthesize materials with well design morphology. Thus, in recent years there has been a growing interest in studies of ionic liquids (ILs). The physicochemical properties of ILs as thermal stability, viscosity, density, melting temperature can be modify by selecting appropriate cations and anions. The extremely low vapor pressure and non-flammability of most ionic liquids makes them good candidates to replace some organic solvents and ILs are often called green solvents. It has been shown that ILs are very efficient media for nanoparticles synthesis, as they can act as in-situ stabilizer and the template for forming particles.

We already presented the using of ILs based method for the synthesis of luminescent efficient nanophosphors – fluorides and phosphates, and we are devolving this method to obtain highly luminescent and water-free materials of $\text{LnPO}_4:\text{Nd}^{3+}$ emitting in NIR range.

Our recent studies of application of ILs in photonic are also devoted to polymerizable ILs, which could replace currently using polymers. Low vapour pressure makes ILs good candidates to use in vacuum techniques and consequently put a substrate with an ionic liquid layer into a chamber of SEM (scanning electron microscope) equipped with FIB (focused ion beam) source. Moreover, a thin layer of this material can be obtained without using a solvent, which might be crucial in many technological processes.

The ILs role as in-stabilizer and reactant for nanoparticales synthesis as well as the useful photonic materials will be shown and discuss, these kind of compounds can find wide application in photoluminescence and photonic.

Acknowledgements

We would like to express our gratitude to the National Science Center of Poland for the grants HARMONIA 9 No UMO-2017/26/M/ST5/00563 and Opus UMO-2015/19/B/ST8/02761.

Site selective spectroscopy as an efficient tool for structural and spectroscopic studies of Nd³⁺-doped LuPO₄ micro-powders

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For over 70 years ortho-phosphates are widely applied as efficient hosts for luminescent materials due to their high chemical stability and ease of synthesis.

Activated by different rare earth (RE) ions they found potential applications as luminophores. Nd³⁺-doped ortho-phosphates are a subject of considerable interest for potential applications as scintillators due to their very fast, short-wavelength emission that originates in the parity allowed transitions from the lowest level of the excited 4f²5d configuration of the Nd³⁺ ion down to the 4f³ configuration levels of this ion. From the other hand they are considered as a laser materials. However, recently Nd³⁺-doped phosphates luminescence materials have attracted increasing attention in biomedical applications. Among them, lanthanide-doped LuPO₄ nanophosphors have potential for multimodal bio imaging due to good biocompatible and luminescence features and excellent X-ray absorption properties. Nevertheless, the path of research on potential bio application of LuPO₄ requires intensive research.

Surprisingly, despite many studies conducted by various researchers for well-known luminescent material i.e. RE³⁺-LuPO₄ the basic structural research is still missing.

So, using the advantage of neodymium ion as structural probe and by applying the low-temperature high-resolution techniques like absorption spectroscopy at 4.2 K and laser site selective spectroscopy at 77 K detailed structural and spectroscopic studies of Nd³⁺-doped LuPO₄ micro-powders were performed.

Micro-powdered samples with Nd³⁺ concentrations fixed from 0.1 to 20 mol% were obtained by using solid state reaction. The LuPO₄ crystallize in the tetragonal system conforming to space group model *I*4₁/amd (*D*¹⁹_{4h}, No. 141), *Z* = 4. Dependence of the dopant concentration on the structure and spectroscopic properties of Nd³⁺-doped LaPO₄ will be discussed. Low-temperature absorption measurements and luminescence measurements at 77 K under site-selective laser excitation in the spectral region of laser interest involving the ⁴F_{3/2} → ⁴I_{11/2} transition allowed to fixed a number of Nd³⁺ sites in this host lattice. A larger than expected number of Nd³⁺ sites was found and an energy levels diagram was constructed from the acquired data. Also, the dynamics of the Nd³⁺ excited states were studied by decay times measurements.

This work was helpful to better understanding of exact structure of Nd³⁺-doped LuPO₄ micro-powders.

Acknowledgments

We would like to express our gratitude to the National Science Center of Poland for the grant HARMONIA 9 No UMO-2017/26/M/ST5/00563.

Lanthanides: Biologically relevant.

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Lanthanides (Ln) are biologically essential metals.^[1] This statement was until recently, unthinkable. Here, the recent developments in the emerging field of lanthanide biochemistry from a coordination chemist's point of view will be presented. Why bacteria prefer for example the light Ln has been a subject of debate.^[2,3] We have previously reported the cultivation of the strictly Ln-dependent methanotrophic bacterium *Methylophilum fumariolicum* SolV with europium(III), as well as the purification, structural and kinetic analyses of the first Eu-dependent methanol dehydrogenase (MDH).^[4] Our studies showed, that although lanthanides have similar properties, the differences in ionic radii caused by the lanthanide contraction across the series impact MDH efficiency and even lanthanide uptake by bacteria.^[5]

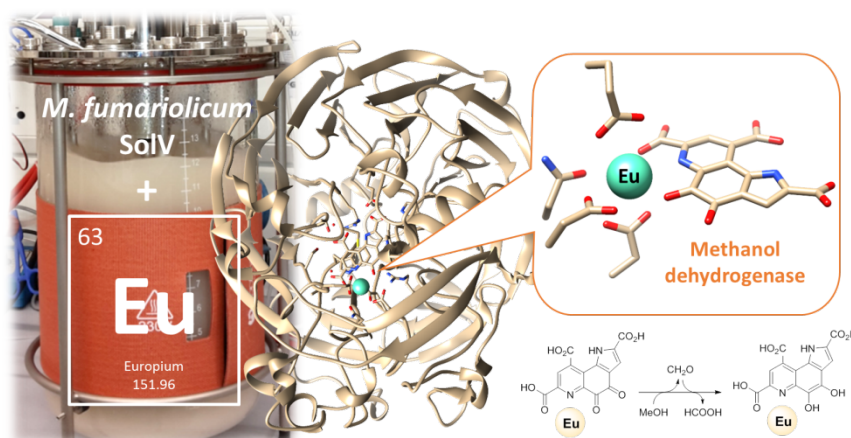


Figure 1. Fermenter for the cultivation of *Methylophilum fumariolicum* SolV with europium(III), structure of Eu-MDH and active site, and the catalyzed MeOH and formaldehyde oxidation.

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What are the prospects of using $\text{Ag}(\text{C}_6\text{F}_5)$ or $\text{Bi}(\text{C}_6\text{F}_5)_3$ instead of HgAr_2 reagents in redox transmetallation/protolysis reactions of free lanthanoid metals?

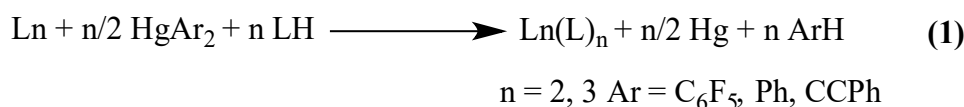
Glen B. Deacon,^{a*} Zhifang Guo,^a Jenny Luu,^a Victoria Blair,^a Peter C. Junk^b

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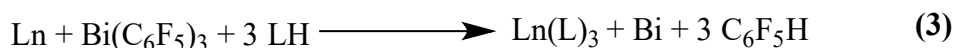
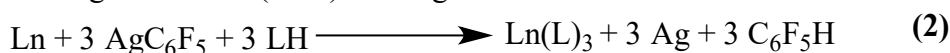
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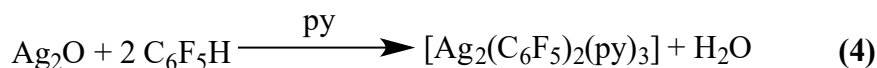
Over many years we have established redox transmetallation/protolysis (RTP) reactions of lanthanoid metals with diarylmercurials and protic agents (phenols, amines, pyrazoles, formamidines, and cyclopentadienes) to be an effective synthesis of highly reactive rare earth compounds.^[1]



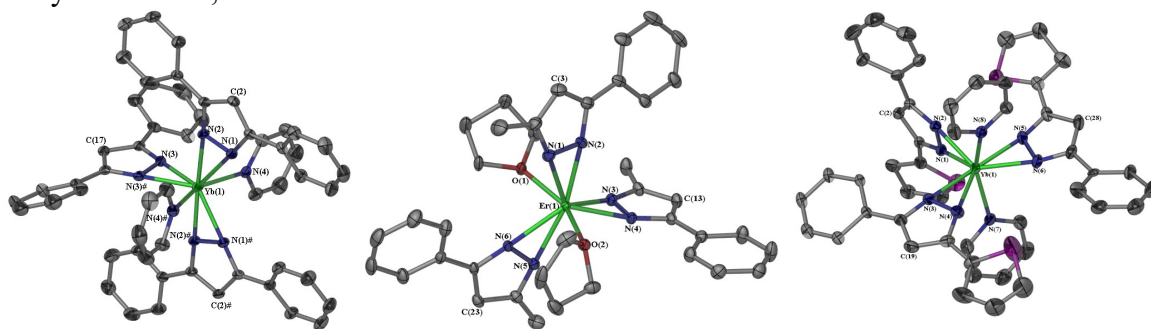
The method is competitive with metathesis. However, the synthetic method would be more attractive if a less toxic metal could be employed. In the search for alternatives, we have examined both AgC_6F_5 and $\text{Bi}(\text{C}_6\text{F}_5)_3$ as reagents.^[2, 3]



Use of AgC_6F_5 has been greatly aided by a new synthesis from commercially available, air-, stable reagents.^[2]



Both AgC_6F_5 and $\text{Bi}(\text{C}_6\text{F}_5)_3$ have been tested in the synthesis of lanthanoid pyrazolates for a wide range of Ln metals and several pyrazoles.^[2, 3] These results are compared with the use of diarylmercurials, and their limitations outlined.^[4]



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- [4]. Support of the Australian Research Council is gratefully acknowledged.

Towards a responsive Lanthanide complex for ROS sensing

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Reactive Oxygen Species (ROS) play a fundamental role in biological systems. Ranging from positive effects (cell signaling, host defense) to harmful ones (damage to lipids and proteins, disease), these reactive molecules are worth being investigated. [1] Reported probes are mostly based on organic dye scaffolds, leading to issues with the autofluorescence of the sample due to the dyes' short lifetimes (ns). [1] Lanthanides offer an exciting alternative: their attractive luminescence properties make for their well-known applications in bioimaging and, more specifically, their long excited state lifetimes sidestep any background fluorescence issue by time gated detection. [2] By attaching a ROS responsive arm to a kinetically inert Lanthanide (III) complex, a cage-on / cage-off mechanism is expected to result in a change in the luminescence properties of the complex. (Figure 1.) The reactive unit has been designed from the results of α -Tocopherol's oxidation by HOCl: the chromanol moiety is oxidized to quinone with cleavage of the cyclic ether bond (Table 1.). A series of esters of hydroquinone and durohydroquinone have been synthesized and investigated as potential responsive arms for the Lanthanide (III) complex.

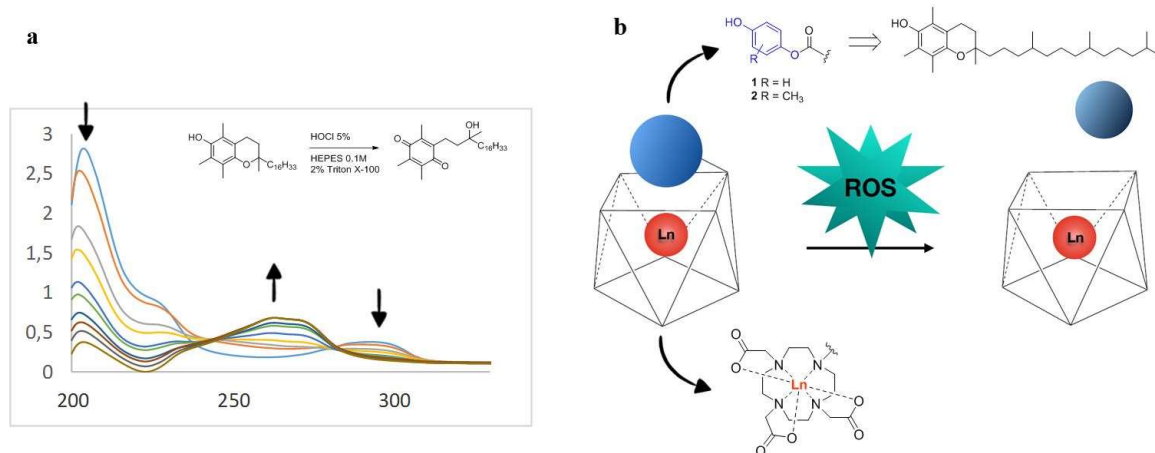


Figure 1. **a** Absorption spectrum of the oxidation of α -Tocopherol by increasing equivalents (0-2.25) of HOCl 5% in HEPES 0.1 M + 2% Triton X-100, pH = 7 **b** Schematic representation of the scaffold and cage-on / cage-off mechanism considered in the study

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Giant Coercivity and Magnetic Blocking in Radical-Bridged Lanthanide Single-Molecule Magnets

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Molecules that possess an energy barrier to spin inversion have intriguing potential applications in areas such as magnetic refrigeration, molecular spintronics and high-density information storage. For these applications, however, key performance characteristics such as large spin-relaxation barriers and high magnetic blocking temperatures are required. Lanthanides have been proven to be particularly well-suited for the design of single-molecule magnets owing to their large magnetic moments and magnetic anisotropy that stem from strong spin-orbit coupling of the 4f orbitals. By using lanthanide ions such as Tb^{3+} , Dy^{3+} , and Er^{3+} which possess intrinsically large orbital angular momentum, significantly higher barriers and blocking temperatures can be achieved. A general methodology to enhance single-molecule magnet properties in mononuclear lanthanide complexes comprises matching the ligand field symmetry with the anisotropic electron density distribution of the maximal M_J state. Employing this methodology, we will present the synthesis of mononuclear rare-earth metallocene complexes that function as new lanthanide-based single-molecule magnets [1-3]. Another particularly successful approach to improve blocking temperatures is to generate strong magnetic exchange between lanthanide centers through the employment of radical bridging ligands. If the magnetic exchange coupling is large enough then quantum tunneling of the magnetization can be attenuated. Here, we will further present the synthesis of multiple bimetallic radical-bridged lanthanide single-molecule magnets and describe effective suppression of quantum tunneling pathways using various organic bridging radical ligands [4-7]. In addition, we combine both methodologies and demonstrate with the first series of N_2^{3-} radical-bridged metallocene complexes that the combination of axial magnetic anisotropy provided by the cyclopentadienyl ligands with the strong magnetic exchange coupling enabled by the inorganic N_2^{3-} radical results in exceptionally large magnetic hysteresis loops which remain open up to high temperatures, Figure 1.[8]

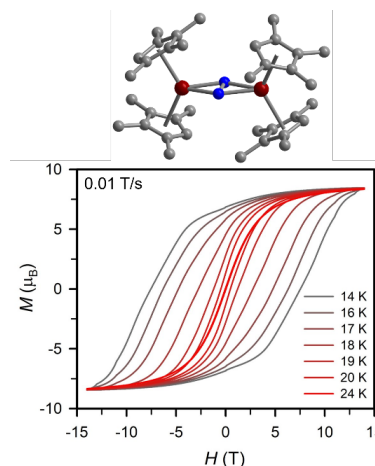


Figure 1. Magnetic hysteresis data and structure for $[(\text{Cp}^{\text{Me4H2Tb}})_2(\mu\text{-N}_2^{\bullet})]^{-.8}$

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Black current: Structure, characterization and optoelectronic properties of $\text{Ce}_3\text{Cl}_3[\text{MoO}_6]$

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The title compound $\text{Ce}_3\text{Cl}_3[\text{MoO}_6]$ ^[1,2] crystallizes in the hexagonal space group $P6_3/m$ (no. 176, $a = 964.93(4)$, $c = 538.86(2)$ pm) with two formula units per unit cell and is thus isotypic to the $\text{Ln}_3\text{Cl}_3[\text{MO}_6]$ representatives for $\text{Ln} = \text{La}$, Pr, and Nd ($M = \text{Mo}$)^[2,3] and $\text{Ln} = \text{La} - \text{Nd}$, Sm – Er, Dy ($M = \text{W}$)^[2,4–9].

The title compound comprises non-condensed trigonal-prismatic $[\text{MoO}_6]^{6-}$ entities, which show the expected vibration bands in the IR and Raman spectra, respectively (Fig. 1, *left*). However, the optical properties for $\text{Ce}_3\text{Cl}_3[\text{MoO}_6]$ are very outstanding: The optical bandgap of only $E_g = 1.35(2)$ eV (Fig. 1, *middle left*) is located in the IR region of the electromagnetic spectrum which causes the black colour of the compound (see Fig. 1, *middle right*), and the specific resistivity of the obtained single crystals can be changed as a function of the utilized IR light source (scheme of measurement see Fig. 1, *right*). Therefore, $\text{Ce}_3\text{Cl}_3[\text{MoO}_6]$ ^[1,2] might be an interesting material for optoelectronic applications *e.g.* for the use in a remote control of home appliances or electronics.

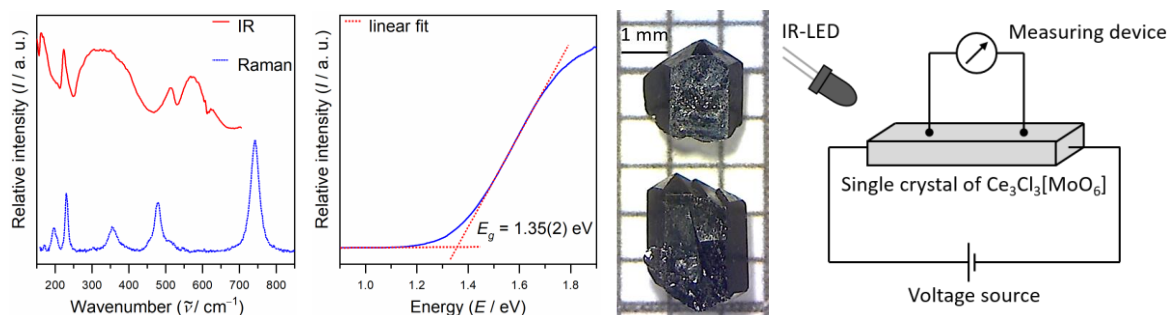


Figure 1. FTIR spectrum (*left, top*), single-crystal Raman spectrum (*left, bottom*) under excitation with a red LASER ($\lambda_{\text{exc}} = 638$ nm), diffuse reflectance spectrum (*middle left*), single crystals of $\text{Ce}_3\text{Cl}_3[\text{MoO}_6]$ (*middle right*) and scheme of the measurement technique of the specific resistivity of a single crystal (*right*).

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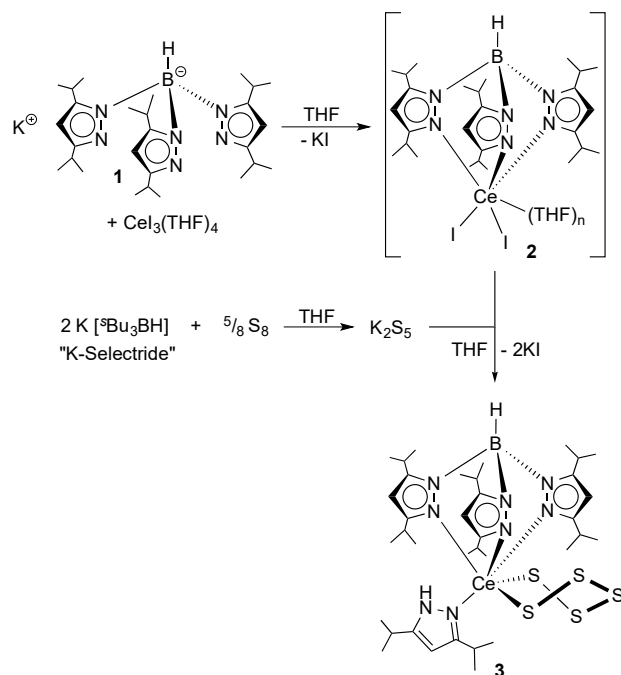
Deliberate synthesis and structural characterization of a scorpionate-supported cerium(III) pentasulfide complex

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For the first time, a scorpionate-supported lanthanide pentasulfide complex has been synthesized in a deliberate manner starting from *in situ*-prepared K_2S_5 . Reaction of K_2S_5 with *in situ*-formed $(\text{Tp}^{\text{iPr}_2})\text{CeI}_2(\text{THF})_n$ (Tp^{iPr_2} = hydro-tris(3,5-diisopropylpyrazolyl)borate) according to Scheme 1 afforded the yellow-brown cerium(III) pentasulfide complex $(\text{Tp}^{\text{iPr}_2})(3,5\text{-}^i\text{Pr}_2\text{pz})\text{CeS}_5$ (**3**) in 62% isolated yield. Compound **3** has been fully characterized, including single-crystal X-ray structural analysis (*cf.* Figure 1).



Scheme 1. Synthetic route to the title compound **3**.

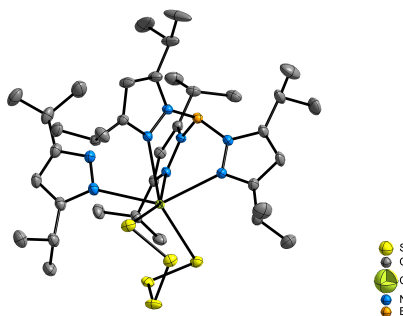


Figure 1. Molecular structure of $(\text{Tp}^{\text{iPr}_2})(3,5\text{-}^i\text{Pr}_2\text{pz})\text{CeS}_5$ (**3**).

Functional Properties and Applications of Lanthanide(III)-Based Metallacrowns Emitting in the Near-Infrared Range

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We have demonstrated that characteristic emission signals of lanthanide(III) ions, particularly in the near-infrared range, are efficiently sensitized in $\text{Zn}^{\text{II}}/\text{Ln}^{\text{III}}$ and $\text{Ga}^{\text{III}}/\text{Ln}^{\text{III}}$ metallacrowns (MCs, Figure 1) [1-3]. In addition, the applicability of $\text{Zn}^{\text{II}}/\text{Ln}^{\text{III}}$ MCs for the selective labelling of necrotic cells [4] or the simultaneous cell fixation and counter staining [5] have been envisaged. Herein, we will discuss how functional properties of near-infrared emitting lanthanide(III)-based MCs can be finely tuned bearing in mind applications for optical and computed tomography imaging modalities.

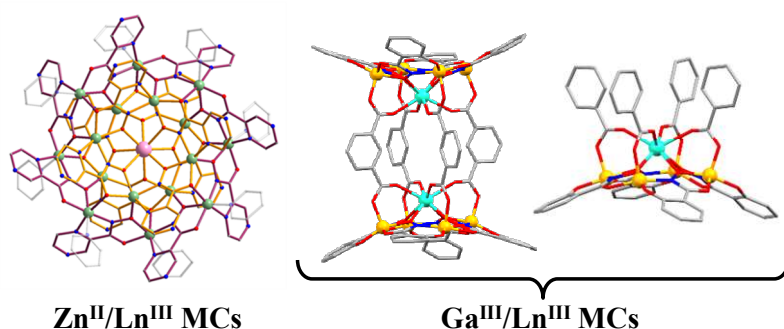


Figure 1. Crystal structures of $\text{Zn}^{\text{II}}/\text{Ln}^{\text{III}}$ and $\text{Ga}^{\text{III}}/\text{Ln}^{\text{III}}$ metallacrowns.

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Modular Synthesis of Rare Earth-Transition Metal Complexes Utilizing a Redox-Active Ligand

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The chemistry of multi-metallic complexes containing *f*-elements is significantly less well developed than that of transition metals. This is attributable to the fact that the directed synthesis of *f-d* complexes is non-trivial. The potential applications of complexes containing both transition metals and lanthanides are significant. We have used a redox-active bridging ligand with multiple and selective binding sites as the template for a general and modular synthetic route to *d-f* or *f-f'* complexes (Figure 1).¹⁻³ The coordination complexes $[\text{Ln}(\text{hfac})_3(\text{N},\text{N}'\text{-pd})]$ ($\text{Ln} = \text{Y}, \text{Sc}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Yb}$; $\text{hfac} = \text{hexafluoroacetylacetonate}$) and $[\{\text{La}(\text{hfac})_3\}_2(\text{N},\text{N}'\text{-O},\text{O}'\text{-pd})]_\infty$ ($\text{Ln} = \text{La}, \text{Ce}$) were synthesised and fully characterised using a range of spectroscopic techniques. The reaction between $[\text{Ln}(\text{hfac})_3(\text{N},\text{N}'\text{-pd})]$ ($\text{Ln} = \text{Y}, \text{Sc}, \text{La}, \text{Ce}, \text{Gd}$) and VCp_2 or VCp^t_2 ($\text{Cp}^t = \text{tetramethylcyclopentadienyl}$) resulted in the isolation of the heterobimetallic complexes, $[\text{Ln}(\text{hfac})_3(\text{N},\text{N}'\text{-O},\text{O}'\text{-pd})\text{VCp}_2]$ ($\text{Ln} = \text{Y}, \text{Sc}, \text{La}, \text{Ce}$ and Gd) or $[\text{Ln}(\text{hfac})_3(\text{N},\text{N}'\text{-O},\text{O}'\text{-pd})\text{VCp}^t_2]$ ($\text{Ln} = \text{Y}, \text{Gd}$). The solid-state molecular structures were determined by X-ray crystallography where possible. The spectroscopic data are consistent with oxidation of V(II) to V(IV) and reduction of pd to pd^{2-} in the heterobimetallic complexes.

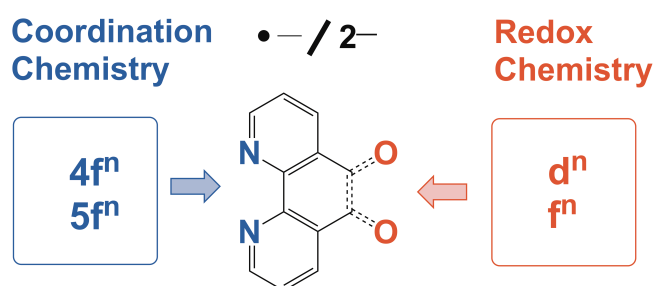


Figure 1. Synthetic template for multi-metallic complexes based on pd

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Access to Divalent lanthanide NHC complexes by redox-transmetallation from silver and CO₂ insertion reactions

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Through the seminal work of Deacon and Junk *et al.*, redox-transmetallation from Hg^{II} has become a common route to access lanthanide complexes.¹ Herein the reactivity of NHC-Ag^I complexes was investigated towards redox-transmetallation with lanthanide metals as a new synthetic approach.

Stirring of IMes-Ag^I (**1**^{Mes}; IMes = 1,3-dimesitylimidazol-2-ylidene) with excess of freshly filed Eu or Yb metal in THF at room temperature for two days resulted in a gradual colour change of the solution from colourless to orange-red. In addition, a fine black precipitate, presumably elemental silver, was formed. After decantation and filtration of the insoluble material, slow evaporation of the solution afforded [LnI₂(IMes)(THF)₃] (Ln = Eu (**2**^{Mes}), Yb (**3**^{Mes})) as bright yellow and orange crystals, respectively, in 33-41% isolated yield (Scheme 1). The Eu^{II} complex **2**^{Mes} exhibits a bright yellow-green luminescence under UV light ($\lambda_{\text{exc}} = 365$ nm) both in the solid-state (Figure 1, bottom right) and in C₆D₆ solution, suggesting that the molecular structure of **2**^{Mes} is retained in non-polar aromatic solvents.

Furthermore the lability of the NHC-Ln^{II} bond was investigated and treatment with CO₂ led to insertion reactions without oxidation of the metal centre.²

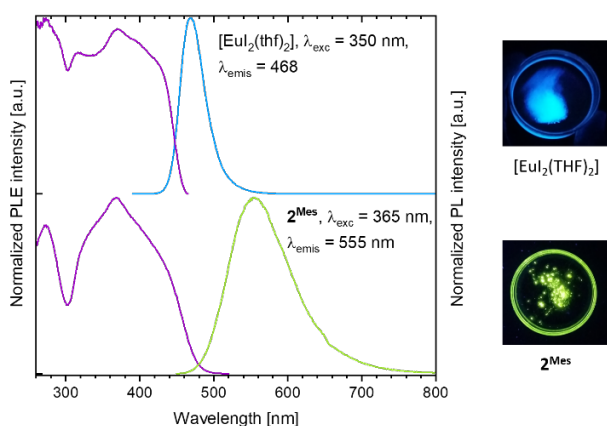
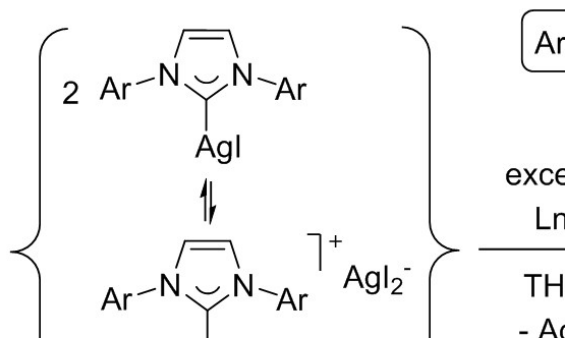


Figure 1 (left). Photoluminescence emission (PL) and excitation (PLE) spectra (left) and photograph under UV light (365 nm) (right) of [EuI₂(THF)₂] and **2**^{Mes} in the solid state at ambient temperature. PL quantum yields for an excitation at 350 nm and a centre of emission at 468 nm ([EuI₂(THF)₂]) and 555 nm (**2**^{Mes}), respectively: $\phi([EuI_2(THF)_2]) = 0.31$; $\phi(\mathbf{2}^{\text{Mes}}) 0.53$.

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Halide-Containing Oxidoarsenates(III) of the Rare-Earth Metals

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Compounds containing rare-earth metals and complex oxoanions are interesting materials because of their luminescence properties^[1]. The simple ternary oxidoarsenates(V) with the composition $Ln[AsO_4]$, which crystallize with the *monazite*-, *xenotime*- or *scheelite*-type structure, are known since 1934^[2] for example. The corresponding $Ln[AsO_3]$ phases with As^{3+} cations have seen less attention so far^[3,4]. If halide-containing fluxing agents in solid-state reactions are used, very often quaternary compounds with incorporated halide anions occur. These oxidoarsenates(III) make a promising material class, since they behave indifferently towards water and air and therefore show long-term stability. The As^{3+} cations carry non-binding, stereochemically active lone-pair electrons, which often lead to the formation of empty channels in the resulting crystal structures. Depending on the size of the Ln^{3+} cation, different quaternary compounds with the compositions $Ln_5Cl_3[AsO_3]_4$, $Ln_3OCl[AsO_3]_2$ and $Ln_3Cl_2[As_2O_5][AsO_3]$ are formed^[5–7]. Different extra anions (O^{2-} and/or Cl^-) and degrees of condensation of the oxidoarsenate(III) units are observed. In the first two compound classes, only isolated ψ^1 -tetrahedral $[AsO_3]^{3-}$ groups with a lone-pair of electrons occur. The latter one contains both $[AsO_3]^{3-}$ anions and *pyro*-anionic $[As_2O_5]^{4-}$ oxidoarsenate(III) entities built up by two corner-connected $[AsO_3]^{3-}$ units. All substances can be prepared through solid-state reactions of the corresponding rare-earth metal sesquioxide (Ln_2O_3), rare-earth metal trichloride ($LnCl_3$), arsenic sesquioxide (As_2O_3) and an excess of caesium chloride (CsCl) as a fluxing agent in evacuated glassy silica ampoules at 800 °C for four days. In the talk, the variety of the structural chemistry of quaternary rare-earth metal(III) halide oxidoarsenates(III) will be presented.

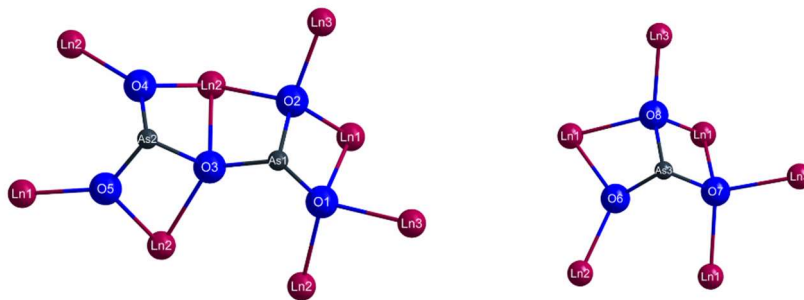


Figure 1. The complex oxoanions $[As_2O_5]^{4-}$ and $[AsO_3]^{3-}$ in the $Ln_3Cl_2[As_2O_5][AsO_3]$ structure.

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Tunable emission in naphthylsalophen dinuclear lanthanide(III) sandwich complexes

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The Schiff- base ligand 1,1'-((1E,1'E)-(1,2-phenylenebis (azanylylidene)) bis(methanylylidene))bis(naphthalen-2-ol) ("naphthylsalophen" = L) was used to prepare metal complexes with a series of lanthanide(III) metal salts.¹ Previously, these ligands have been characterized in complexes with Th(IV), Ce(IV), and U(VI) - as the uranyl UO_2^{2+} cation.^{2,3} Eleven lanthanide double decker sandwich complexes (Ln_2L_3), where Ln = Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), or Lu(III), were synthesized and characterized in the solid-state and in solution. The resultant complexes were found to self-assemble as triple decker sandwich complexes of the type (Ln_2L_3). The structural differences between the Nd_2L_3 , Gd_2L_3 , Tb_2L_3 , Dy_2L_3 , Ho_2L_3 , Yb_2L_3 , and Lu_2L_3 analogues are minimal and can be attributed to the decreasing size of the lanthanide series. Small differences in structure afforded similar absorbance spectra, and these were found to be somewhat tunable with the addition of coordinating solvents. In the Nd_2L_3 complex, both metals were found to be 8 coordinate with the ligand, while in the Gd_2L_3 complex, one metal is 8 coordinate, one 7 coordinate. The Ho_2L_3 , Yb_2L_3 , Tb_2L_3 , Dy_2L_3 , and Lu_2L_3 were found to be isostructural with the Gd_2L_3 complex. These were found to have tunable emission based on primarily ligand-centered fluorescence at room temperature across the lanthanide series with a maximum at 556 nm for the Sm_2L_3 complex to 617 nm for Er_2L_3 . Greatly enhanced emission from single crystals of Lu_2L_3 was observed. Here, we describe these distinctive lanthanide complexes and their absorption and emission properties both in solid-state and solutions.

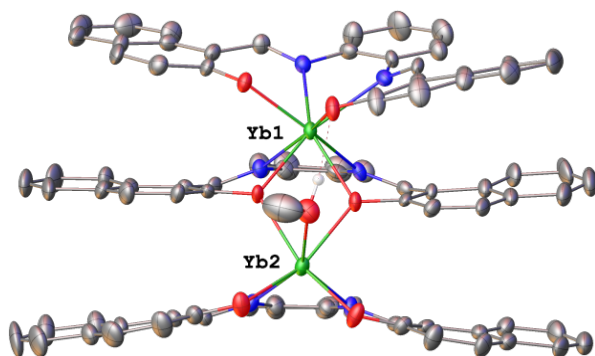


Figure 1. Projection of the side view of Yb_2L_3 . Interstitial solvent and hydrogen, except those involved in hydrogen bonding have been removed for clarity. Carbon atoms are shown in grey, nitrogen in blue, oxygen in red, and ytterbium in green.

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F and d in harmony: Halide derivatives of rare-earth metal molybdates and tungstates as promising materials for luminescence applications

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Halide derivatives of rare-earth metal oxidomolybdates and -tungstates represent promising materials for luminescence applications, since they offer a plethora of different chemical compositions, resulting in host lattices with hardness variations and diverse coordination numbers of the refractory metal cations, as well as various condensation grades of the complex molybdate and tungstate anions, respectively. The latter two adjustment possibilities directly influence the ligand-to-metal charge transfer excitation range, which provides an effective energy transfer towards the activator, usually a trivalent lanthanoid, such as Eu^{3+} or Tb^{3+} . Thus, of luminescence excitation can be accessed by the easily tunable refractory metallates as sensitizer besides energetically fix $f \rightarrow f$ transitions or the ligand-to-activator transfer, which depends on the coordination environment of the latter. The appropriate modifications of those molybdate or tungstate units, respectively, lead to materials which are able to be excited in the visible range, e.g. by a blue LED (see Figure 1).

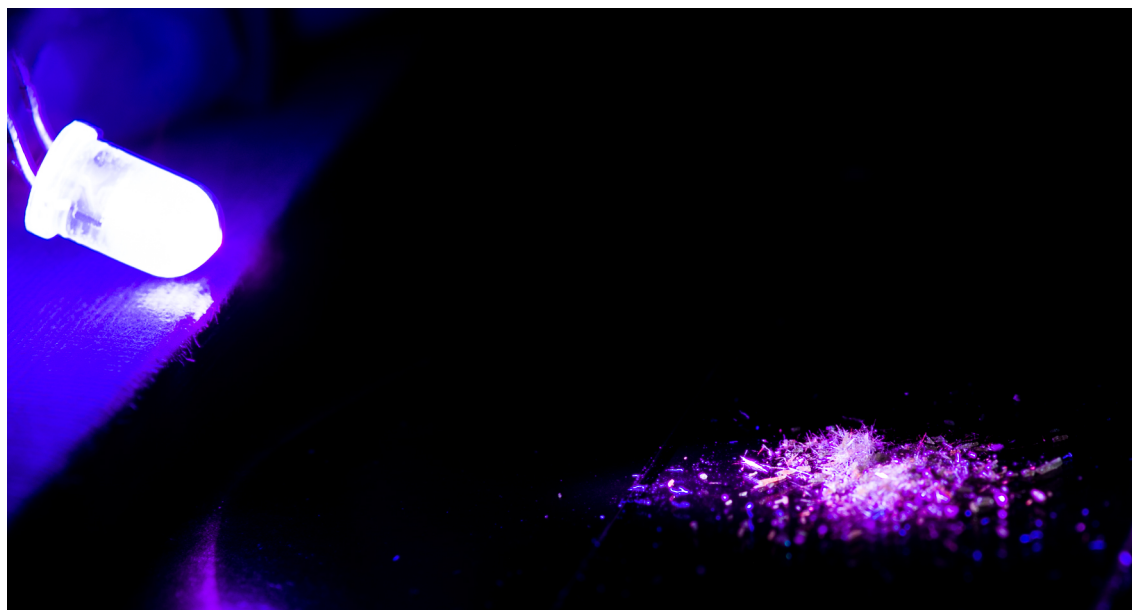


Figure 1. Excitation of $\text{La}_3\text{Cl}_3[\text{MoO}_6]:\text{Eu}^{3+}$ by a blue LED, the visible violet light is a mixed colour of the blue LED and the red emission of the material.^[1]

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The Lanthanide Co-ordination Chemistry of the Redox-Active Ligand 1,10-phenanthroline-5,6-dione

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Multimetallic *d-f* and *f-f'* compounds are well-known for their enhanced and often unique properties.^[1] However, their synthesis can be challenging. We have used the redox-active bridging ligand 1,10-phenanthroline-5,6-dione (pd, Figure 1) to synthesise lanthanide monometallic and lanthanide-transition metal bimetallic complexes.^[2] The co-ordination compounds [Ln(hfac)₃(*N,N'*-pd)] (Ln = Eu, Tb, Yb) have now been synthesised, and the sensitisation of their fluorescence has been probed.^[3] We also recently synthesised the first structurally characterised molecular examples of compounds of the radical anion pd^{•-}.^[4] The compound [CoCp₂]⁺[pd]^{•-} was synthesised and its co-ordination chemistry was utilised to synthesise the lanthanide radical compound [CoCp₂]⁺[Y(hfac)₃(*N,N'*-pd)]^{•-}. Solution and solid-state spectroscopic analysis of these compounds by EPR, UV-visible, and IR methods and single crystal X-ray diffraction, in conjunction with DFT calculations have allowed us to interrogate the effects of lanthanide co-ordination on the ligand in this unusual oxidation state. Present work is targeting the synthesis of *f-f'* multimetallic compounds of the radical anion pd^{•-}, containing optically active and magnetically important lanthanides. Synthetic strategies and initial results towards this goal will also be discussed.

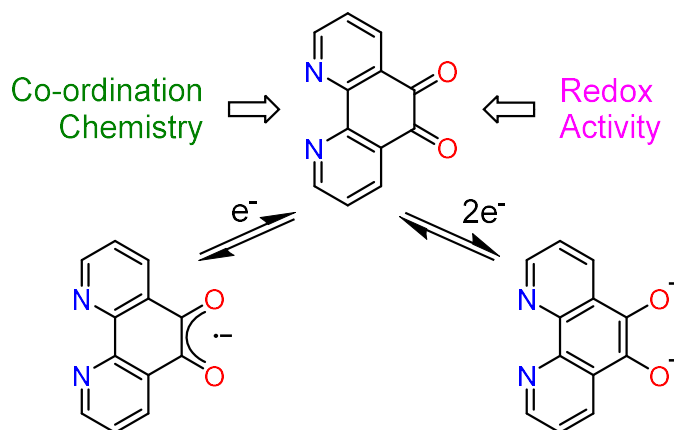


Figure 1. The 1,10-phenanthroline-5,6-dione ligand. Showing the two distinct binding sites and the three accessible oxidation states.

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Lutetium Trigermanide LuGe_3 : High-Pressure Synthesis, Chemical Bonding and Superconductivity

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The element semiconductors silicon or germanium form a rich variety of binary phases with electropositive partners of the alkaline-, alkaline earth- and rare earth metal groups. These compounds often exhibit significant contributions of classical covalent two-center two-electron and ionic interactions, whereby chemical bonding and electron count normally follow the principles established by the Zintl-Klemm concept [1].

Although, compounds violating these electron counting rules or possessing unusual coordination environments in the covalent partial structure of the p-block element, often possess remarkable properties, like superconductivity. The application of high-pressure methods is one strategy to obtain such phases.

A systematic study of tetrel connectivities exceeding the scope of the 8- N rule revealed the special suitability of the structure MTt_3 ($M = \text{Y, La, Eu, Ho, Yb, Lu}$; $Tt = \text{Si, Ge}$) [2-7] for obtaining interesting physical properties. Among the series of rare-earth metals, lutetium, normally occurring as Lu^{3+} in the bound state, provides absence of a magnetic moment, setting the stage for the occurrence of phonon-mediated superconductivity in these so-called covalent metals. Hitherto, the superconducting LuSi_3 [6] has been described, but no analogue phases are known in the system Lu-Ge.

The new metastable binary compound LuGe_3 has been synthesized under high-pressure, high-temperature conditions at pressures between 8(1) and 14(2) GPa and temperatures in the range of 1100(150) to 1500(150) K.

The atomic arrangement of LuGe_3 is isotypic to DyGe_3 , containing double layers of condensed Ge_2 dumbbells as well as Ge zig-zag chains, with the space group $Cmcm$ and the lattice parameters $a = 3.97547(3)$ Å, $b = 20.3771(2)$ Å and $c = 3.86966(3)$ Å. Chemical bonding analysis reveals multicentre polar interactions between Lu and Ge, as well as a lone pair on each Ge. A transition into a BCS-type superconducting state below $T_c = 3.3(3)$ K is indicated by magnetic susceptibility, specific heat, and electrical conductivity measurements.

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New synthetic pathways towards bulky highly luminescent divalent europocene complexes

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Molecular divalent europium complexes are increasingly studied for their photophysical properties, leading for example to the first application of an aza-cryptand based complex in visible-light photoredox catalysis.[1] In Eu^{2+} complexes, f-d transitions become available, leading to broad emission bands across the whole range of the visible spectrum, depending on the ligand environment. Following Harder's ground-breaking report on the bright orange luminescence of $\text{Eu}(\text{Cp}^{\text{BIG}})_2$ ($\text{Cp}^{\text{BIG}} = \text{C}_5(4\text{-}n\text{-butylC}_6\text{H}_4)_5$),[2] we have synthesized the divalent complexes $\text{Eu}(\text{C}_5\text{Ph}_5)_2$ and $\text{Eu}(\text{C}_5\text{Ph}_4\text{H})_2(\text{dme})$ by redox-transmetallation protolysis (RTP) reactions using organomercury reagents (Figure 1).[3] Both complexes emit in the orange region with high quantum yields and relatively long lifetimes. We herein report on two mercury-free syntheses of luminescent divalent europocenes starting from europium metal: a) the new divalent ansa-complexes were obtained by reductive dimerization of the corresponding tetraphenylfulvene; and b) an octaphenyleuropocene was synthesized by selective C-P bond cleavage of $\text{C}_5\text{Ph}_4\text{HPPH}_2$ (Figure 1). Structural and photophysical properties of the bridged and non-bridged complexes will be compared and further developments will be discussed.

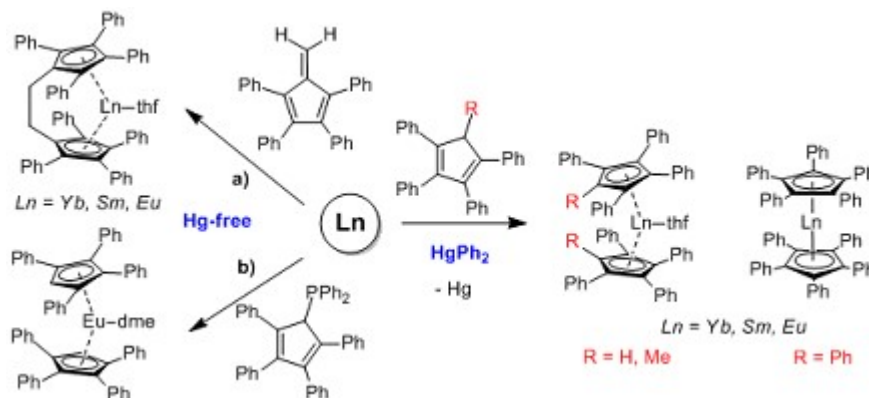


Figure 1. Various synthetic pathways to bulky divalent europocenes starting from europium metal.

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Synthesis, characterisation and reactivity of halogenoaluminate complexes of rare earths and alkaline earths,

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Rare-earth complexes featuring π -bonded arenes are among the most exciting and challenging organometallic compounds. Chloroaluminate π -arene complexes of lanthanoids $[\text{Ln}(\text{arene})(\text{AlCl}_4)_n]$ ($n = 2, 3$) have been known for over three decades with most work focussing on the trivalent^[1] compounds with only few reports on divalent^[2] species. Our work focuses on the synthesis and characterisation of bromo- and iodoaluminate complexes of rare earths having π -bonded arenes. Both divalent and trivalent lanthanoid complexes are accessible by a convenient synthetic route. Catalytic activity of iodoaluminate complex of neodymium for the isoprene polymerisation has been investigated. The π -bonded arene complexes of some heavy alkaline earths have also been synthesised for the first time.

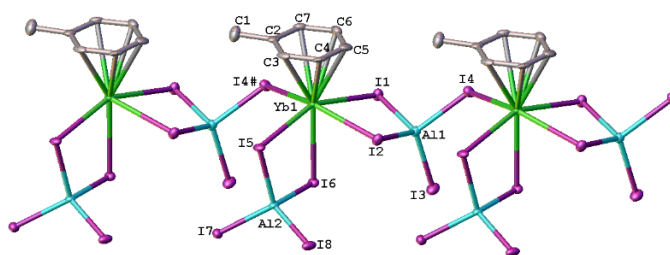


Figure 1: Iodoaluminate complex of ytterbium

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Bimetallic Complexes and Catalyst Systems Combining Rare Earth Elements and Transition Metals

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In the talk, an overview of the activities of the Kempe group in developing bimetallic coordination compounds including those having unsupported bonds between a rare earth element and a transition metal is given[1]. In addition, bi- or multi-metallic catalyst systems combining such metals are discussed[2]. Starting from the “Ap for Cp Concept”, an initiative to replace Cyclopentadienyl (Cp) ligands by Aminopyridinato (Ap) ligands, the benefit of Ap ligands in stabilizing bimetallic compounds is discussed. Unfortunately, unsupported bond could not be observed leading to a conceptual change to address this challenge.[1] To also look into applications of bimetallics, we recently developed bi- and multi-metallic catalyst systems to solve key issues in polymerization chemistry [2] and deoxygenation catalysis.

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Soft chemistry approaches to REE doped nanomaterials

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Uniform doping of nanoparticles and complex oxide nanostructures is a considerable challenge. An attractive solution for it can be application of so-called Soft Chemistry routes, where the nucleation of the oxide phase occurs on decomposition of precursors bearing organic ligands through hydrolytic and thermolytic transformations. The emerging oxide surfaces often act also as catalysts in other organic condensation reactions resulting in formation of oxo-ligands and generation and growth of the oxide phase. In the present contribution, we will consider the structure, stability and reactivity of metal-organic derivatives of Rare Earth elements bearing alkoxide, beta-diketonate and carboxylate ligands. The morphology, structure and compositions of the emerging oxide phases will be discussed and a number of possible applications outlined, including potential use in bio-imaging and drug delivery applications.

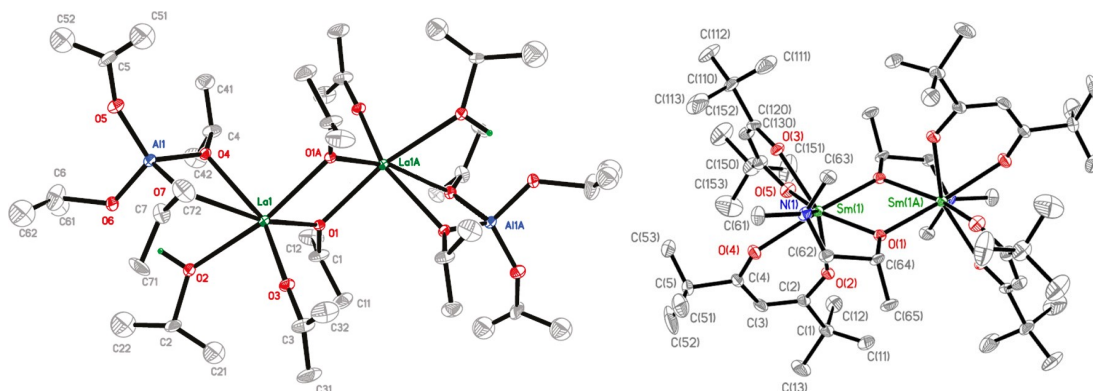


Figure 1. Molecular structure of $\text{La}_2\text{Al}_2(\text{O}^i\text{Pr})_{12}(\text{}^i\text{PrOH})_2$ [1], molecular structure of $\text{Sm}_2(\text{OCHMeCH}_2\text{NMe}_2)_2(\text{thd})_4$ [2]

References

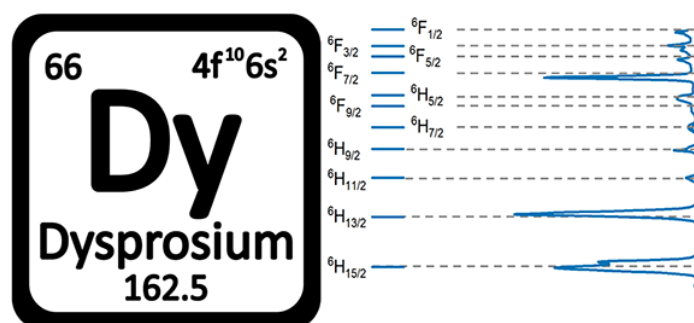
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Electronic Energy Levels of Dysprosium(III) in Solution

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The luminescence arising from the formally forbidden $f-f$ transitions of the trivalent lanthanide ions has found applications in a large number of fields such as lighting, optical fibers and bioimaging.[1-2] However, the exact nature of these transitions is not well understood. A striking example is that of dysprosium: While the electronic ground state, $^6H_{15/2}$, of Dy(III) has been extensively studied the last decade due to the promising magnetic properties of Dy(III) complexes[3], the understanding of the excited state manifold of the ion has remained largely unchanged since the days of Dieke and Carnall.[4-5] In this work, we revisit the assignment made by Carnall by investigating the electronic transitions by electronic absorption spectroscopy as well as steady state and time resolved emission spectroscopy of $Dy(CF_3SO_3)_3$ in water, methanol and dimethyl sulfoxide.[6] We find that the assignment made by Carnall cannot describe the experimental results, and we can identify a second, thermally populated, emitting energy level, the $^4I_{15/2}$. More importantly, we conclude that the m_J manifold arising from the ligand field perturbation of the electronic states, must be taken into account when determining the energy levels of lanthanide ions. We also show that the transition probabilities of the optical transitions can be used to probe the structure of the complexes in solution.



Emission spectra and energy levels of $Dy(CF_3SO_3)_3$ in DMSO- d_6 determined in this study

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Metal-semiconductor transition in hydrides of Laves phases $LnMg_2$

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Laves phase hydrides play an important role in hydrogen storage, e. g. $ZrCr_2$ based materials for rechargeable battery application. They reversibly take up considerable amounts of hydrogen to form metallic hydrides, e. g. ZrV_2H_6 with hydrogen in tetrahedral voids of the parent crystal structure. Lanthanide magnesium based Laves phases $LnMg_2$ are an exception as they form ionic hydrides $LnMg_2H_7$ ($Ln = La, Ce, Pr, Nd, Sm$) or $EuMg_2H_6$ [1-3]. They have the highest hydrogen content of all Laves phase hydrides, exhibit mainly ionic bonding and thus show a metal-semiconductor transition during hydrogenation.

$LnMg_2H_7$ ($Ln = La, Ce, Pr, Nd, Sm, Nd_{0.95}Sm_{0.05}, Nd_{0.95}Tb_{0.05}$) crystallize in the $LaMg_2H_7$ type structure, which is a tetragonal distortion variant of the cubic Laves phase type, as determined by X-ray, synchrotron and neutron powder diffraction [1-2]. $EuMg_2H_6$ crystallizes in a unitary structure type, which may be described as a vacancy derivative of the cubic perovskite type [2]. $CeMg_2H_7$ and $NdMg_2H_7$ are paramagnetic with effective magnetic moments of $2.49(1) \mu_B$ and $3.62(1) \mu_B$, respectively, in good agreement with the calculated magnetic moments of the free trivalent rare-earth cations ($\mu_{calc}(Ce^{3+}) = 2.54 \mu_B$; $\mu_{calc}(Nd^{3+}) = 3.62 \mu_B$) [3]. Despite the high hydrogen capacity, the Laves phases $LnMg_2$ are not well-suited for hydrogen storage. The formation condition with hydrogen gas pressures of 9.0 MPa and higher are not practical, and the decomposition temperatures of the hydrides above 660 K are rather high.

Hydrides with hydrogen content lower than for the above mentioned examples were found by hydrogenation of the hexagonal Laves phases $LnMg_2$ ($Ln = Eu, Gd, Tb$). $EuMg_2H_x$ shows an orthorhombic structure, which is a distortion variant of the parent hexagonal Laves phase type of $MgZn_2$. The lattice parameters suggest the same to be the case for $GdMg_2H_x$ and $TbMg_2H_x$. Laves phase hydrides $LnMg_2H_x$ ($Ln = Eu, Gd, Tb$; $x < 6$) are interesting intermediates of the presumably topotactic hydrogen-incorporation driven metal-semiconductor transitions.

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Slow Er^{3+} Spin Relaxation in $\text{Cs}_3\text{Er}_2\text{Br}_9$

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$\text{Cs}_3\text{Er}_2\text{Br}_9$ and diluted $\text{Cs}_3\text{Lu}_2\text{Br}_9$: Er^{3+} crystals were grown from non-stoichiometric melt by the Bridgman method. They adopt the $\text{Cs}_3\text{Tl}_2\text{Cl}_9$ structure with space group $R\bar{3}c$ (No. 167) [1]. Crystal structures of $\text{Cs}_3\text{Er}_2\text{Br}_9$ [2,3] and $\text{Cs}_3\text{Lu}_2\text{Br}_9$ [3] were previously determined. Magnetic properties were investigated by DC susceptibility, magnetization, and AC susceptibility measurements on a Quantum Design MPMS-5XL SQUID magnetometer between 1.9 K and 300 K.

Er^{3+} ions have a distorted octahedral coordination in $\text{Cs}_3\text{Er}_2\text{Br}_9$. Two octahedra share a face and form dimer units $[\text{Er}_2\text{Br}_9]^{3-}$ with a close Er-Er distance of 3.9 Å. Cs^+ ions separate the dimers from each other and give rise to significantly longer interdimer distances of 5.8 Å along the c -axis and 7.9 Å in the a - b plane. Er^{3+} ions have a C_3 point symmetry and the dimer axis is aligned parallel to the c -axis. The magnetic susceptibility shows a strong anisotropy with much higher values along the c -axis at low temperature. Below $T_C = 0.9$ K 3D magnetic order is observed by neutron diffraction with magnetic moments along the c -axis and ferromagnetic coupling in the dimer. $\text{Cs}_3\text{Er}_2\text{Br}_9$ shows a strong out-of-phase signal in AC magnetic susceptibility. A direct process dominates the spin relaxation below 2.8 K, see Fig. 1. At higher temperature an Orbach process prevails with an activation energy of 59 K, corresponding to the energy difference between the lowest crystal field levels of the $^4\text{I}_{15/2}$ ground state.

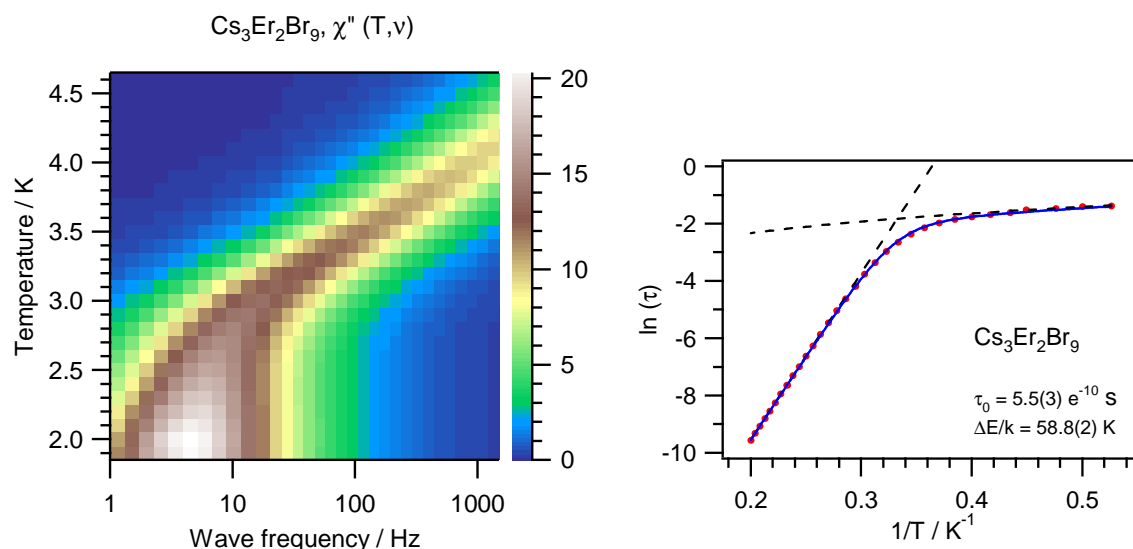


Figure 1. (left) Imaginary part of the zero-field AC susceptibility χ'' of $\text{Cs}_3\text{Er}_2\text{Br}_9$. (right) Relaxation time τ versus reciprocal temperature $1/T$ revealing a direct process below 2.8 K and an Orbach process at higher temperature.

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Optical properties of rare earth doped mixed anionic hydrides and borohydrides

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Mixed anionic hydrides have recently attracted a lot of attention, because the partial substitution of anions by hydride can significantly change the physical and chemical properties of a material [1]. Beside neutron and X-ray diffraction as a characterization tool, the use of local probes can be helpful to obtain additional information, for example on polarizability and local symmetry.

Rare earths ions can serve both as local probes for optical as well as electron paramagnetic resonance spectroscopy. 5d-4f transitions are very sensitive towards differences in the polarizabilities in the local environment. On the other hand, 4f-4f transitions are sensitive towards local symmetries. Here, we study rare earth doped mixed hydride halide compounds and discuss new insights into examples where Eu^{2+} emission can be shifted from 4f-4f emission in the UV in fluoride rich compounds to 5d-4f emission shifted towards the red in hydride rich compounds, allowing for an estimation of the hydride content based on optical spectra [2]. Furthermore, we study optical properties of Eu^{2+} in borohydride chlorides, where high quantum efficiencies and temperature-dependent shifts of the emission maxima are found [3]. We also investigate partial substitution of fluoride by hydride in compounds that may potentially serve as host materials for trivalent lanthanide ions.

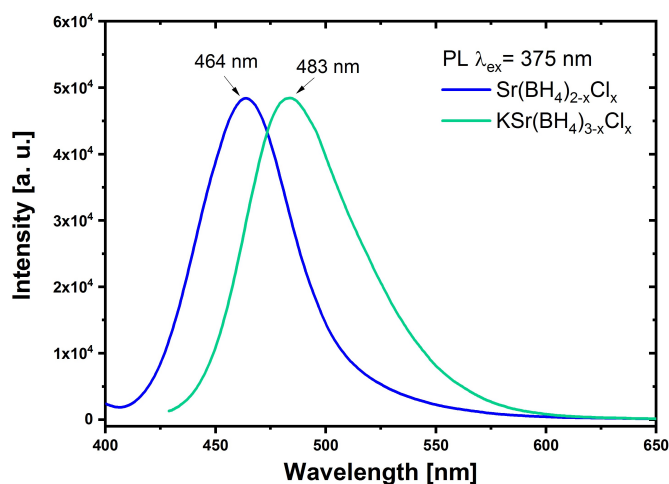


Figure 1. Photoluminescence emission of Eu^{2+} in $\text{Sr}(\text{BH}_4)_{2-x}\text{Cl}_x$ and $\text{KSr}(\text{BH}_4)_{3-x}\text{Cl}_x$ (λ_{ex} 375 nm).

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Synthesis of $\text{Na}_3[\text{R}(\text{NH}_2)_6]$, Intermediates during the Ammonothermal Synthesis of Rare-Earth Metal Nitrides

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Due to the successful growth of high quality group III nitride semiconductors (GaN, InN) and increasing commercial applications, research interests in ammonothermal syntheses routes were considerably rising in recent time. Compared to traditional methods (solid-state synthesis, vapour phase epitaxy), reactions under ammonothermal conditions provide several benefits like comparatively low synthesis temperatures, very good scalability and low defect concentration because of the inherent chemical transport. Since several important device technologies (solar thermophotovoltaics, photocatalysis, etc.) require materials and heterostructure metamaterials that are not possible to archive with traditional III-V nitride semiconductors, alternate materials are necessary. Although the synthesis is quite challenging rare-earth metal containing nitrides such as ScN, $\text{Al}_x\text{Sc}_{1-x}\text{N}$ or $\text{Ga}_x\text{Sc}_{1-x}\text{N}$ are promising materials that could overcome the limitations of group III-V nitride semiconductor materials.

We present new possible intermediates during the ammonothermal synthesis of binary rare-earth metal nitrides and simultaneously new possible reactants for the synthesis of ternary nitrides, $\text{Na}_3[\text{R}(\text{NH}_2)_6]$ ($\text{R} = \text{Nd}, \text{Pr}, \text{Er}$). The neodymium and praseodymium containing compounds crystallize isotypic to $\text{Na}_3[\text{La}(\text{NH}_2)_6]$ ^[1] (orthorhombic in space group *Fddd*), while the erbium containing compound crystallizes isotypic to $\text{Na}_3[\text{Yb}(\text{NH}_2)_6]$ ^[2] (orthorhombic in space group *Pbca*). In both structures all metal atoms are coordinated octahedrally by amide anions. The materials with the larger rare-earth metals comprise two crystallographically unique sodium positions and one rare-earth metal position, forming isolated $[\text{R}(\text{NH}_2)_6]^{3-}$ octahedra. These latter octahedra around the rare-earth metal atoms are vertex-connected with two octahedral coordination spheres and edge-connected with eight octahedral coordination spheres of the sodium atoms. The compound with the smaller rare-earth metal contains three crystallographically unique sodium positions and one rare-earth metal position. The octahedron around the erbium is vertex-sharing with two, edge-sharing with six and face-sharing with one octahedral coordination of the sodium atoms due to the smaller ionic radius of the metal.

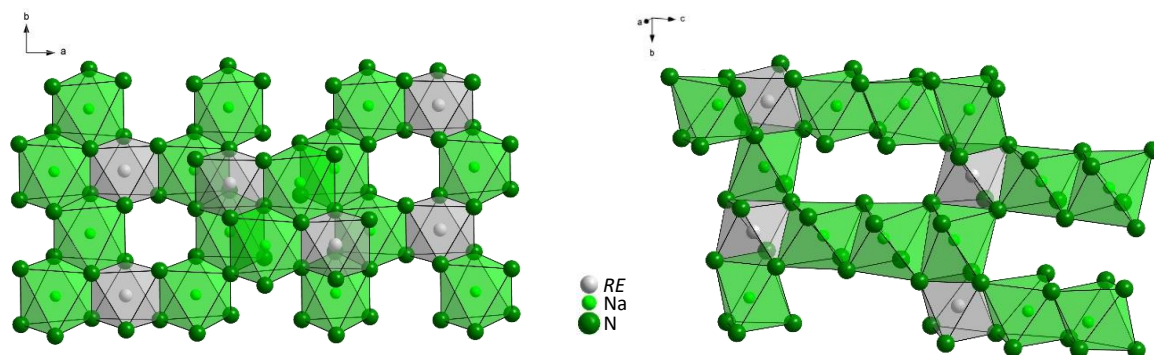


Figure 1. Sections of the crystal structures of $\text{Na}_3[\text{R}(\text{NH}_2)_6]$ with (left) and Er (right) emphasizing the coordination polyhedra around sodium and rare-earth metal atoms as well as their interconnection.

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Electronic Structures of Bent, Formally Two-Coordinate Lanthanide(III) Cations

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Low coordinate metal complexes can exhibit superlative physicochemical properties, but achieving low coordination numbers for the lanthanides (Ln) is problematic due to the tendency to maximize electrostatic contacts in their predominantly ionic bonding regimes.¹ Despite these challenges, formally two-coordinate bent, $[\text{Ln}\{\text{C}(\text{SiMe}_3)_3\}_2]$ (Ln = Sm, Eu, Yb),² and near-linear, $[\text{Ln}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}_2]$ (**1-Ln**; Ln = Sm, Eu, Tm, Yb),³ Ln^{2+} complexes have been isolated. However, examples of formally two-coordinate Ln complexes in the most common +3 oxidation state have remained elusive due to the greater charge density and electrostatic forces of Ln^{3+} centers.

Here we report the isolation and characterization of bent, formally two-coordinate Ln^{3+} complexes $[\text{Ln}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2-Ln**; Ln = Sm, Tm, Yb), which were synthesized by halide abstraction of the heteroleptic three-coordinate precursors $[\text{Ln}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}_2(\text{X})]$, (**3-Ln**; X = Cl, Ln = Sm,⁴ Tm; X = F, Ln = Yb) using $[\text{H}(\text{SiEt}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$.⁵ Complexes **3-Ln** were accessed by the oxidation of **1-Ln** with either $^t\text{BuCl}$ or $[\text{FeCp}_2][\text{PF}_6]$; a Eu^{3+} analogue could not be accessed by adapting these methods. Interrogation of the electronic structures of **2-Ln** and **3-Ln** by EPR spectroscopy, magnetic studies and *ab initio* calculations revealed that the bent complex **2-Yb** expresses a *pseudo*-planar rather than a *pseudo*-axial crystal field in the solid state. This unanticipated result is in opposition to the predicted electronic structure for two-coordinate systems; our calculations indicate that the geometries of these $4f^{13}$ complexes are more important than the identity of the metal ion in dictating the magnetic ground state, providing crucial information for the construction of Ln complexes with enhanced magnetic and optical properties through molecular design.

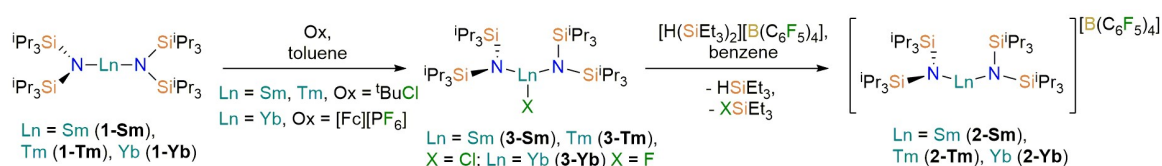


Figure 1. Synthesis of **2-Ln** and **3-Ln**; the synthesis of **3-Sm** has been previously reported.⁴

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Synthesis and grafting of yttrium neosilyl complexes onto mesoporous silica

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Since their initial synthesis in 1973 by Lappert and Pearce, rare-earth metal neosilyl (silylmethyl) complexes emerged as most useful precursors according to tetramethylsilane elimination and silylmethyl abstraction pathways. [1,2] By using surface organometallic chemistry (SOMC) on well-defined support materials highly isolated metal sites can be generated, which perform as immensely active heterogeneous catalysts for a plethora of processes. [3] Moreover, tailor-made siloxy complexes are widely regarded as molecular models for silica surface species. [4]

Here we wish to report the synthesis of a series of donor-stabilized complexes $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{do})_x$ including their full structural and spectroscopic characterization. By varying the donor (do) molecules, the stability of such alkyl complexes is significantly affected. Using a SOMC approach on mesoporous silica nanoparticles, silica-supported yttrium alkyl species could be generated.

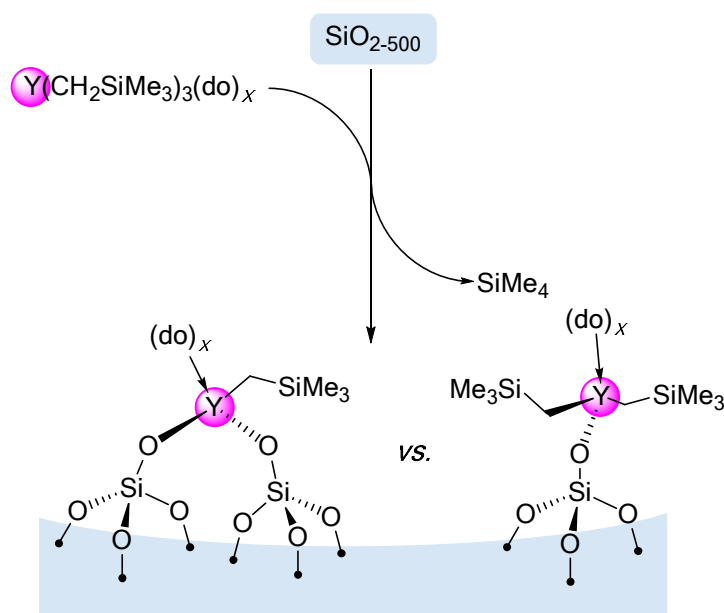


Figure 1. Reactivity of alkyl complexes $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{do})_x$ towards dehydroxylated silica.

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Samarium Polypnicogenides derived from highly activated nanoscale Arsenic and Antimony

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Zintl ions in molecular compounds are of fundamental interest for basic research and application. As part of this research project different reactive arsenic and antimony, sources were used to directly access molecular polypnicogenide compounds. These are Sb amalgam (Sb/Hg), Sb⁰ nanoparticles (d = 6.6 ± 0.8 nm) and As⁰ nanoparticles (d = 7.2 ± 1.8 nm).

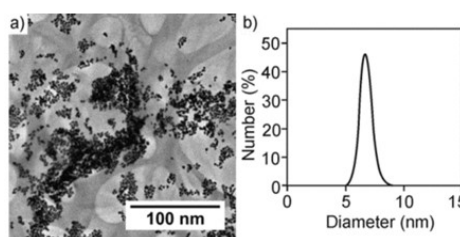


Figure 1. a) TEM-image of the prepared Sb⁰ nanoparticles; b) Size distribution based on 150 nanoparticles from (a).

All three were independently used as precursors for the synthesis of [(Cp*₂Sm)₄E₈] (E = As, Sb), the largest f-element polyarsenide and polystibide, respectively.

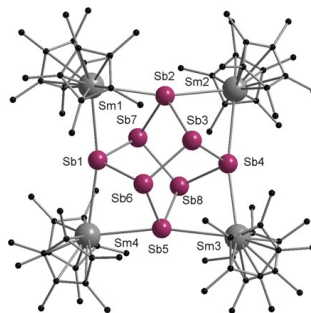


Figure 2. a) Molecular structure of [(Cp*₂Sm)₄Sb₈] in the solid state, Hydrogen Atoms as well as solvent molecules (toluene) are omitted for clarity. The corresponding Arsenic compound is isostructural

Upon reacting the As⁰ nanoparticles with [Cp*₂Sm], [(Cp*₂Sm)₂(μ-η²:η²-As₂)] and [(Cp*₂Sm)₄Sb₈] could independently be isolated depending on the reaction conditions, whereas the reaction of the Sb⁰ nanoparticles with [Cp*₂Sm] directly led to [(Cp*₂Sm)₄Sb₈]. In contrast different Sm/Sb/Hg intermediates were isolated and structurally characterized, when using Sb/Hg as precursor, giving insight in the formation mechanism of polystibide compounds.

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DIRECT DETERMINATION OF SOLUTION STRUCTURE OF EUROPIUM(III) DIPICOLINATE COMPLEXES

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The intensities and degeneracies of the m_J states observed in f-block elements is governed by the coordination geometry that is imposed by the ligand-field. This is theoretically well-established from group-theory[1] but has only been proved experimentally to some extent[2]. Previous studies of ligand field effects in the f-elements has employed europium(III) ions in model compounds due the non-degenerate absorbing and emissive state of europium(III), that ensures that transition spectroscopy is not a convolution of a multitude of m_J states. To study the effects of the ligand-field on transition degeneracies, the tridentate ligand 2,6-pyridinecarboxylate (DPA) has been used extensively[3, 4]. This can be surprising considering how difficult the solution chemistry of this complex is to control. The aqueous, mono-, bis- and tris-ligated europium(III)-DPA species all have different point group symmetries that will give different spectroscopic fingerprints. Previous studies have oversimplified the change in properties by refraining from identifying the bis-species and ignored the weighted average emission fingerprints arising from the long excited state lifetimes of lanthanides[5].

Here, the work done on the $\text{Eu}(\text{DPA})_n^{3-2n}$ system is revisited in order to identify the missing components and evaluate the effect of weighted averages in this very fundamental model system. Rigorous modelling of evolutions in intensities, degeneracies, and peak shifts as a function of ligand concentration is presented. And to investigate the effect of ligand field changes emission, excitation, absorption and NMR spectroscopy, emission lifetimes, and total scattering is used.

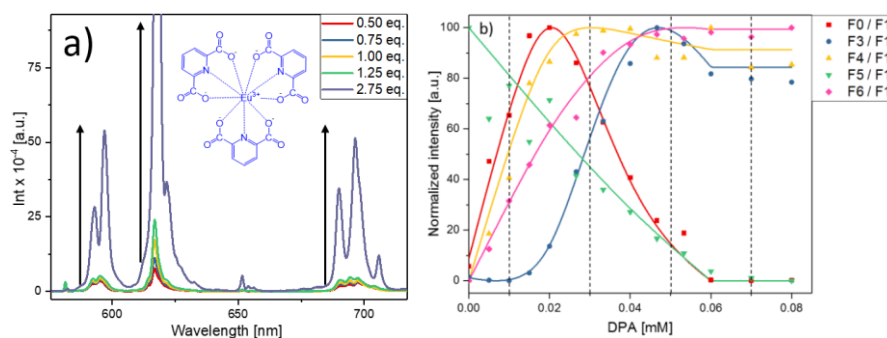


Figure 1. a) Emission spectra at selected Eu: 2,6-pyridinecarboxylate ratios, showing the evolution of the transition band intensity and crystal-field splitting. Insert: Representation of the complex structure at a ratio of 1:3. b) Modelling of transition band intensities of the Eu(III) $^5D_0 \rightarrow ^7F_0$ transition as a function of added ligand. Different bands gain intensity from certain point group symmetries.

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Tetradentate α -diimine ligands for redox-active actinide and lanthanide complexes

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The redox-active Schiff base ligand “phen-BIAN” (N,N'-bis(iminophenol)acenaphthene), which combines the mixed-donor O-N-N-O binding pocket typical of salens with the redox-non-innocent α -diimine backbone of Ar-BIANs, has recently been established¹. The uranyl complex of this ligand adopts a μ -oxo-bridged dimeric structure that exhibits unusual oxo interactions with solvent H-atoms in the solid state, and has a rich electrochemical profile consistent with the reduction of a U(VI)-U(VI) complex to a U(IV)-U(IV) through a series of reversible one-electron steps via the formation of mixed-valent states. Studies of analogous complexes of gbha (glyoxal-bis(hydroxyanil)) ligands which lack the conjugated backbone of phen-BIANs show similar behavior but are much more limited in their electronic flexibility, highlighting the utility of the accessible π -system of phen-BIAN ligands in studying the reductive behavior of uranyl². These gbha species are however useful in examining the effects of equatorial ligand substituents on the uranyl (VI/V) couple. Given that the phen-BIAN framework shows potential for accessing low or unusual uranium oxidation states, it is currently being investigated as a ligand for lanthanides and tetravalent actinides. The characterization of such complexes is pertinent to developing a more thorough understanding of some of the fundamental properties of 4f and 5f elements, and the use of this ligand system offers a unique opportunity to view a variety of metal oxidation states across these series under the same lens. The structural and electrochemical features of these systems will be highlighted.

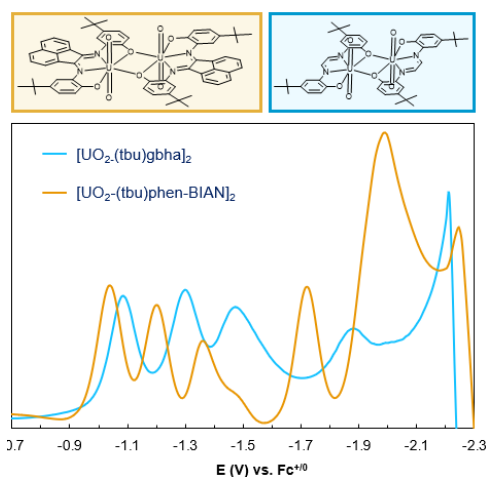


Figure 1. DPV traces of phen-BIAN and gbha complexes of uranyl showing differences in reductive behaviour.

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Synthesis and characterization of alkaline earth – rare earth – borates $\text{Me}_3\text{REE}_2(\text{BO}_3)_4$

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A great interest in phosphors has been brought rapid developments in the promising display and illumination technologies. Since the research on $\text{Sr}_3\text{Nd}_2(\text{BO}_3)_4$ and $\text{Ba}_3\text{Nd}_2(\text{BO}_3)_4$, showed interesting structural and spectral properties, different promising optical materials related to alkaline earth - rare earth borates were prepared. These orthoborate materials have many advantages, such as congruent melting, convenient synthesis, low thermal conductivity, high stability, and the ability to accommodate defects [1, 2].

The search for new host lattices for long lasting phosphorescent materials needs a systematic study on a large family of synthetic borates $\text{Me}_3\text{REE}_2(\text{BO}_3)_4$ (Me = Ca, Sr, Ba and REE = La, Nd, Sm, Eu, Gd, Dy, Y, Yb). The synthesised compounds were studied by X-ray powder diffraction analysis, IR, TG, REM and calorimetry. The unit lattice parameters were refined by Pawley method using the program High Score Plus.

Powder samples were synthesised by a standard solid-state reaction. Analytical grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, H_3BO_3 , $\text{La}(\text{OH})_3$, Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Dy_2O_3 , Y_2O_3 and Yb_2O_3 were used as starting materials. A stoichiometric mixture of the starting materials was finely ground and sintered in a temperature range from 1100°C to 1300°C. The synthesis steps of grinding and sintering was repeated several times until the desired monophasic phase was obtained. The total sinter time varies from 10 h to 24 h.

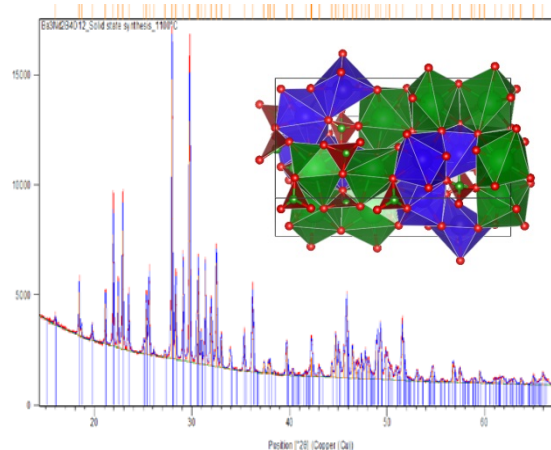


Fig 1: Powder XRD of $\text{Ba}_3\text{Nd}_2(\text{BO}_3)_4$ and its polyhedral structure

24 monophasic phases with the composition of borate $\text{Me}_3\text{REE}_2(\text{BO}_3)_4$ (Me = Ca, Sr, Ba and REE = La, Nd, Sm, Eu, Gd, Dy, Y, Yb) could be synthesized by solid state synthesis method. These compounds crystallize in an orthorhombic lattice. It consists of distorted Me-oxygen polyhedrals, distorted REE-oxygen polyhedral and four sets of BO_3 planar triangles, as shown in Figure 1, using $\text{Ba}_3\text{Nd}_2(\text{BO}_3)_4$ as example. A change of space group from $\text{Pna}2_1$ to Pnma could be observed in the studied compounds depending on the alkaline earth element incorporated in the phase.

Furthermore $\text{Me}_3\text{Eu}_2(\text{BO}_3)_4$ are doped with Dy^{3+} and Sm^{3+} to study its potential use in white light emitting diodes (W-LED).

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Exploratory studies in the *RE*–Mn–Au systems (*RE* = rare-earth metal)

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Chemical and physical properties of gold and its compounds are hallmarked by strong relativistic effects. The high electronegativity of gold is one of the consequences of the relativistic stabilization of the $6s^2$ electronic configuration, which can be adopted upon combination with electropositive elements, such as alkali, alkaline-earth or rare-earth metals [1].

In this contribution, we present results of the exploratory studies in the *RE*–Mn–Au systems (*RE* = rare-earth metal), which were only scarcely explored before [2,3].

Our investigations revealed the existence of a new ternary compound $\text{LaMn}_{0.79(1)}\text{Au}_{5.21}$ crystallizing in the $\text{LaMg}_{1.1}\text{Ag}_{4.9}$ structure type (space group $P4/nmm$, Pearson code $tP14$, $a = 7.111(1)$ Å, $c = 5.3803(7)$ Å), which can be viewed as a derivative of the YbMo_2Al_4 type (Figure 1) [4]. The latter is adopted in particular by other intermetallic compounds containing anionic gold, e.g., CeZn_2Au_4 [5].

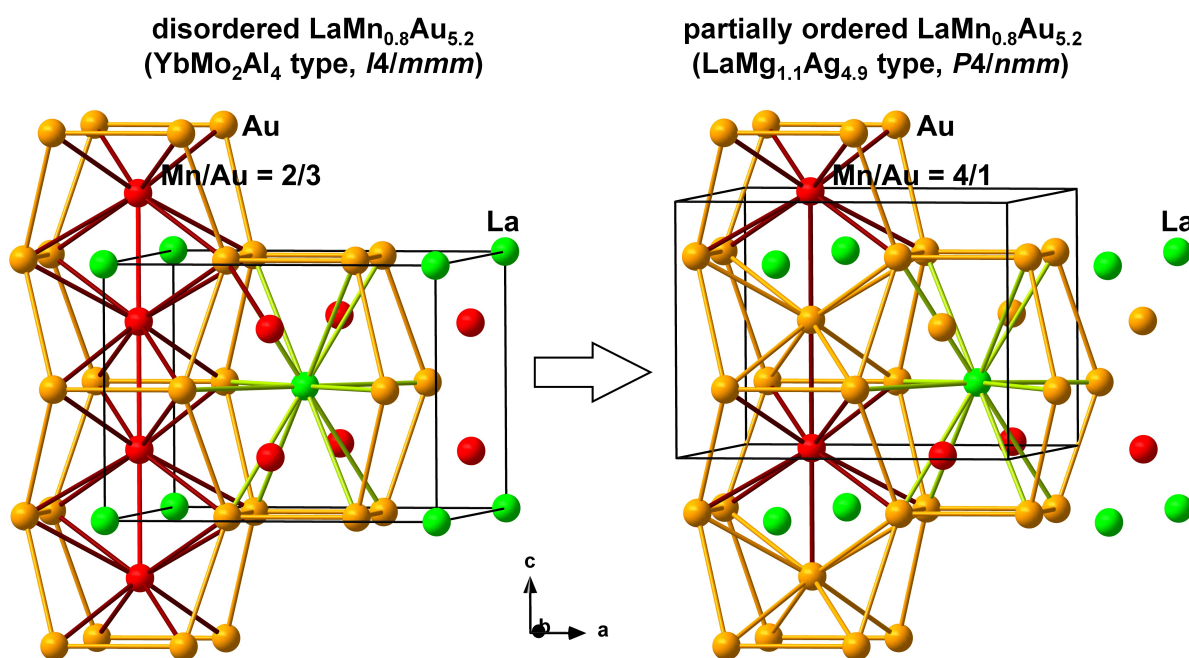


Figure 1. Crystal structures and selected atomic coordination environments of $\text{LaMn}_{0.8}\text{Au}_{5.2}$ in the hypothetical disordered YbMo_2Al_4 type (left) and in the experimentally observed partially ordered $\text{LaMg}_{1.1}\text{Ag}_{4.9}$ type (right). Unit cells are outlined.

Synthetic attempts in the La-rich region of the La–Mn–Au system yielded a hitherto unreported binary compound La_7Au_3 with the Fe_3Th_7 structure (space group $P6_3mc$, Pearson code $hP20$, $a = 10.5726(7)$ Å, $c = 6.5801(5)$ Å). Analysis of the diffraction data did not indicate any potential stabilization by a third element.

Preliminary results in other *RE*–Mn–Au systems and magnetic properties of the new compounds will be also discussed.

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New Lanthanide Compounds and Perspectives for Near-infrared Optical Imaging: Small Molecules, Macromolecules and MOF Nanomaterials

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For biological research and medical diagnostic, optical imaging is an increasingly attractive tool for in vitro and in vivo biological imaging due to the high sensitivity of detection, versatility, low cost of instruments and high resolution at the cellular level. A common characteristic of biologic systems is the presence of complex matrices such as blood, cells, tissue and organs. These matrices emit a significant background fluorescence in the visible domain (autofluorescence), strongly limiting the sensitivity of detection.

The luminescence of lanthanide cations possesses several complementary advantages over the fluorescence of organic fluorophores and semiconductor nanocrystals, such as sharp emission bands for spectral discrimination from background emission, long luminescence lifetimes for temporal discrimination and strong resistance to photobleaching.

Several lanthanide cations emit near-infrared (NIR) photons which result in improved detection sensitivity due to the absence of native NIR emission from tissues and cells (autofluorescence). In addition, NIR photons can potentially cross tissues for non-invasive imaging and diagnostic. [1]

The key requirement to take advantage of lanthanide emission is to sensitize them with appropriate chromophores (“antenna effect”).

We will present here several complementary NIR emitting systems with increasing sizes associated with their applications for biologic imaging: 1) small monometallic complexes that possess excitation and emission wavelengths within biological diagnostic window, 2) macromolecular systems [2-4] and 3) nanoMOFs with high density of lanthanide emitters and sensitizers per unit volume.[5]

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Targeted Synthesis, Crystal Structures and Chemical Bonding of the Valence Electron rich phases RE₄CuGe₂ (RE = La, Ce, Pr)

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Abstract: We present the targeted synthesis of the new phases RE₄CuGe₂ (RE = La, Ce, Pr) to understand the impact of an incremental increase of valence electron count (VEC) on the structure and bonding of the virtual series of phases with nominal composition RE_nTE₂ (T = mid-transition metal; E = Si, Ge, Sn). We noticed the existence of many representatives of the *n* = 1 member such as RENiSi₂ (BaCuSn₂ type, *Cmcm*), and of the *n* = 3 member such as RE₃NiSi₂ (*Pnma*) that are reported for RE = La, Ce, Sm, Gd, Tb, Dy, Ho. However, representatives of the *n* = 2 member are missing, suggesting a possible composition gap in the virtual series. The *n* = 2 members RE₂TE₂ are speculated to adopt the ubiquitous Mo₂FeB₂ type and related structures (space group *P4/mbm* or *P4₂/mnm*) or the W₂CoB₂ type (*Immm*), depending on the RE size.¹ Hence, the targeted synthesis and to confirm the non-existence of the *n* = 2, and the possibility to expend the series to *n* = 4 members or further. The three isostructural title compounds crystallize in a new structure type, monoclinic space group *C2/m*, *Z* = 4, Pearson code *mC28*, Wyckoff sequence *i⁶da*. The most remarkable structural features in these phases are the Cu zigzag chains with unusual homonuclear Cu...Cu interactions (Cu–Cu distances as short as 2.60 Å) and Ge atoms in trigonal prismatic environment of RE, typical of the Mo₂FeB₂ type, indicating close structural relationship. Band structure calculations were carried out to investigate the electronic structure and chemical bonding of La₄CuGe₂.

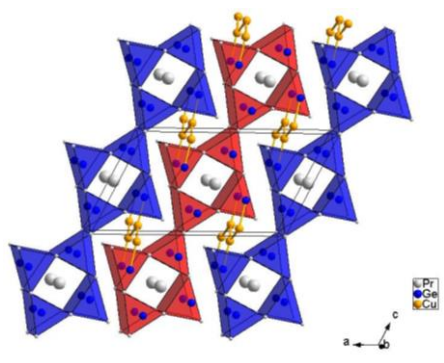


Figure 2. Polyhedral view along the *b*-axis of RE₄CuGe₂ structure showing Ge atoms in trigonal prismatic coordination geometry of RE atoms typical of the Mo₂FeB₂ type.

¹ M. Lukachuk, R. Pöttgen, *Z. Kristallogr.* **2003**, 218, 767 and references cited therein.

The structurally related $\text{Gd}_5\text{Pt}_2\text{In}_4$ and $\text{Gd}_{11}\text{Pd}_4\text{In}_9$ compounds

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The ternary R-T-X phases (R = rare earth, T = transition metal, X = *p*-block element) have been and are always rising lots of interest due to their unique crystal structures and new and unusual physical properties. Among them, the Ni-poor R-Ni-In phases with stoichiometry $\text{R}_5\text{Ni}_2\text{In}_4$ [1,2] and $\text{R}_{11}\text{Ni}_4\text{In}_9$ [3-5] phases have been investigated recently. These two series of intermetallic compounds show a strictly close composition and similar crystal structure, with large and complicated unit cell in form of slabs (almost the same *c* axis of ≈ 3.6 Å and long *a* and *b* axes). The structural prototypes are the orthorhombic $\text{Lu}_5\text{Ni}_2\text{In}_4$ -type (*oP22*, *Pbam*) for the former and the orthorhombic $\text{Nd}_{11}\text{Pd}_4\text{In}_9$ -type (*oC48*, *Cmmm*) for the latter. They are layered, formed by AlB_2 and CsCl fragments, where layers of R alternate with layers of Ni/In. Three and five crystallographic sites are occupied by the R atoms, respectively, in the two compounds. Despite the similarities in the structures, the $\text{R}_{11}\text{Ni}_4\text{In}_9$ compounds reveal a unique and peculiar property: they naturally crystallize in a bundle of self-assembled microfibers when cooled from the melt, leading to very anisotropic physical properties depending on the fibers orientation. The fibers grow unidirectionally along the temperature gradient, with the growth direction along the *c*-axis (orthogonal to the *a-b* plane) [3,4]. The two Gd compounds $\text{Gd}_5\text{Pt}_2\text{In}_4$ and $\text{Gd}_{11}\text{Pd}_4\text{In}_9$ have never been measured; here we present the preliminary results of the investigation of their physical properties. Both compounds show a ferrimagnetic ordering (Figure 1).

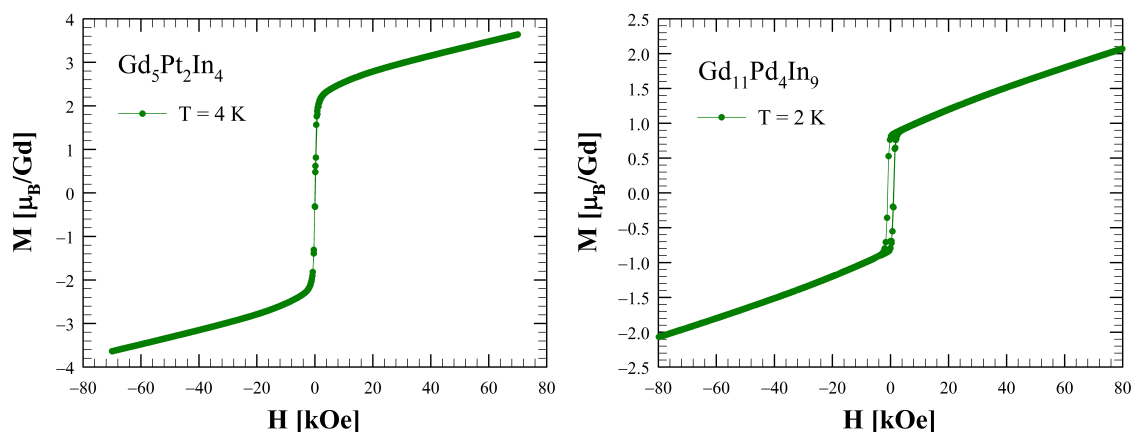


Figure 1. Isothermal magnetization, $M(H)$, of $\text{Gd}_5\text{Pt}_2\text{In}_4$ ($T = 4$ K) and $\text{Gd}_{11}\text{Pd}_4\text{In}_9$ ($T = 2$ K).

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Chemical Vapor Deposition of Phase-Pure Uranium Dioxide Thin Films from Uranium(IV) Amidate Precursors^[1]

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Homoleptic uranium(IV) amidate complexes have been synthesized and applied as single-source molecular precursors for the chemical vapor deposition of UO_2 thin films. These precursors decompose by alkene elimination to give highly crystalline phase-pure UO_2 films with an unusual branched heterostructure

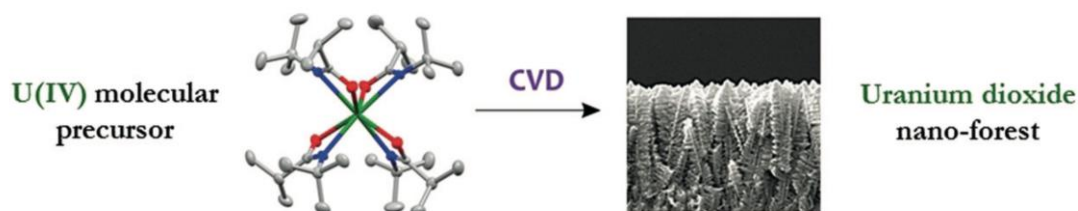


Figure 1. UO_2 nanotree: Volatile uranium(IV) amidate complexes are used as single-source molecular precursors to uranium oxide films. Chemical vapor deposition (CVD) of these single-source precursors yields crystalline, phase-pure UO_2 films with a fir tree-like microstructure and a high surface area.

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Synthesis and development of bis-trialkylsilanide lanthanide chemistry

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The chemistry of complexes containing lanthanide-silicon bonds is largely underdeveloped in comparison to that of lanthanide alkyls.¹ Renewed interest in the field of lanthanide silanide chemistry has been inspired the use of hypersilanide $\{\text{Si}(\text{SiMe}_3)_3\}$ and its derivatives; this research has predominantly focused on Ln^{2+} chemistry,² with fewer examples of Ln^{3+} complexes.³ The development of this field is vital to better understand how softer silicon centres bond to hard lanthanide ions; these advances will provide the foundations for developing actinide silanide chemistry, where there is currently a paucity of examples.⁴

In this work we report the synthesis of the first examples of $\text{Ln}(\text{II})$ bis(trialkyl)silanide complexes **1-Ln** (**1**: $[\text{Ln}(\text{Si}^t\text{Bu}_2\text{Me})_2(\text{THF})_3]$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$), **2-Ln** (**2**: $[\text{Ln}(\text{Si}^t\text{Bu}_3)_2(\text{THF})_3]$ ($\text{Ln} = \text{Sm}, \text{Eu}$) and **3** ($[\text{Yb}(\text{Si}^t\text{Bu}_3)_2(\text{THF})_2]$) by salt metathesis reactions (Figure 1). A reduction in the number of bound THF molecules in **3** is attributed to a combination of the increased steric requirements of tri-*tert*-butylsilanide and the small ionic radius of Yb^{2+} . We have studied $4f^7$ **1-Eu** and **2-Eu** by EPR spectroscopy to gain new insights into the electronic structures of these complexes. We are currently performing reactivity studies on **1-Sm** to benchmark its single electron transfer and bond insertion chemistry.

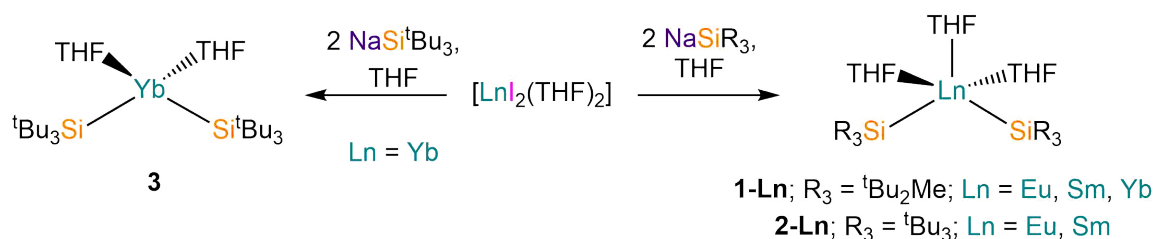


Figure 1. Synthesis of complexes **1-Ln**, **2-Ln** and **3**.

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[C₄mim][AlCl₄] used as solvent to oxidize lanthanide metals at low temperature

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Ionic liquids (ILs) are salts with a melting point below 100°C. In addition, ILs present some interesting properties including good electric conductivity, low to no vapour pressure and easily tailored structure. They can be utilized as solvents, templating agent or even reagents^[1]. Lanthanide containing ILs can present good optical or magnetic properties^[2]. This makes them good candidates for an array of interesting applications such as light emitting electrochemical cells, chemical thermometers, electrically conducting magnetic lubricants, etc.

We report here the successful oxidation of several lanthanide metal (Ln⁰) into Ln^{III} utilizing [C₄mim][AlCl₄] (figure 1). The reaction yields two phases: in the solid phase, the metal powder is converted into the lanthanide-containing ionic liquid [C₄mim]₃[LnCl₆], while in the liquid phase, aluminium chloride is enriched by a significant percentage of Ln^{III}.

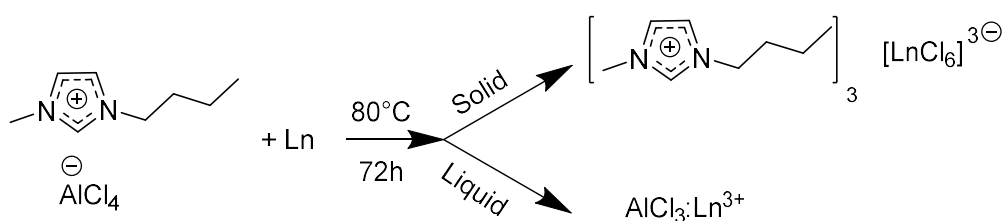


Figure 1. Reaction between [C₄mim][AlCl₄] and lanthanide metal (Ln=Eu, Dy).

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Molecular Lanthanide Zintl-Phases

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For some time, we are interested in the reactions of divalent organometallic lanthanide compounds with group 15 and 16 elements. As products, molecular Zintl ions and other polymeric anion structures stabilized in the coordination sphere of the 4f metals were isolated.^[1]

Herein, the recent progress in this area is reported. Besides the synthesis and structural characterization of lanthanide polypnictogenide and polychalcogenide compounds new activation methods of group 15 elements are shown. Thus, the application of group 15 nanoparticles and group 15 alloys is demonstrated (Figure 1). In addition, as shown by others and us, the product formation initiated by divalent lanthanides depends on the steric demand and on the electronic properties of the ligand.^[2] In detail, the reactions of various divalent lanthanide compounds, e.g. samarocene, with white phosphorous,^[3] yellow arsenic,^[4] gray antimony,^[5] elemental sulfur,^[6] and other small molecules^[7] will be discussed.

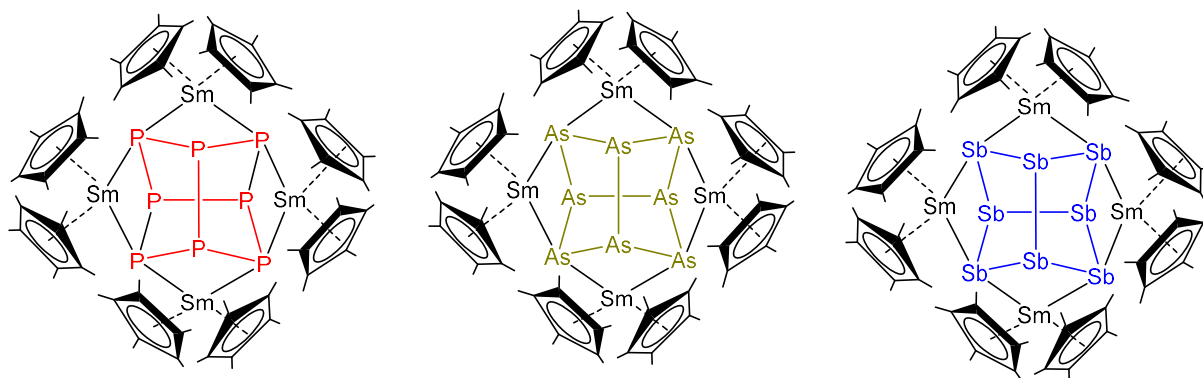


Figure 1. A polyphosphide, a polyarsenide, and a polystibide of the lanthanides.

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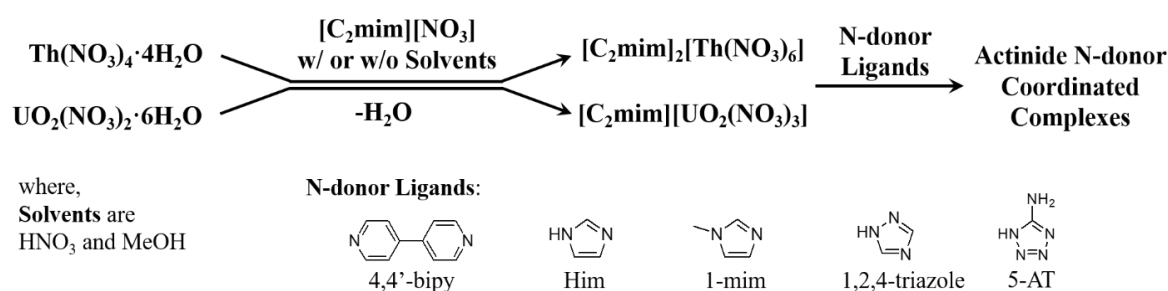
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Dehydrating f-Element Salt Hydrates with Ionic Liquids and Using the Anhydrous Salts as Labile Intermediates for Bench top N-Donor Chemistry

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We report a unique strategy to readily prepare crystalline N-donor f-element coordination complexes from readily available hydrated f-element salts by first dehydrating them with an ionic liquid containing a common anion and then reacting the anhydrous complexes with N-heterocyclic ligands. This presentation will discuss our results of this approach with both lanthanide and with actinide salts. Here, illustrated with actinide salts, the hydrated actinide salts, $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, were dissolved in 1-ethyl-3-methylimidazolium nitrate ($[\text{C}_2\text{mim}][\text{NO}_3]$) to prepare anhydrous $[\text{C}_2\text{mim}]_2[\text{Th}(\text{NO}_3)_6]$ and $[\text{C}_2\text{mim}][\text{UO}_2(\text{NO}_3)_3]$. Reaction of these anhydrous salts with N-donor heterocycles yielded several new actinide N-donor coordinated complexes, $[\text{H}(1\text{-mim})_2][\text{Th}(\text{NO}_3)_5(1\text{-mim})_2]$, $[\text{C}_2\text{mim}]_2[\text{UO}_2(\text{NO}_3)_3]_2(4,4'\text{-bipy}) \cdot 2\{\text{UO}_2(\text{NO}_3)_2(4,4'\text{-bipy})\}$, $(\text{UO}_2(\text{NO}_3)_2(1\text{-mim})_2)_2$, and $\text{UO}_2(\text{NO}_3)_2(\text{H-im})_2$ (1-mim = 1-methylimidazole; H-im = imidazole). These results challenge the concept that f-elements prefer O-donors over N-donors, suggesting it is the acidic hydrogen atoms from water which compete with the f-elements for access to the N-donor that impedes access to the more elusive N-donor coordination complexes. Other current results will be discussed as time allows.



Scheme 1. Dehydration and complexation strategy.

Organolanthanides with aryl-substituted cyclopentadienyl ligands, structural peculiarities and luminescence

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Aryl-substituted Cp ligands could be useful to provide an effective steric control over Ln³⁺ ion coordination sphere and to improve the photophysical properties of the complexes. We have used polyphenylcyclopentadienyl¹ and diphenyl-aryl-cyclopentadienyl ligands to design different types of neodymium, gadolinium, terbium and dysprosium complexes with different number of cyclopentadienyl ligands in the metal coordination sphere. The use of arylsubstituted Cp ligands with bulk aryl substituents derived from condensed arenes and arenes, containing heteroatoms, allowed us to obtain new structural types of complexes due to the non-valent and covalent interaction involving aryl substituents.

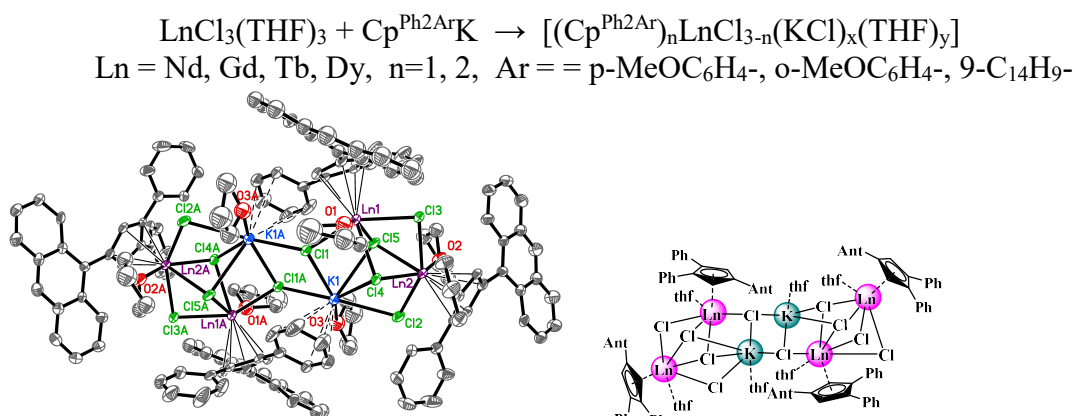


Figure 1. Molecular structure and scheme of $[(1-(9\text{-anthracenyl})-3,4\text{-Ph}_2\text{C}_5\text{H}_2)\text{Ln}(\text{thf})\text{Cl}_2]_2\text{KCl}(\text{thf})]$

Using of polyarylsusbstituted cyclopentadienyl ligands allowed to develop a new approach to design of “antenna-ligands” for Ln³⁺ ions and to enhance the photoluminescence of lanthanide complexes. Variation of the aryl substituent in the cyclopentadienyl rings allowed to regulate photophysical properties of the complexes.

Synthesis, structural diversity and photophysical properties of different types of polyaryl-substituted cyclopentadienyl complexes of Nd, Gd, Tb, Dy will be discussed in the presentation.

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

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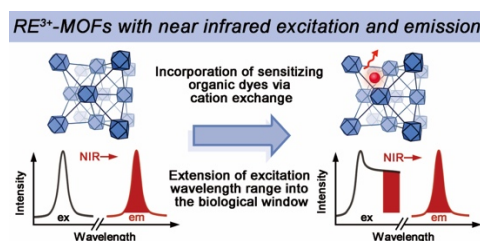
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Metal-Organic Frameworks as Platform Materials for Creating NIR-Emitting BioAnalytical Probes

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Metal-organic frameworks (MOFs) are presented as a platform material for creating near infrared (NIR) emitting materials. Specifically, a selection of lanthanide-ion based MOF materials designed for bioanalytical and biological imaging applications are presented. Various strategies for controlling and systematically tuning the excitation energy of these materials will be discussed. It will be demonstrated that lanthanide-based MOF materials are sufficiently bright for biological imaging applications and that they can be excited at energies that lie within the ideal biological imaging window. Three strategies will be presented for designing MOFs with excitation wavelengths suitable/ideal for biological imaging applications. In the first, MOFs are prepared with extended conjugated linkers; in the second, post-synthetic MOF modification strategies are implemented to systematically shift the excitation wavelength of the MOF to the low energy visible region of the spectrum; in the third, a dye encapsulation strategy is developed whereby long wavelength dyes are encapsulated within a MOF and used for low energy Ln sensitization.



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Separations of Rare Earth Metals: Challenges and Opportunities Using a Molecular Basis

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The rare earth metals (La-Lu, Sc, and Y) are the most challenging inter-element separations. The industry standard method for separating rare earth metals, countercurrent solvent extraction, is typically operated at or near equilibrium for a single pass extraction or stripping step. Each step of this process has low selectivity for separating a given rare earth. We have been working to develop different modes of separation for rare earths. And we recently initiated a program to examine separations of rare earth metals by kinetic means. For example, rate differences for a chemical process tied to rare earth cations was shown to provide means for separation. We have used variable rates of oxidation reactions to partition late rare earth metals. And simple rate equation models also allow for prediction of separations factors. The presentation will highlight recent efforts in this area for the simplified separations of pairs of rare earth species, especially for applications in recycling rare earths from spent materials.

The Structural Variety of Rare-Earth Metal Selenidophosphates

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Due to their wide range of structures and properties, thiophosphates of the rare-earth elements with and without alkali metals have been studied very well in the past years [1,2]. Moreover, the interest in selenidophosphates with rare-earth metals has increased in the last few years, since they also show interesting physical properties. In contrast to the thiophosphates, the isotypic examples of selenidophosphates have proven to be elusive, so far, especially the series of $Ln[PSe_4]$ compounds. While the $Ln[PS_4]$ representatives with isolated $[PS_4]^{3-}$ tetrahedra have been investigated in the last forty years [1,2], analogous $[PSe_4]^{3-}$ tetrahedra are only known in structures, which include transition [3] or alkali metals [4]. The only compounds with alkali, rare-earth metals and $[PSe_4]^{3-}$ tetrahedra are $Rb_3Ce[PSe_4]_2$ [5] and most amazingly $K_4Eu[PSe_4]_2$ [6], $KEu[PSe_4]$ [7] and $LiEu[PSe_4]$ [8], all with divalent europium. In addition, compounds with ethane-like $[P_2Se_6]^{4-}$ anions and the structured formula $ALn[P_2Se_6]$ are well known for $A = Tl$ and Ag [9] and a few alkali metals ($A = Na$ and K) with $Ln = La$ and Ce [10–13].

During the characterization of the new $ALn[P_2Se_6]$ series with $A = K, Rb$ and Cs it was observed that the structure of the $KLn[P_2Se_6]$ representative varies with the size of the Ln^{3+} cation. $KSm[P_2Se_6]$ with mid-size Sm^{3+} crystallizes in the monoclinic space group $P2_1$. The representatives with the light lanthanoids ($Ln = Ce - Nd$) adopt the $KLn[P_2Se_6]$ -type structure (monoclinic, $P2_1/c$) [10], whereas the smaller ones ($Ln = Gd - Dy$) prefer the orthorhombic $KY[P_2Se_6]$ -type structure (space group: $P2_12_12_1$) [11]. For the composition $ALn[P_2Se_7]$ three selenidophosphate representatives are known with $Ln = Ce, Pr$ and Gd for $A = Rb$ and Cs [11,12]. The caesium praseodymium selenidophosphates having the empirical formula $Cs_2PrP_2Se_7$ and $Cs_2GdP_2Se_7$ crystallize in the monoclinic space group $P2_1/n$ and contain both $[PSe_4]^{3-}$ and $[P_2Se_6]^{4-}$ anions according to $Cs_4Ln_2[PSe_4]_2[P_2Se_6]$ [13].

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Nanotechnology for extraction and separation of Rare Earth Elements

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The increased demand for REE resulted in their enlarged production from ores (i.e. mining) and also in a strong research focus on the development of technologies for their recycling. The strategic importance of developing a general approach capable of producing a new technology for separation of REE is recognized. Application of selectively acting hybrid magnetic nanoparticles has been accepted as one of the promising directions by European Union. New hybrid organic–inorganic materials acting as complex adsorbents bearing specific ligands for uptake of trivalent rare-earth (RE) ions have been developed. The binding and release of trivalent rare earth element (REE) cations from solutions by a new fully characterized magnetic nano adsorbent material, consist of specific ligand grafted onto SiO_2 covered $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles [1, 2]. To understand the chemistry of REE binding to complexone-bearing nanoparticles and to provide insight into the molecular origins of the possible selectivity in this process it is necessary to investigate the molecular models revealed the coordination of cations occurring via concerted action of the grafted anions. The binding modes were highly varied for cations with slightly different sizes in the coordination polymer like surface layers. The insight into the molecular aspects and potential maximal capacity of hybrid organic–inorganic adsorbents has been obtained [3,4].

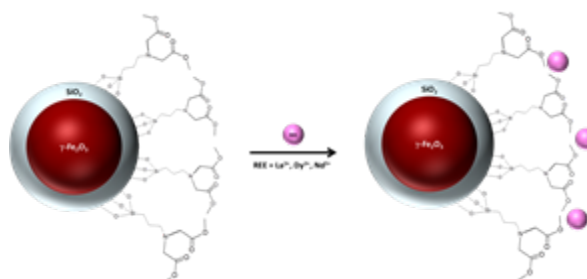


Figure 1. Scheme of the conventional proposed mechanism of hybrid magnetic nanoadsorbents.

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A Hidden Island of Rare Earth Rich Intermetallics

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Although the rare-earth–transition-metal phase diagrams have been intensively explored, our recent studies on rare-earth metal cluster complex halides with endohedral transition metal atoms has uncovered new binary intermetallics that are mimicking others in the present database but are “non-existent”. All the reported compounds belong to a narrow region with approximately 71 at% of the rare-earth metal but represent four different structure types. The binaries Tb_7Pd_3 , $\text{Er}_{17}\text{Pd}_7$ and $\text{Pr}_{17}\text{Co}_7$ are compositionally approaching (less than 1 at% difference) the reported $\text{Tb}_{2+x}\text{Pd}_{1-x}$, $\text{Er}_{2+x}\text{Pd}_{1-x}$ and Pr_5Co_2 [1, 2], respectively, and apparently form by peritectoidic transformation, hard to detect by fast cooling. Tb_7Pd_3 crystallizes in the Th_7Fe_3 structure type ($hP20$, $P6_3mc$, $a = 9.8846(4) \text{ \AA}$, $c = 6.2316(3) \text{ \AA}$, $Z = 2$) while $\text{Er}_{17}\text{Pd}_7$ belongs to the newly discovered $\text{Pr}_{17}\text{Co}_7$ type being its second reported representative ($cP96$, $P2_13$, $a = 13.365(2) \text{ \AA}$, $Z = 4$). $\text{Er}_{17}\text{Pd}_7$ is almost overlapping with the reported cubic F -centered cell of $\text{Er}_{2+x}\text{Pd}_{1-x}$ with practically identical unit cell parameters, but with a significantly different structure and appears to be a low temperature modification of the latter. Cubic structures can be described in terms of polyhedral Heusler type packing (Figure 1) and contain close-packed polyicosahedral clusters. The application of different fluxes allowed to obtain good quality single crystals of all compounds. Electronic structure calculations confirm that heteroatomic R – T (R = rare-earth element, T = transition-metal elements) bonding strongly dominates in all structures; Pd–Pd and Co–Co bonding interactions are usually strong but do not play a significant role in the total bonding.

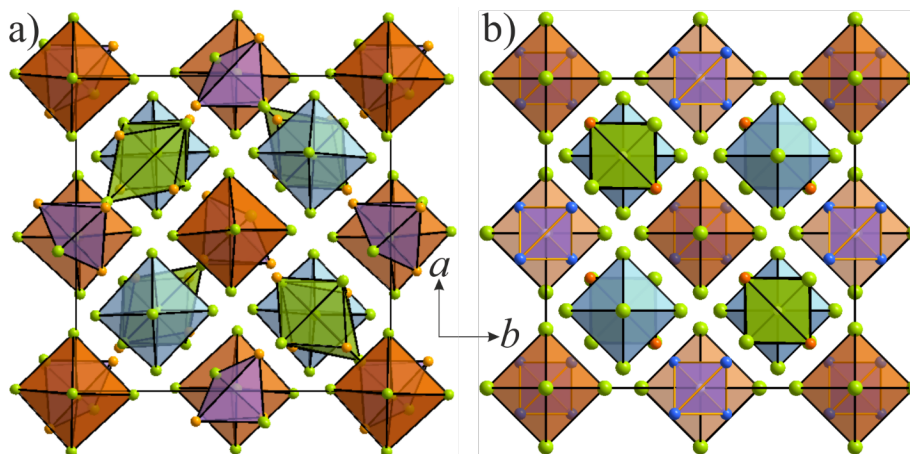


Figure 1. Heusler-type polyhedral packing in the crystal structures of (a) $\text{LT-Er}_{17}\text{Pd}_7$ and (b) Gd_4PdCd . Er and Gd atoms are green, Pd orange and Cd blue.

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Influence of synthesis route and grain size on structural and spectroscopic properties of cubic Nd³⁺-doped Y₆MoO₁₂ nano- and micro-powders as optical materials

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Rare earth (RE)-doped tungstates and molybdates are known as optical materials for over 50 years. They find application as phosphors, scintillators and laser materials. Although, the knowledge about structure and spectroscopic properties of these materials crystallizing in cubic structure is very limited. Cubic nano-crystalline powders can be used to fabricate new optical transparent ceramics. One of the potential candidate could be RE³⁺-doped Y₆MoO₁₂ molybdate, so far not investigated as optical material. We already reported structure and spectroscopic properties of Yb³⁺-doped Y₆MoO₁₂ micro-powder [1].

Here, we present the synthesis and structure, morphology, as well as the spectroscopic properties investigations for cubic Nd³⁺-doped Y₆MoO₁₂ (0.07–10 mol% of Nd³⁺) solid solutions. Nano-crystalline powders were obtained by the combustion method at 600°C/3h (grain size 5–10 nm) and then annealed at 800°C/3h and 1050°C/3h (10–20 nm and 35–40 nm, respectively). All nano-powdered samples were compared with micro-powders synthesized by high-temperature solid state reaction at 1550°C (4–5 μm).

Detailed structural analysis by XRD, as well as microscopic (SEM, TEM) techniques were performed to study dependence of the synthesis route and annealing temperature for the phase transformation. Main spectroscopic results are presented in relationship with the average size of grains and the multisite effect of Nd³⁺ ions, observed by site selective and time-resolved spectroscopies, which, in addition, points out evidence of traces of Nd³⁺-doped Y₂O₃. High-resolution low temperature spectroscopy with a selective excitation was indispensable in our research. We believe that our contribution of both structural and spectroscopic properties of Nd³⁺-doped Y₆MoO₁₂ nano/micro powders brought out a better knowledge of this molybdate material [2].

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Ionic liquid-assisted facile hydrothermal synthesis of nanocrystalline Nd³⁺-doped BiPO₄ NIR emitting phosphor

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Rare earth³⁺ (RE³⁺)-doped BiPO₄ phosphors could be applied in photonic and as the temperature sensors. Moreover, RE³⁺-doped BiPO₄ orthophosphors are interesting as luminescent materials and show up-conversion luminescence [1].

Aim of our research is to obtain new optical materials based on REPO₄ -doped with Nd³⁺ or Yb³⁺ ions. Due to the fact that Nd³⁺ and Yb³⁺ act as structural probe and host materials are not toxic, the materials can be applied in cellular imaging as well.

It is known that luminescent properties depend on morphology of the sample and size of grains [2]. Therefore there is a need to develop new synthesis routes leading to the powder with the highest photoluminescence efficiency. By using task specific ionic liquid (IL) as a donor of PO₄³⁻ anion, the size of the obtained grains is lower than using standard reactants as the IL covers the surface of nanoparticles and limits the growth process. The choice of using choline dihydrogen phosphate as IL was explained previously [3].

One of the synthesis methods leading to obtain nanocrystalline powders is hydrothermal one. Depending on the synthesis conditions at temperature range 20-1100°C can exists in one of three phases: hexagonal (trigonal), low-temperature monoclinic phase (LTMP) and high-temperature monoclinic phase (HTMP). Hydrothermal synthesis promotes the LTMP. At high temperature the phase changes to HTMP. By doping the matrix with Nd³⁺ ion, some changes in the crystal structure have been observed.

Herein, we present synthesis, structure analysis, morphology and spectroscopic properties of BiPO₄ -doped with Nd³⁺ in the form of nanocrystalline powder.

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Crystal structure and physical properties of the novel complex intermetallic compounds $R_8Pt_{32}Be_{66}$ ($R = Y, La-Nd, Sm-Lu$)

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Crystallographically complex compounds often possess peculiar physical properties, the evolution of which can be tracked by changing one of the constituent elements at a time. We report the discovery and synthesis of a $R_8Pt_{32}Be_{66}$ ($R = Y, La-Nd, Sm-Lu$) series of compounds. These materials crystallize in the same cubic structure type (space group $I\bar{4}3d$) with lattice parameters ranging from $a = 13.4366(3)$ Å ($R = Lu$) to $a = 13.6682(4)$ Å ($R = La$). $R_8Pt_{32}Be_{66}$ compounds exhibit a wide range of ground states -- from superconducting ($R = Y, La$, and Lu) to ferromagnetic ($R = Ce, Pr, Nd, Sm, Gd, Tb, Dy$, and Ho), antiferromagnetic ($R = Eu$), and paramagnetic ($R = Er, Tm$, and Yb). These diverse properties can likely be attributed to the level of hybridization of $4f$ orbitals with the $5d$ conduction electrons of Pt , which, in turn, is driven by the complex crystal structure of these compounds – in each case, R atoms are coordinated by 8 Pt atoms and 12 Be atoms.

Lanthanide tris- and tetrakis complexes with 4-(cyclohexanecarbonyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one – an update

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The title ligand was introduced in synthetic practice in 2000 by the group of Claudio Pettinari [1] and since that time it was extensively used for the preparation of variety of complexes with *d*-elements and selected lanthanides. Two main type of complexes were obtained for this ligand – neutral tris complexes (1) and anionic tetrakis complexes (2), bearing cation on the outer sphere of complex. In some cases free acids with H_3O^+ or $(\text{H}_5\text{O}_5)^+$ cations were isolated. The coordination polyhedron for Ln^{3+} in tetrakis complexes is represent by virtually perfect square antiprism, and such environment is favorable for manifestation of SMM properties.

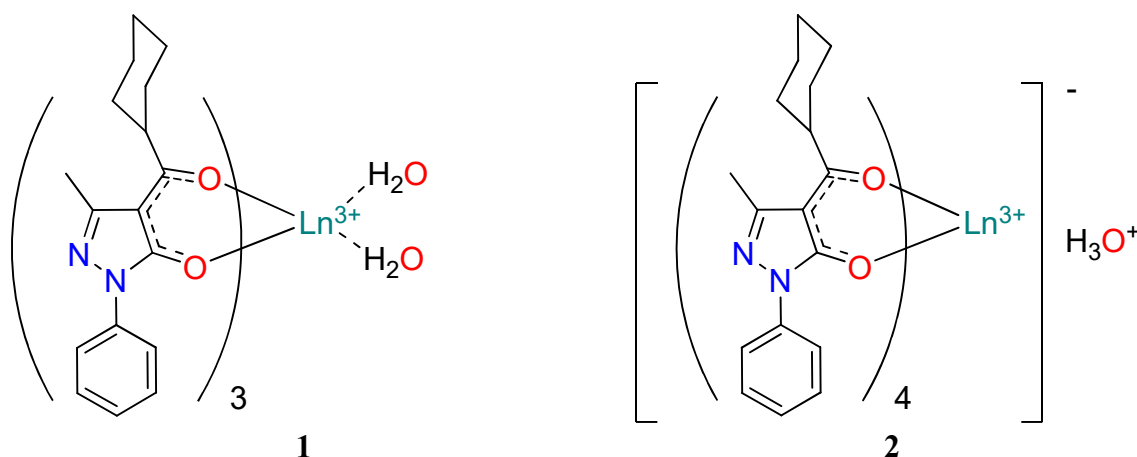


Figure 1. Chemical structures of lanthanide tris (1) and tetrakis (2) complexes with acylpyrazolone ligand.

Unfortunately, known synthetic pathways to these complexes are unreliable and often led to unpredictable result. We have investigated complicated temperature-depended equilibrium between tris and tetakis species in solutions and elaborated direct pathways to both types of complexes. Besides, some interesting aspects of crystal structures and luminescent properties of lanthanide complexes with different composition will be discussed in the report.

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Ln doped materials by solution processing

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There is an increasing demand for complex multi-functional materials of high elemental and structural complexity, often hierarchically structured with sizes down to a few nm. These structures also have to be of high quality and be produced at low cost, which means few and fast processing steps why it is anticipated that molecular based solution processes will be the main route for fabrication. Although the last decade has seen a rapid development of solution based processing routes there is still a strong need for new molecular based processes, where there is a strong connection between the target composition and micro-structure and the precursor structure and process steps in-between. By using low temperature synthesis and suitable molecules there are also great possibilities to achieve far from thermodynamically stable doping levels, composites and inorganic materials built with memory of the molecular precursors. Here we will describe solution processes to Ln doped glasses and oxide sponges and connect the final structures with the precursors and steps in-between. Some examples showing scalability of the processes through applications and up-scalings will also be given. The processes have been studied with a large range of techniques including; TG, DSC, XRD, XPS, SEM-EDS, TEM-EDS, and IR spectroscopy.

Molecular and electronic structure of the dithiooxalato radical ligand stabilised by rare earth coordination

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Multi-metallic complexes containing rare earth elements (RE) are substantially less well understood and developed than their transition metal counterparts. This comes down to the fact that the synthesis of *RE-d* compounds is complex and often stochastic in nature. There is a plethora of possible applications of complexes containing both transition metals and RE, from catalysis to materials science. Non-innocent ligand systems are an important key to unlocking hidden properties exhibited by multimetallic complexes. We have adopted the well-known dithiooxalato (dto)²⁻ non-innocent bridging ligand with asymmetric binding sites favouring coordination to particular metal ions based on their chemical hardness. This provides a synthetic pathway towards new *RE-d* complexes with interesting redox activity (Figure 1).

Heterometallic *RE-d* complexes of dithiooxalato (dto)²⁻, [Ni^{II}{(dto)RE^{III}Tp₂}₂] (RE = Y (**1**), Gd (**2**); Tp = hydrotris-(pyrazol-1-yl)borate) were synthesised in high yields via precipitation from a one-pot reaction, under aqueous conditions at room temperature. Compounds **1** and **2** exhibited quasi-reversible one electron redox chemistry and were chemically reduced by cobaltocene (CoCp₂) yielding [CoCp₂]⁺[Ni^{II}{(dto)RE^{III}Tp₂}₂]^{•-} (RE = Y (**3**), Gd (**4**)). The reduction of **1** and **2** is shown spectroscopically to be ligand-based. Compounds **3** and **4** are the first reported examples of molecular and electronic structure characterisation of the dithiooxalato ligand radical (dto)^{3•-}.

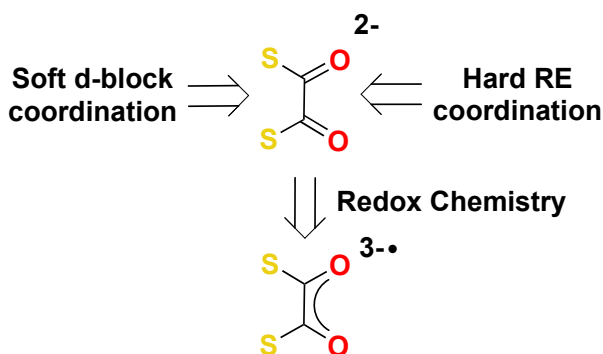


Figure 1: Synthetic template for *RE-d* complexes based on dto²⁻ ligand system

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