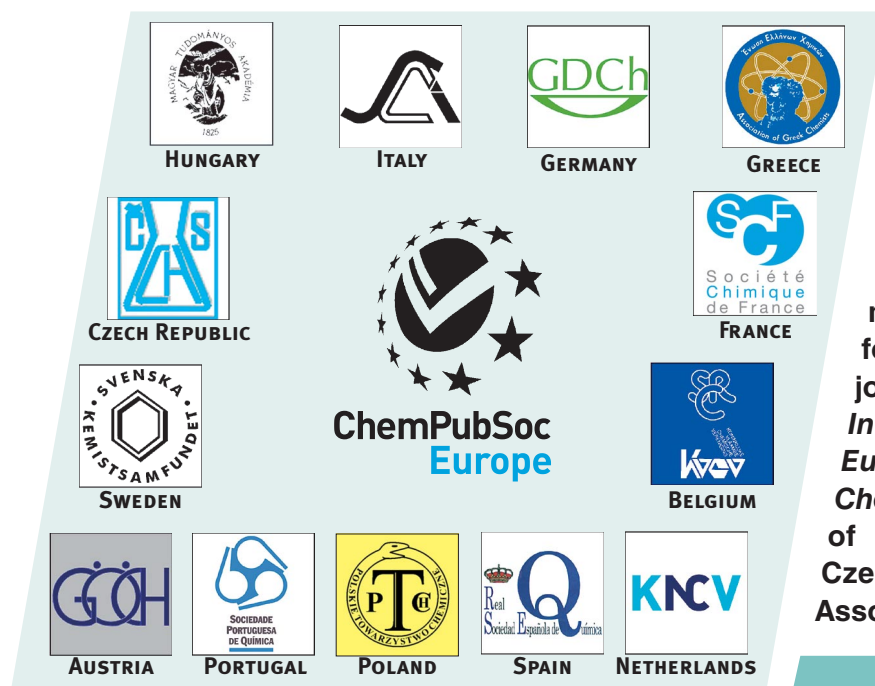


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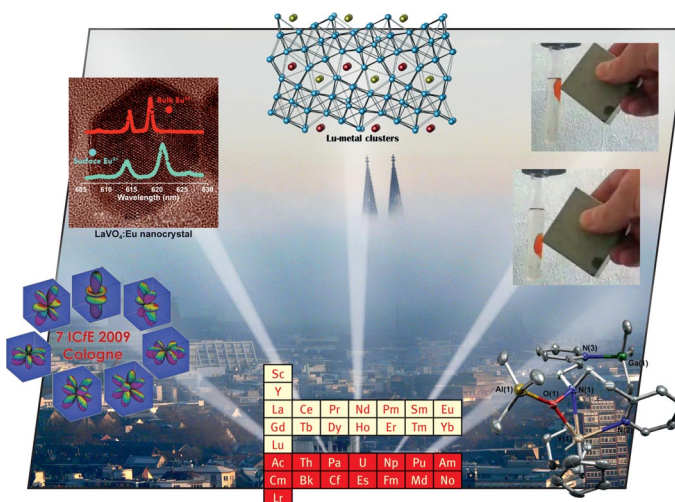


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Other ChemPubSoc Europe journals are *Chemistry – A European Journal*, *ChemBioChem*, *ChemPhysChem*, *ChemMedChem*, *ChemSusChem* and *ChemCatChem*.

## COVER PICTURE

The cover picture highlights a few of the fine collection of articles assembled in this Cluster Issue on f elements, based on presentations at the 7th International Conference on f Elements held in Cologne (23–27 August 2009). The individual graphics making up the composite design are set against a background depicting Cologne, with the Cathedral only just visible in the mist. Just as the sun clears the mist to reveal a beautiful view, our deepened understanding of f-element chemistry opens up new avenues in the chemistry landscape. The diversity of the f elements is reflected in the contributions shown on the cover. The solid-state chemistry of Lu–Bi–Te clusters is highlighted by J. D. Corbett et al. (p. 2620ff), and the importance of ionic liquids in f-element chemistry, as illustrated by the response of the lanthanide ionic liquid to an externally applied magnetic field, is reviewed by A.-V. Mudring et al. (p. 2569ff). The binding mode in rare-earth metal complexes with donor-functionalised hydroxylamino ligands is featured by N. W. Mitzel et al. (p. 2774ff), and the luminescence behaviour of  $\text{LaVO}_4\text{:Eu}$  nanocrystals is revealed by C.-H. Yan et al. (p. 2626ff). A hearty thanks to the authors for their valuable contributions to the cover.



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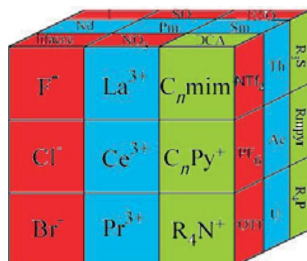
## MICROREVIEWS

### Ionic Liquids

A.-V. Mudring,\*  
S. Tang ..... 2569–2581

Ionic Liquids for Lanthanide and Actinide Chemistry

**Keywords:** Actinides / Homogeneous catalysis / Ionic liquids / Lanthanides / Luminescence



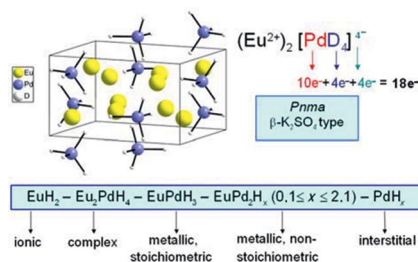
The widely tuneable class of ionic liquids has become important for lanthanide and actinide coordination chemistry, f-element spectroscopy, f-element electrochemistry and electrodeposition, organic synthesis and catalysis as well as inorganic nanomaterial synthesis.

### Solid-State Hydrides

H. Kohlmann\* ..... 2582–2593

Solid-State Structures and Properties of Europium and Samarium Hydrides

**Keywords:** Europium / Samarium / Hydrides / Neutron diffraction / X-ray diffraction



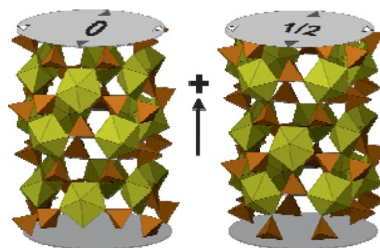
A survey on the available crystal structural data shows that europium and samarium hydrides exhibit rich crystal chemistry, ranging from ionic to complex and interstitial type compounds. While europium is always divalent, samarium is also found to be trivalent in its hydrides. Practical solutions are given to perform neutron diffraction with highly absorbing samples, such as <sup>nat</sup>Eu and <sup>nat</sup>Sm.

### Modeling Actinide Compounds

S. V. Krivovichev\* ..... 2594–2603

Actinyl Compounds with Hexavalent Elements (S, Cr, Se, Mo) – Structural Diversity, Nanoscale Chemistry, and Cellular Automata Modeling

**Keywords:** Actinides / Uranium / Crystal structure / Nanotubes / Cellular automata



Basic features of the structural chemistry of actinyl compounds with TO<sub>4</sub> tetrahedral oxyanions (T = S, Cr, Se, and Mo) are outlined with particular attention to structural topologies, nanoscale units, and algorithmic generation of structures by using cellular automata.

## SHORT COMMUNICATIONS

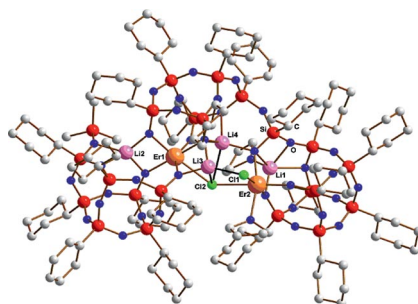
### Erbium Silsesquioxane Clusters

V. Lorenz, S. Blaurock, C. G. Hrib,  
F. T. Edelmann\* ..... 2605–2608



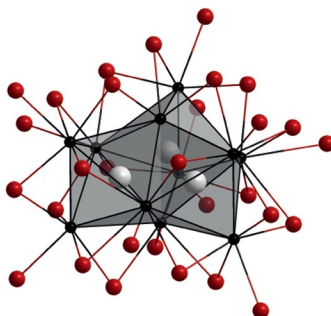
Coupling of Silsesquioxane Cages in the Coordination Sphere of Erbium

**Keywords:** Lanthanides / Silsesquioxanes / Metallasilsesquioxanes / Erbium / Cluster compounds



Reaction of in situ prepared (*c*-C<sub>6</sub>H<sub>11</sub>)<sub>7</sub>-Si<sub>7</sub>O<sub>9</sub>(OLi)<sub>3</sub> with ErCl<sub>3</sub> in thf solution afforded the large heterometallic (Er/Li) metallasilsesquioxane cluster (*c*-C<sub>6</sub>H<sub>11</sub>)<sub>21</sub>-Si<sub>21</sub>O<sub>36</sub>-(SiMe<sub>3</sub>)Er<sub>2</sub>(thf)<sub>2</sub>Li<sub>4</sub>Cl<sub>2</sub> in good yield (65%). An X-ray structure determination of it revealed several unusual features, including the coupling of two silsesquioxane cages through an –O<sub>3</sub>Si(*c*-C<sub>6</sub>H<sub>11</sub>)– unit as well as trimethylsilylation of an Si–OH functionality.

The trimeric cluster  $\{\text{Ir}_3\text{Gd}_{11}\}$  with a structure analogous to that of the cesium suboxide  $\{\text{O}_3\text{Cs}_{11}\}$  (face-sharing octahedra) was observed as embedded in the cluster complex  $\{\text{Ir}_3\text{Gd}_{11}\}\text{Br}_{30}$ . These are connected according to the formulation  $\{\text{Ir}_3\text{Gd}_{11}\}\text{Br}^{i-i}_{12/2}\text{Br}^{i-a}_{9/2}\text{Br}^{a-i}_{9/2}$ .



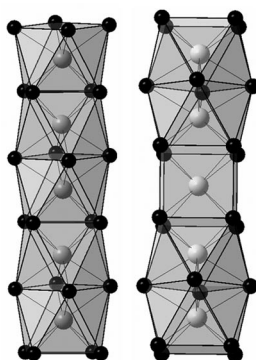
M. Brühmann, G. Meyer\* ..... 2609–2611

A Topological Link between Lanthanide and Alkali-Metal Clusters: Face-Sharing Gadolinium Octahedra Centered by Endohedral Iridium Atoms in  $\{\text{Ir}_3\text{Gd}_{11}\}\text{Br}_{15}$

**Keywords:** Bromides / Cluster compounds / Gadolinium / Iridium / Rare earths

## FULL PAPERS

Eight-coordinate endohedral atoms of sixth-period elements ( $Z = \text{Re}, \text{Os}, \text{Ir}$ ) are present in the extended cluster complexes  $\{\text{ReGd}_4\}\text{Br}_4$ ,  $\{\text{OsSc}_4\}\text{Cl}_4$ ,  $\{\text{Ir}_3\text{Sc}_{12}\}\text{Br}_{16}$ , and  $\{\text{Os}_3\text{Sc}_{12}\}\text{Br}_{16}\text{Sc}$  with different  $\{\text{ZR}_{4/2}\}$  chains for the two formula types. Chemical bonding is dominated by endohedral atom–cluster atom ( $Z\text{--R}$ ) and cluster atom–halide ( $\text{R--X}$ ) interactions.



### Cluster Halides

S. Zimmermann, M. Brühmann, F. Casper, O. Heyer, T. Lorenz, C. Felser, A.-V. Mudring,\* G. Meyer\* ... 2613–2619

Eight-Coordinate Endohedral Rhenium, Osmium and Iridium Atoms in Rare-Earth Halide Cluster Complexes

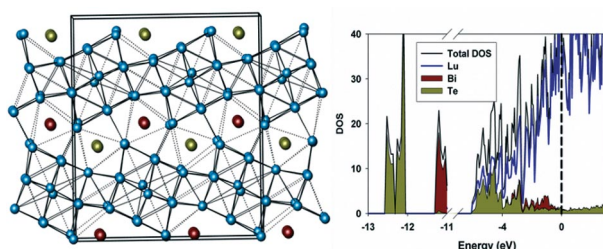
**Keywords:** Cluster compounds / Crystal structures / Electronic structure / Endohedral atoms

### Condensed Clusters

S. Gupta, P. A. Maggard, J. D. Corbett\* ..... 2620–2625

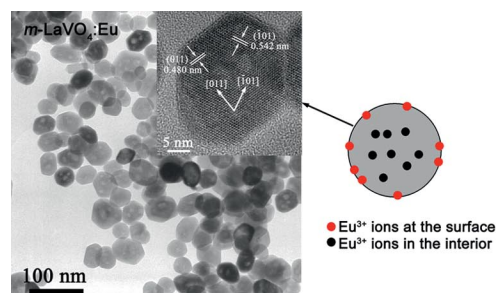
A Bismuth-Stabilized Metal-Rich Telluride  $\text{Lu}_9\text{Bi}_{\approx 1.0}\text{Te}_{\approx 1.0}$  – Synthesis and Characterization

**Keywords:** Rare earths / Cluster compounds / Tellurium / Solid state chemistry / Hamilton populations

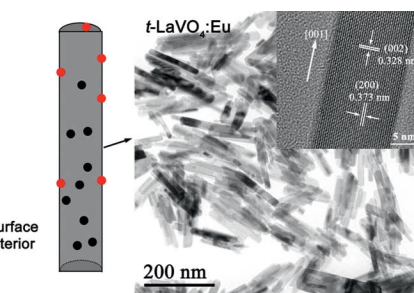


Incorporation of bismuth into a lutetium-rich telluride system produces the new ternary phase  $\text{Lu}_9\text{Bi}_{\approx 1}\text{Te}_{\approx 1}$  with the orthorhombic  $\text{Sc}_9\text{Te}_2$  structure. Partial oxidation

of the Lu component is evident from the significant number of empty Lu 5d states above the Fermi level (dashed line).



Pure monoclinic (m) and tetragonal (t)  $\text{LaVO}_4\text{:Eu}$  nanocrystals were prepared by the facile hydrothermal method assisted with citric and EDTA anions, respectively.



Relative to  $\text{m-LaVO}_4\text{:Eu}$ ,  $\text{t-LaVO}_4\text{:Eu}$  nanocrystals are promising phosphors with high quantum yields and low cost.

### Doped Ln Vanadate Nanocrystals

C.-J. Jia, L.-D. Sun,\* Z.-G. Yan, Y.-C. Pang, S.-Z. Lü, C.-H. Yan\* ..... 2626–2635

Monazite and Zircon Type  $\text{LaVO}_4\text{:Eu}$  Nanocrystals – Synthesis, Luminescent Properties, and Spectroscopic Identification of the  $\text{Eu}^{3+}$  Sites

**Keywords:** Rare earths / Nanocrystals / Vanadates / Europium / Doping / Luminescence



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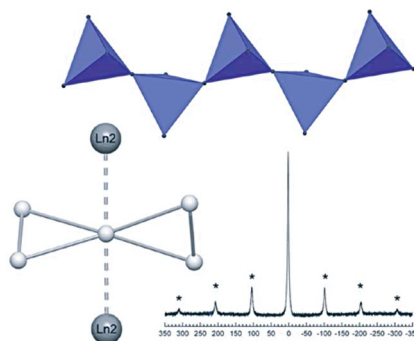
## Lithium Nitridosilicates

S. Lupart, M. Zeuner, S. Pagano,  
W. Schnick\* ..... 2636–2641



Chain-Type Lithium Rare-Earth Nitrido-  
silicates –  $\text{Li}_5\text{Ln}_5\text{Si}_4\text{N}_{12}$  with  $\text{Ln} = \text{La}, \text{Ce}$   
[dc0]"

**Keywords:** Solid-state structures / Lithium /  
Nitridosilicates / Silicon



Two new quaternary lithium rare earth nitridosilicates  $\text{Li}_5\text{Ln}_5\text{Si}_4\text{N}_{12}$  ( $\text{Ln} = \text{La}, \text{Ce}$ ) with nonbranched  $\text{SiN}_4$  zweier single-chains have been characterized. The method of using lithium melts in closed systems at moderate temperatures has been extended to the synthesis of rare earth element containing compounds. The  $^7\text{Li}$  solid-state NMR spectrum of  $\text{Li}_5\text{La}_5\text{Si}_4\text{N}_{12}$  is reported.

## Non-Centrosymmetric Crystals

L. Bohatý, R. Fröhlich, P. Held,  
P. Becker\* ..... 2642–2648

Non-Centrosymmetric Ammonium Rare  
Earth Nitrates  $(\text{NH}_4)_2\text{Ln}(\text{NO}_3)_5 \cdot 4\text{H}_2\text{O}$  –  
Crystal Structure, Crystal Growth and Op-  
tical Properties

**Keywords:** Crystal growth / Refractive indi-  
ces / SHG phase matching / Structure eluci-  
dation / Rare earths



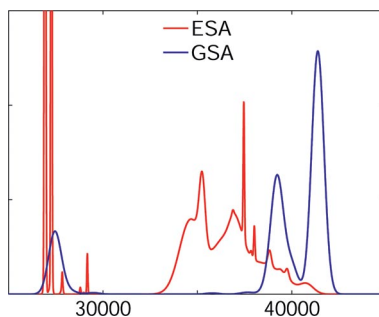
Crystals of  $(\text{NH}_4)_2\text{Ln}(\text{NO}_3)_5 \cdot 4\text{H}_2\text{O}$  ( $\text{Ln} = \text{La}, \text{Ce}$ ) are piezoelectric and pyroelectric and therefore non-centrosymmetric and polar. Crystals with  $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$  are isomorphic and belong to the space group  $Cc$ . Large single crystals of the La and the Ce compounds were grown. Their refractive indices and dispersion allow the realization of phase-matching conditions for second harmonic generation.

## High-Energy Lanthanide States

M. F. Reid,\* L. Hu, S. Frank, C.-K. Duan,  
S. Xia, M. Yin ..... 2649–2654

Spectroscopy of High-Energy States of  
Lanthanide Ions

**Keywords:** Lanthanides / Rare earths /  
Crystal field / Ab initio calculations / UV/  
Vis spectroscopy / Laser spectroscopy



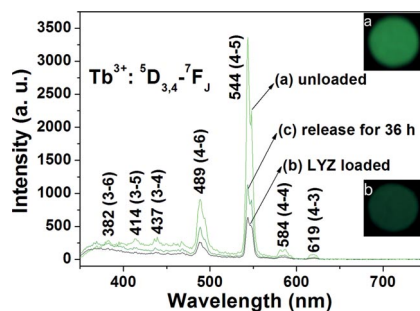
High-energy states of lanthanide ions in crystals may be analyzed by a combination of quantum-chemical calculations and phenomenological crystal-field models. We show that sharp lines may be obtained in excited-state absorption (ESA) spectra, and hence more information about the excited states could be obtained by using ESA than broad-band ground-state absorption (GSA) spectra.

## Luminescent Composites

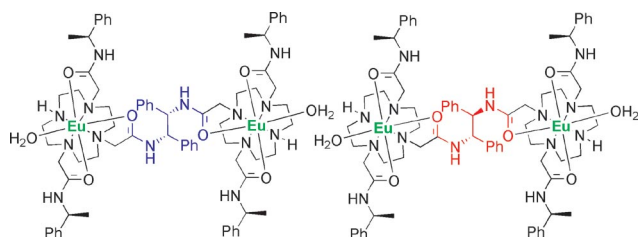
S. Huang, C. Li, P. Yang, C. Zhang,  
Z. Cheng, Y. Fan, J. Lin\* ..... 2655–2662

Luminescent  $\text{CaWO}_4\text{:Tb}^{3+}$ -Loaded Meso-  
porous Silica Composites for the Immo-  
bilization and Release of Lysozyme

**Keywords:** Immobilization / Luminescence /  
Mesoporous materials / Lanthanides / Bio-  
inorganic chemistry



Luminescent  $\text{CaWO}_4\text{:Tb}^{3+}$ -loaded meso-  
porous silica composites with various mor-  
phologies were synthesized to serve as sup-  
ports for lysozyme immobilization and re-  
lease. These composites show specific lyso-  
zyme adsorption capacities at different  
solution pH values. The release of the en-  
zyme can be tracked by the change in the  
photoluminescence of  $\text{Tb}^{3+}$  in  $\text{CaWO}_4\text{:Tb}^{3+}$ @rod-like SBA-15.



Complexes of  $\text{Ln}^{\text{III}}$  ( $\text{Ln} = \text{Eu}, \text{Tb}, \text{Yb}$ ) with diastereomeric ditopic ligands reveal differing anion binding profiles; circularly

polarised luminescence studies of Eu systems show significant differences in the local helicity at the metal centre.

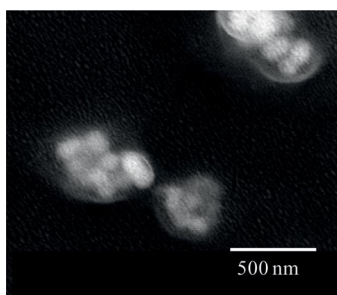
**B. S. Murray, D. Parker,\***  
**C. M. G. dos Santos,**  
**R. D. Peacock** ..... 2663–2672

Synthesis, Chirality and Complexation Phenomena of Two Diastereoisomeric Dinuclear Lanthanide(III) Complexes

**Keywords:** Lanthanides / Europium / Luminescence / Chirality

## NIR Bioimaging

Liposome-encapsulated, Er-doped  $\text{Y}_2\text{O}_3$  nanoparticles were developed as near-infrared (NIR) bioimaging probes. The characteristics of the liposomes with surface modification and their distribution after injection into the body of a mouse are reported with microscopic and macroscopic NIR fluorescence images.



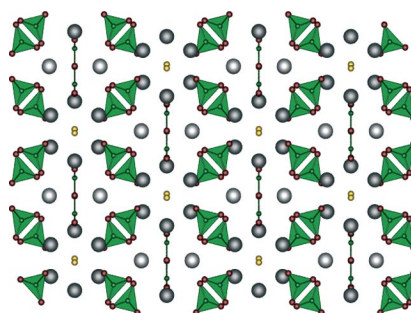
**K. Soga, K. Tokuzen, K. Tsuji, T. Yamano, H. Hyodo, H. Kishimoto** ..... 2673–2677

NIR Bioimaging: Development of Liposome-Encapsulated, Rare-Earth-Doped  $\text{Y}_2\text{O}_3$  Nanoparticles as Fluorescent Probes

**Keywords:** Bioimaging / Rare earths / Liposomes / Ceramics / Fluorescent probes / Nanoparticles

## Europium(II) Borate Fluoride

$\text{Eu}_5(\text{BO}_3)_3\text{F}$ , structurally similar to fluorapatite, is the first europium(II) borate fluoride and exhibits an ordered distribution of the O and F atoms.



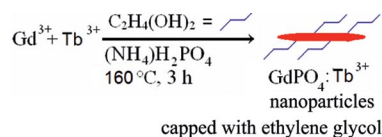
**K. Kazmierczak, H. A. Höppe\*** ..... 2678–2681

Synthesis, Crystal Structure and Optical Spectra of Europium Borate Fluoride  $\text{Eu}_5(\text{BO}_3)_3\text{F}$

**Keywords:** Structure elucidation / Europium / Borates / Fluorides / Optical spectroscopy

## Phosphor Nanoparticles

Nanoparticles of  $\text{Tb}^{3+}$ -doped  $\text{GdPO}_4$  have been prepared at a low temperature and show green luminescence. There is a strong energy transfer from  $\text{Gd}^{3+}$  to  $\text{Tb}^{3+}$ . These nanoparticles are dispersible in polar solvents and can be incorporated in polyvinyl alcohol polymer to make a film.



**N. Yaiphaba, R. S. Ningthoujam,\***  
**N. R. Singh,\* R. K. Vatsa** ..... 2682–2687

Luminescence Properties of Redispersible  $\text{Tb}^{3+}$ -Doped  $\text{GdPO}_4$  Nanoparticles Prepared by an Ethylene Glycol Route

**Keywords:** Lanthanides / Luminescence / Nanoparticles / Dispersion / Polymers

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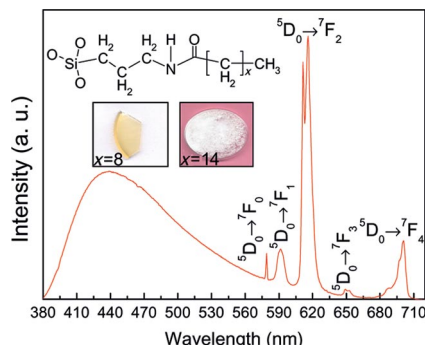
## Eu-Doped Alkyl/Siloxane Hybrids

S. C. Nunes, J. Planelles-Aragó,  
R. A. S. Ferreira, L. D. Carlos,\*  
V. de Zea Bermudez\* ..... 2688–2699



Eu<sup>III</sup>-Doping of Lamellar Bilayer and Amorphous Mono-Amide Cross-Linked Alkyl/Siloxane Hybrids

**Keywords:** Organic–inorganic hybrid composites / Sol–gel processes / Luminescence / Europium



Two structurally different but chemically similar series of mono-amidosil alkyl/siloxane hosts have been doped with a wide range of concentrations of Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>. The influence of the structure of the two mono-amidosils (lamellar bilayer or amorphous matrix) on the photoluminescence features is addressed by using Eu<sup>3+</sup> ions as a local probe.

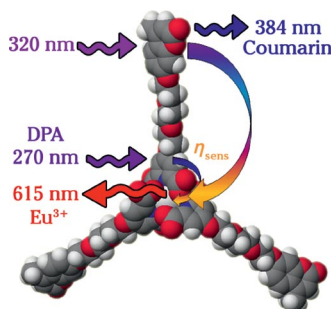
## Double Europium(III) Sensitization

J. Andres, A.-S. Chauvin\* ..... 2700–2713



Europium Complexes of Tris(dipicolinato) Derivatives Coupled to Methylumbelliferone: A Double Sensitization

**Keywords:** N, O ligands / Lanthanides / Luminescence / Europium / Sensitization



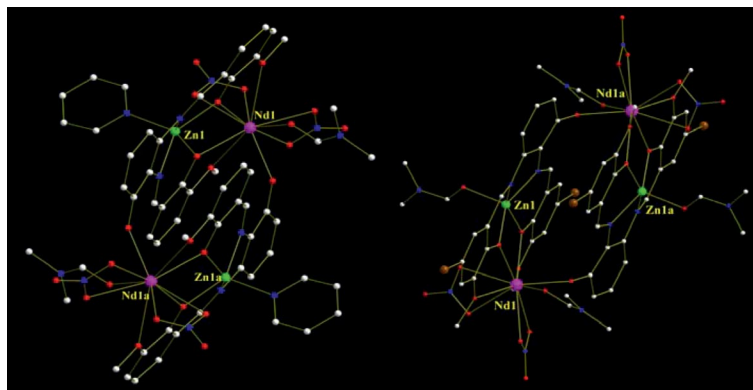
A dipicolinic acid ligand coupled to a polyoxyethylene chain with a coumarin chromophore at its extremity was used to complex Eu<sup>3+</sup>, which affords a stable 1:3 Eu/L complex. The sensitization of the Eu<sup>3+</sup> can occur by an excitation of the dipicolinato part ( $\lambda_{\text{ex}} = 270$  nm) or through the coumarin moiety ( $\lambda_{\text{ex}} = 320$  nm).

## Heterometallic Schiff Base Complexes

X.-Q. Lü,\* W.-X. Feng, Y.-N. Hui,  
T. Wei, J.-R. Song, S.-S. Zhao,  
W.-Y. Wong, W.-K. Wong,\*  
R. A. Jones\* ..... 2714–2722

Near-Infrared Luminescent, Neutral, -Cyclic Zn<sub>2</sub>Ln<sub>2</sub> (Ln = Nd, Yb, and Er) Complexes from Asymmetric Salen-Type Schiff Base Ligands

**Keywords:** Zinc / Schiff bases / Lanthanides / Luminescence / Energy transfer



Upon excitation at 200–550 nm corresponding to the intraligand  $\pi \rightarrow \pi^*$  transitions of the Schiff base, complexes [Zn<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(py)<sub>2</sub>Ln<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>(dmf)<sub>2</sub>·3Et<sub>2</sub>O and [Zn<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>Ln<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>(dmf)<sub>4</sub>] (Ln = Nd, Yb, Er, Gd) emit strong NIR luminescence of the

Ln<sup>3+</sup> ions with lifetimes in ms ranges, whereas the ligand-centered singlet (<sup>1</sup>LC) visible luminescence is mostly quenched by energy transfer from the <sup>1</sup>LC excited state to Ln<sup>3+</sup> ions.

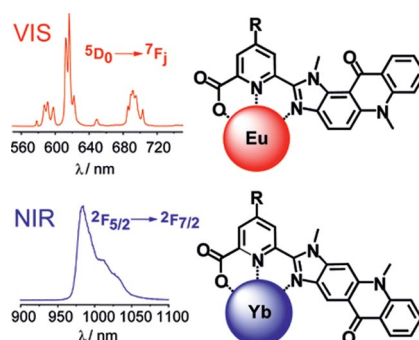
## Lanthanide Luminescence

E. Deiters, F. Gummy,  
J.-C. G. Bünzli\* ..... 2723–2734



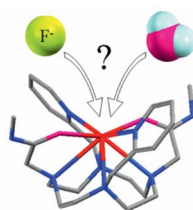
Acridone-Benzimidazole Ring-Fused Ligands: A New Class of Sensitizers of Lanthanide Luminescence via Low-Energy Excitation

**Keywords:** Tridentate ligands / Luminescence / Energy transfer / Lanthanides / Sensitizers / Radiative lifetime / Sensitization efficiency




Two new tridentate ring-fused acridone-benzimidazole ligands have been prepared. They sensitize europium and ytterbium luminescence upon excitation with visible light (410–430 nm).

Positively charged  $\text{Ln}^{\text{III}}$  complexes bind  $\text{F}^-$  anions with a high selectivity over  $\text{Cl}^-$  and  $\text{Br}^-$ . Fluoride binding replaces an inner-sphere water molecule, which results in important changes in the shape and intensity of the emission spectrum of the  $\text{Eu}^{\text{III}}$  complex. Thus, these systems show promise in the field of fluoride sensing.



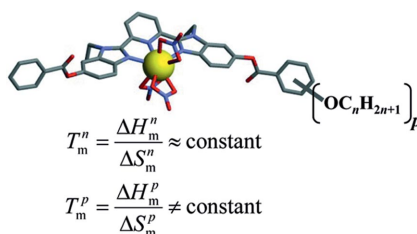
**R. Tripier,\* C. Platas-Iglesias, A. Boos, J.-F. Morfin, L. Charbonnière\*** ..... 2735–2745

Towards Fluoride Sensing with Positively Charged Lanthanide Complexes 


**Keywords:** Lanthanides / Macrocyclic ligands / Luminescence / Anions / Sensors

## Lanthanidomesogens

Enthalpy/entropy compensation occurs for the simple increase ( $n$ ) of the length of the peripheral flexible alkyl chains in lanthanide-containing thermotropic liquid crystals. The connection of an increasing number of divergent chains in polycatenar ligands ( $p$ ) circumvents this limitation and allows some deliberate tuning of the melting temperatures in lanthanidomesogens.



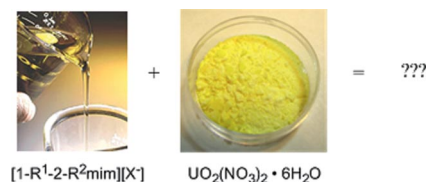
**A. Escande, L. Guénée, E. Terazzi, T. B. Jensen, H. Nozary, C. Piguet\*** ..... 2746–2759

Enthalpy/Entropy Compensation in the Melting of Thermotropic Nitrogen-Containing Chelating Ligands and Their Lanthanide Complexes: Successes and Failures 

**Keywords:** Thermodynamics / Lanthanides / Liquid crystals / Thermotropic behavior / Polycatenar compounds

## Uranyl Salts from Ionic Liquids

Initial studies in the crystallization of uranyl species from ionic liquids or by reaction with ionic liquid precursors led to the isolation of three new imidazolium-based salts of bis- $\mu$ -hydroxo-bis[bis(nitrato- $O,O$ )dioxouranate(VI)] and one of trichlorobis(nitrato- $O,O$ )dioxouranate(VI).



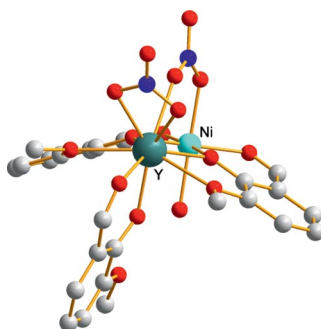
**V. Cocalia, M. Smiglak, S. P. Kelley, J. L. Shamshina, G. Gurau, R. D. Rogers\*** ..... 2760–2767

Crystallization of Uranyl Salts from Dialkylimidazolium Ionic Liquids or Their Precursors

**Keywords:** Actinides / Uranium / Uranyl salts / Ionic liquids

## Magnetic Ni–Ln Complexes

*ortho*-Vanillin can yield two types of heterodinuclear  $\text{Ni}^{\text{II}}\text{--Ln}^{\text{III}}$  complexes that differ by their formulation and structure, depending on the solvent used. A  $D_{\text{Ni}}$  zero field splitting (zfs) term is active in these complexes. The departure from planarity of the equatorial *ortho*-vanillin ligands is responsible for the slight decrease in the ferromagnetic  $\text{Ni--Gd}$  interaction.



**J.-P. Costes,\* L. Vendier** ..... 2768–2773

Structural and Magnetic Studies of New  $\text{Ni}^{\text{II}}\text{--Ln}^{\text{III}}$  Complexes 

**Keywords:** Coordination Chemistry / Nickel / Lanthanides / Structure elucidation / Magnetic properties



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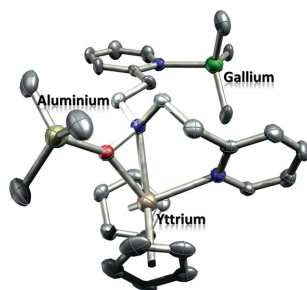
## RE Metal Complex Adducts

B. J. Hellmann, A. Mix,  
B. Neumann, H.-G. Stammer,  
N. W. Mitzel\* ..... 2774–2786



AlMe<sub>3</sub>, GaMe<sub>3</sub> and InMe<sub>3</sub> Adducts of *N,N*-Bis(2-{pyrid-2-yl}ethyl)hydroxylaminato Rare-Earth Metal Complexes and Their Molecular Dynamics

**Keywords:** Rare earths / Hydroxylamines / Hemilability / N,O-Ligands / Molecular dynamics



Three in one: The *N,N*-bis(2-{pyrid-2-yl}ethyl)hydroxylaminato ligand allows generating heterobi- and -trimetallic complexes by adduct formation of [Cp<sub>2</sub>Ln{η<sup>2</sup>-ON(C<sub>2</sub>H<sub>4</sub>-*o*-Py)<sub>2</sub>}] with AlMe<sub>3</sub>, GaMe<sub>3</sub> and InMe<sub>3</sub>. All complexes exhibit a highly dynamic behaviour in solution.

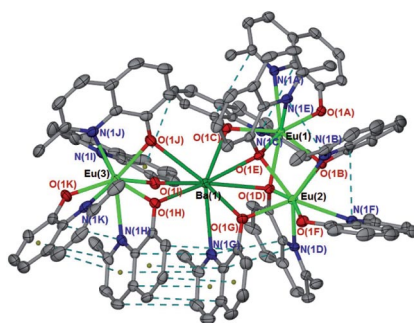
## Pseudo-Solid-State Syntheses

G. B. Deacon, C. M. Forsyth, P. C. Junk,\*  
A. Urbatsch ..... 2787–2797



Syntheses at Elevated Temperature and Structures of Lanthanoid/Alkaline Earth Heterobimetallic Derivatives of 2-Methyl-8-hydroxyquinoline

**Keywords:** Lanthanides / Alkaline earth metals / Structure elucidation / N, O ligands



Rearrangement reactions of Ln(MQ)<sub>3</sub> and AE(MQ)<sub>2</sub> compounds (HMQ = 2-methyl-8-hydroxyquinoline) at elevated temperatures in a 1,2,4,5-tetramethylbenzene (TMB) flux provide a useful route to homoleptic [Ln<sub>2</sub>AE(MQ)<sub>8</sub>] complexes, and the new [Eu<sub>3</sub>Ba(MQ)<sub>11</sub>]·2TMB and [Ln<sub>3</sub>(MQ)<sub>7</sub>CO<sub>3</sub>] (Ln = Eu, Er) complexes have also been obtained by this route.

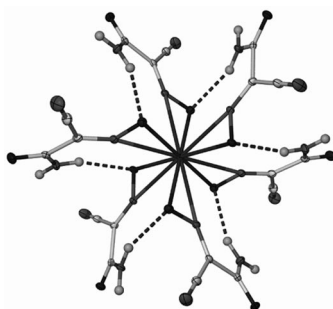
## Rare-Earth Nitroso Complexes

A. S. R. Chesman, D. R. Turner,  
G. B. Deacon, S. R. Batten\* .... 2798–2812



New Approaches to 12-Coordination: Structural Consequences of Steric Stress, Lanthanoid Contraction and Hydrogen Bonding

**Keywords:** Lanthanides / Lanthanide contraction / Nitroso ligand / Hydrogen bonds / Steric hindrance



Rare-earth complexes containing nitroso bonding ligands dicyanonitrosomethanide, C(CN)<sub>2</sub>(NO)<sup>−</sup>, and carbamoylcyanonitrosomethanide, C(CONH<sub>2</sub>)(CN)(NO)<sup>−</sup>, demonstrate a variety of coordination modes from symmetrical η<sup>2</sup>(N,O) to monodentate η<sup>1</sup>(O). The effects upon the coordination environment of the lanthanoid contraction. Intramolecular hydrogen bonding and steric influences of co-ligands are discussed.

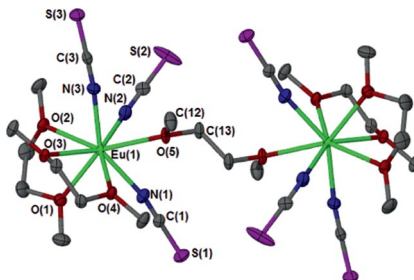
## Synthesis by Redox Transmetalation

J. M. Bakker, G. B. Deacon,\*  
C. M. Forsyth, P. C. Junk,\*  
M. Wiecko ..... 2813–2825



A Structural Investigation of Trivalent and Divalent Rare Earth Thiocyanate Complexes Synthesised by Redox Transmetalation

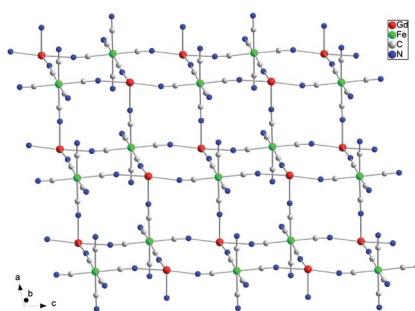
**Keywords:** Rare earths / N ligands / Ether ligands / Redox chemistry / Transmetalation / Solid-state structures



Solvated rare earth thiocyanate complexes synthesised by redox transmetalation between RE metals and Hg(SCN)<sub>2</sub> yield compounds with a wide variety of structural types featuring RE–NCS and/or RE–NCS–RE bonding.



Fourteen cyano-bridged 2D bimetallic 4f–3d arrays with monolayered stair-like, brick-wall-like, or bilayered topologies were rationally prepared by the ball-milling method, and their structures were also characterized. The relationship between the crystal structures and the controllable syntheses was discussed.



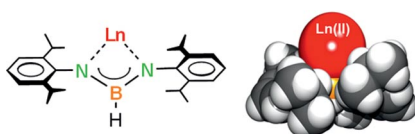
W.-T. Chen, A.-Q. Wu, G.-C. Guo,\*  
 M.-S. Wang, L.-Z. Cai,  
 J.-S. Huang ..... 2826–2835

Cyano-Bridged 2D Bimetallic 4f–3d Arrays with Monolayered Stair-Like, Brick-Wall-Like, or Bilayered Topologies – Rational Syntheses and Crystal Structures

**Keywords:** Lanthanides / N ligands / Synthesis design / Self-assembly / Prussian blue complexes

### Bora-Amidinate Complexes

The first bora-amidinate (*bam*) complexes of the lanthanide metals in the +2 oxidation state could be successfully obtained by reaction of DIPP(H)N–BH–N(H)DIPP with a benzylic lanthanide(II) precursor. The crystal structures show very small N–Ln–N' bite angles (ca. 60°) that leave a large part of the metal coordination sphere available for neutral thf ligands.



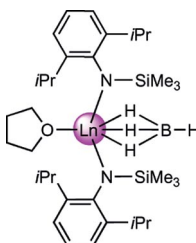
S. Harder,\* D. Naglav ..... 2836–2840

Bora-Amidinate Complexes of Lanthanide(II) Metals

**Keywords:** Lanthanides / Europium / Ytterbium / Samarium

### Controlling ate-Complex Formation

Deliberate choice of the reaction conditions gives access to monomeric alkali metal-free heteroleptic complexes  $Y[N-(SiMe_3)(C_6H_3iPr_2-2,6)]Cl_2(thf)_3$  and  $Ln[N-(SiMe_3)(C_6H_3iPr_2-2,6)]_2(BH_4)(thf)$  ( $Ln = Nd, La$ ; depicted) according to salt metathesis protocols, with solvent effects and type of alkali metal amide precursor deserving closer attention.

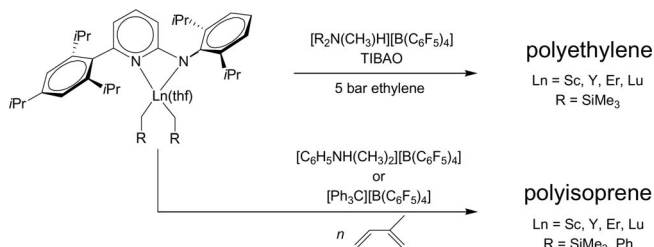


C. Schädle, C. Meermann, K. W. Törnroos,  
 R. Anwender\* ..... 2841–2852

Rare-Earth Metal Phenyl(trimethylsilyl)-amide Complexes

**Keywords:** Rare earths / N ligands / Polymerization

### Ln Polymerization Catalysts



Aminopyridinato ligand-stabilized alkyl-lanthanoid complexes were synthesized and structurally characterized. These complexes are, after activation, active catalysts for the polymerization of ethylene and isoprene.

The obtained polyisoprenes have an increased 3,4-content, which decreases with increasing metal ion radius. An ethylene polymerisation activity maximum is observed for Er.

C. Döring, W. P. Kretschmer,  
 R. Kempe\* ..... 2853–2860

minopyridinato-Stabilized Lanthanoid Complexes: Synthesis, Structure and Polymerization of Ethylene and Isoprene

**Keywords:** Polymerization / Ethylene / Isoprene / Lanthanoids / Aminopyridinato ligands

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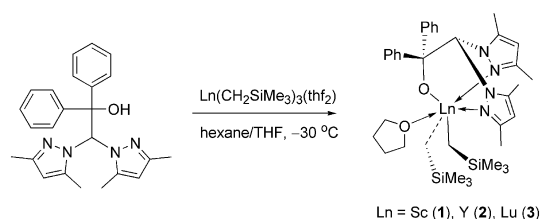
## Rare-Earth Metal Alkyl Complexes

Z. Zhang, D. Cui,\*

A. A. Trifonov ..... 2861–2866

Synthesis and Characterization of Heteroscorpionate Rare-Earth Metal Dialkyl Complexes and Catalysis on MMA Polymerization

**Keywords:** Rare earths / Tridentate ligands / Polymerization



The first heteroscorpionate ligated rare-earth metal dialkyl complexes were prepared via alkane elimination. These complexes were effective catalysts for the poly-

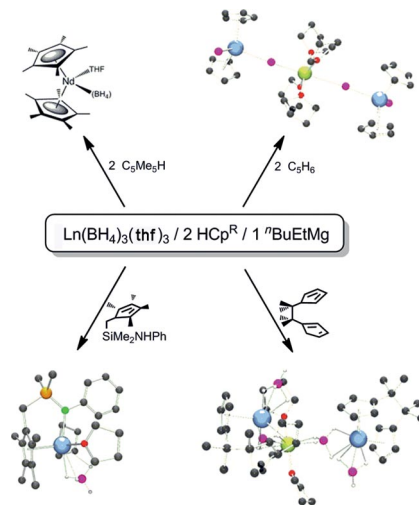
merization of methyl methacrylate to produce syndiotactically enriched poly(methyl methacrylate) with narrow molecular weight distribution.

## Organolanthanide Catalysts

M. Visseaux,\* M. Terrier, A. Mortreux, P. Roussel ..... 2867–2876

Facile Synthesis of Lanthanidocenes by the “Borohydride/Alkyl Route” and Their Application in Isoprene Polymerization

**Keywords:** Lanthanides / Metallocenes / Structure elucidation / Polymerization / Homogeneous catalysis



Borohydrolanthanidocenes were easily prepared by a straightforward synthetic approach, starting from their tris(borohydride)s, a ligand in its protonated form, and the stoichiometric amount of dialkyl-magnesium reagent. These compounds were found to be very efficient in isoprene polymerization. Our approach also enables the rapid screening of a given ligand for polymerization catalysis.

\* Author to whom correspondence should be addressed.

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