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## COVER PICTURE

The cover picture shows the molecular structure of GaCp, a sleeping beauty in organometallic chemistry. An easy synthesis of GaCp, which can be carried out with standard laboratory equipment, opens the way for GaCp to become a useful ligand in organometallic chemistry. Details of the synthesis and first structurally characterized molecular compounds exhibiting GaCp units are discussed in the Short Communication by H. Schnöckel, A. Schnepf et al. on page 3681ff.



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## SHORT COMMUNICATIONS

### Cyclopentadienylgallium

C. Schenk, R. Köppe, H. Schnöckel,\*  
A. Schnepf\* ..... 3681–3685



A Convenient Synthesis of Cyclopentadienylgallium – The Awakening of a Sleeping Beauty in Organometallic Chemistry

**Keywords:** Cyclopentadienyl ligands / Gallium / Subvalent compounds / Main group elements / Synthesis design



An easy synthesis – that can be carried out with standard laboratory equipment – of ( $\eta^5$ -cyclopentadienyl)gallium (GaCp) is presented as the kiss to awake this sleeping beauty in organometallic chemistry.

### Abnormal Carbenes

A. Jana, R. Azhakar, G. Tavčar,  
H. W. Roesky,\* I. Objartel,  
D. Stalke\* ..... 3686–3689

Lithium Complex of an Abnormal Carbene

**Keywords:** Carbenes / Boranes / Lithium



A lithium complex of an abnormal carbene with the composition  $[\text{H}_3\text{BC}\{\{\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\}_2\text{CHLi}(\text{THF})_3\}]$  was synthesized by the lithiation reaction of the N-heterocyclic carbene borane adduct ( $\text{IPr}\cdot\text{BH}_3$ ,  $\text{IPr} = [\text{C}\{\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]\text{-CH}_2\}$ ) with  $n\text{BuLi}$ .

## FULL PAPERS

### Metallophosphazenes

E. W. Ainscough,\* H. R. Allcock,  
A. M. Brodie,\* K. C. Gordon,\*  
M. D. Hindenlang, R. Horvath,  
C. A. Otter ..... 3691–3704

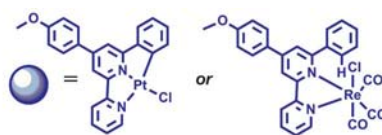


Spectroscopic Studies of Phosphazene Polymers Containing Photoluminescent Metal Complexes

**Keywords:** Phosphazenes / Polymers / Rhenium / Palladium / Platinum



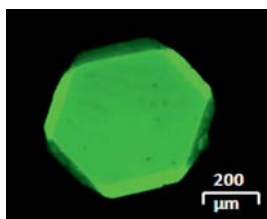
Cyclotriphosphazene ligands substituted with pendant 2,2'-bipyridyl moieties and related polyphosphazenes have been used to synthesise  $\text{Pt}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$  and  $\text{Re}^{\text{I}}$  complexes. Spectroscopic and computational studies



were conducted to compare the small-molecule complexes with the polymers and show that the cyclotriphosphazene complexes are appropriate for modelling the behaviour of polyphosphazenes.

## Luminescent Coordination Polymers

Two families of coordination polymers have been obtained with the respective general chemical formulae  $\{[\text{Ln}_6(\text{aip})_7(\text{H}_2\text{O})_{24}] \cdot 2(\text{aip}) \cdot 6\text{H}_2\text{O}\}_\infty$  in which  $\text{Ln} = \text{Tm}$  or  $\text{Yb}$  (Family 1) and  $\{[\text{Ln}_2(\text{aip})_2(\text{H}_2\text{O})_{10}] \cdot (\text{aip}) \cdot 4\text{H}_2\text{O}\}_\infty$  in which  $\text{Ln} = \text{La} - \text{Er}$  (except  $\text{Pm}$ ) or  $\text{Y}$  (Family 2). The luminescent properties under UV irradiation of compounds belonging to Family 2 have been explored.



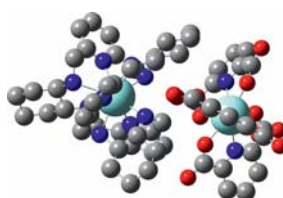
**Y. Luo, G. Calvez, S. Freslon, K. Bernot, C. Daiguebonne,\* O. Guillou** ..... 3705–3716

Lanthanide Aminoisophthalate Coordination Polymers: A Promising System for Tunable Luminescent Properties

**Keywords:** Coordination polymers / Lanthanides / Polymers / Luminescence

## Ion Pairs

Chiral cationic macrocyclic  $\text{Ln}^{\text{III}}$  complexes and anionic tris(dipicolinate)  $\text{Ln}^{\text{III}}$  complexes form hydrogen-bonded ion pairs in solution, indicated by NMR measurements and DFT calculations. In the case of (*M*) diastereomers, the ion-pair formation is accompanied by the Pfeiffer effect and the formation of supramolecular polymers comprising protonated macrocyclic cations and complex anions.



**J. Gregoliński, R. Wieczorek, J. Lisowski\*** ..... 3717–3725

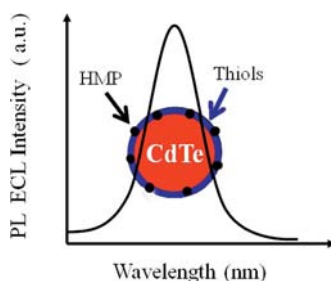
Formation of Chiral Heteronuclear  $\text{Ln}^{\text{III}}$  Assemblies by Ion Pair Formation



**Keywords:** Ion pairs / Lanthanides / Macrocyclic ligands / Supramolecular chemistry / Pfeiffer effect

## Near-Infrared Nanocrystals

The dual-stabilizer-capped CdTe nanocrystals displayed efficient photoluminescence and electrochemiluminescence.



**G.-d. Liang, L.-p. Shen, X.-l. Zhang, G.-z. Zou\*** ..... 3726–3730

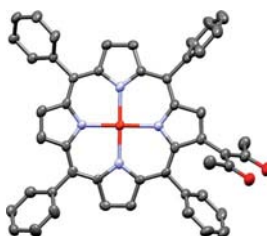
One-Pot Synthesis of Dual-Stabilizer-Capped CdTe Nanocrystals with Efficient Near-Infrared Photoluminescence and Electrochemiluminescence



**Keywords:** Nanocrystals / Cadmium / Tellurium / One-pot synthesis / Near-infrared / Photoluminescence / Electrochemiluminescence

## Porphyrin Dyes

Three porphyrins bearing a 1-acetyl-2-oxopropyl group at a  $\beta$ -pyrrolic position have been synthesized and their structures and photophysical and -voltaic performances in dye-sensitized solar cells have been investigated.



**H. He,\* M. Dubey, Y. Zhong, M. Shrestha, A. G. Sykes** ..... 3731–3738

2-(1-Acetyl-2-oxopropyl)-5,10,15,20-tetraphenylporphyrin and Its Transition-Metal Complexes



**Keywords:** Porphyrinoids / Dyes / Sensitizers / Solar cells / Nanotubes / Transition metals

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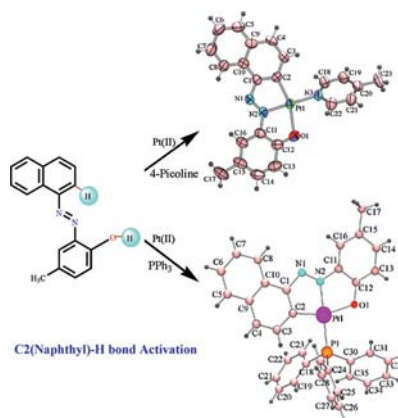
## C–H Activation

A. N. Biswas, P. Das, V. Bagchi,  
A. Choudhury,  
P. Bandyopadhyay\* ..... 3739–3748



Regiospecific C(naphthyl)–H Bond Activation by Platinum(II) – Isolation, Characterization, Reactivity and TD-DFT Study of the Cycloplatinate Complexes

**Keywords:** C–H activation / Cyclometallation / Platinum / Oxidation / Density functional calculations



Regiospecific C(naphthyl)–H bond activation of a group of naphthylazo-2'-hydroxyarenes has been achieved with platinum(II). Oxidative reactions of the divalent cycloplatinate complexes results in the formation of air-stable Pt<sup>IV</sup> complexes; both *cis*- and *trans*-oxidative addition has been realized.

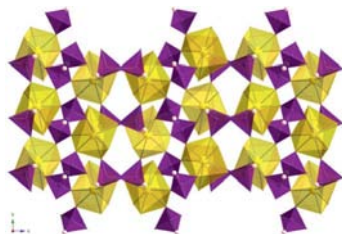
## Actinide Phosphites

E. M. Villa, S. Wang, E. V. Alekseev,\*  
W. Depmeier,  
T. E. Albrecht-Schmitt\* ..... 3749–3754



Facile Routes to Th<sup>IV</sup>, U<sup>IV</sup>, and Np<sup>IV</sup> Phosphites and Phosphates

**Keywords:** Radiochemistry / Actinides / Hydrothermal synthesis / Neptunium / Uranium / Thorium



Reactions of actinides with H<sub>3</sub>PO<sub>3</sub> yield a series of isotopic An<sup>IV</sup> phosphites. An<sup>IV</sup>(HPO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> (An<sup>IV</sup> = Th<sup>IV</sup>, U<sup>IV</sup> or Np<sup>IV</sup>) and Cs[Np<sup>IV</sup>(H<sub>1.5</sub>PO<sub>4</sub>)(PO<sub>4</sub>)<sub>2</sub>] were hydrothermally synthesized and subtle synthetic differences with Np yield either a phosphite or a phosphate structure. The starting pH, phosphite concentration, and solubility appear to control the crystalline products formed.

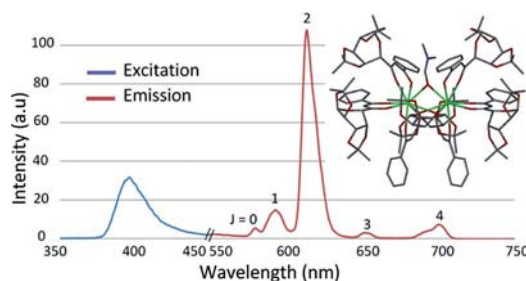
## Chiral Lanthanoid Dimers

W. J. Gee, J. Hierold, J. G. MacLellan,  
P. C. Andrews, D. W. Lupton,  
P. C. Junk\* ..... 3755–3760



Chiral Lanthanoid Dimers Ligated by Carbohydrate-Based Diketonates: Catalytic and Luminescent Properties

**Keywords:** Rare earths / Lanthanoids / Asymmetric catalysis / Luminescence / Enantioselectivity / Lewis acids / Diketonates



The synthesis of a dimeric lanthanoid species ligated by chiral diketonate ligands containing a protected carbohydrate group is reported. The dimers [La (1), Eu (2)] have been characterised by several methods. Additionally, a preliminary investigation regarding the catalytic potential of these chiral species to the thio-Michael reaction has been undertaken. Both 1 and 2 show excellent activity as Lewis acid catalysts, however the transfer of steric information was only observed under poorly yielding reaction conditions.

ral species to the thio-Michael reaction has been undertaken. Both 1 and 2 show excellent activity as Lewis acid catalysts, however the transfer of steric information was only observed under poorly yielding reaction conditions.

## Light-Induced Valence Tautomerism

Y. Teki,\* M. Shirokoshi, S. Kanegawa,  
O. Sato\* ..... 3761–3767



ESR Study of Light-Induced Valence Tautomerism of a Dinuclear Co Complex

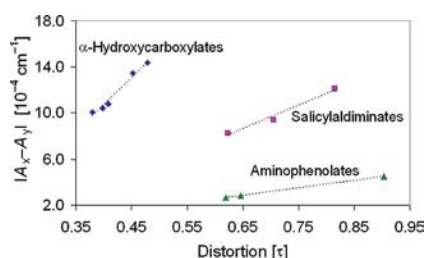
**Keywords:** Light-induced valence tautomerism / ESR / Cobalt / Charge transfer / Glasses



Light-induced valence tautomerism (LIVT) of a dinuclear complex, [{Co(dpqa)}<sub>2</sub>-(dmbq)](PF<sub>6</sub>)<sub>3</sub> (1), was investigated by ESR analysis of dmbq<sup>3-</sup>. LIVT phenomena were observed in the glass matrix as well as in the powder sample. The signal decay and the relaxation, analyzed by double exponential fitting, suggest a two-step mechanism. Quantum tunneling phenomena were clearly observed in the glass matrix.



The effect of trigonal bipyramidal distortion of pentacoordinate  $V^{IV}O^{2+}$  species was calculated by DFT methods. The variation of the structural (bond lengths and angles), electronic (MO composition and electronic structure) and spectroscopic ( $^{51}V$   $A$  and  $g$  tensors,  $\lambda_{max}$ ,  $\nu_{V=O}$ ,  $^{14}N$   $A$  tensor,  $C_Q$  and  $\eta$ ) parameters as a function of the structural index of trigonality,  $\tau$ , is discussed.

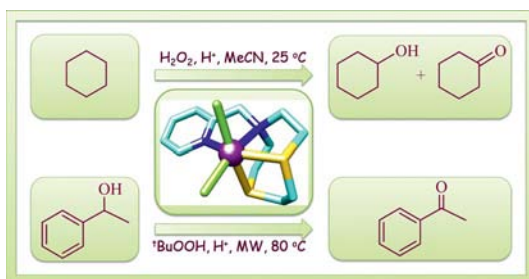


G. Micera, E. Garribba\* ..... 3768–3780

The Effect of Trigonal Bipyramidal Distortion of Pentacoordinate  $V^{IV}O^{2+}$  Species on their Structural, Electronic and Spectroscopic Parameters

**Keywords:** Vanadium / Structure elucidation / EPR spectroscopy / UV/Vis spectroscopy / Vibrational spectroscopy / Density functional calculations

## Azathia Macrocyclic Complexes



New macrocyclic azathia  $N_2S_2$  complexes of  $Fe^{II}$  and  $Cu^{II}$  were prepared and used as

selective catalyst precursors in cyclohexane and 1-phenylethanol oxidations.

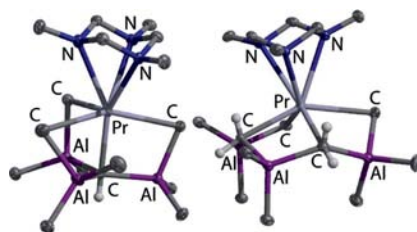
R. R. Fernandes, J. Lasri, A. M. Kirillov, M. F. C. Guedes da Silva, J. A. L. da Silva, J. J. R. Frausto da Silva, A. J. L. Pombeiro\* ..... 3781–3790

New  $Fe^{II}$  and  $Cu^{II}$  Complexes Bearing Azathia Macrocycles – Catalyst Precursors for Mild Peroxidative Oxidation of Cyclohexane and 1-Phenylethanol

**Keywords:** Macrocyclic ligands / Metal complexes / Homogeneous catalysis / Oxidation / Microwave chemistry

## Methylidene/Methyldiyne Complexes

Size does matter: Methylidene and methyldiyne units bound to aluminium and rare-earth metal atoms are formed by the combination of rare earth tetramethylaluminates  $Ln(AlMe_4)_3$  ( $Ln = La, Pr$ ) and 1,3,5-trialkyl-1,3,5-triazacyclohexanes (TRTAC) ( $R = Me, tBu, iPr$ ). Subtle size effects determine the product selectivity.

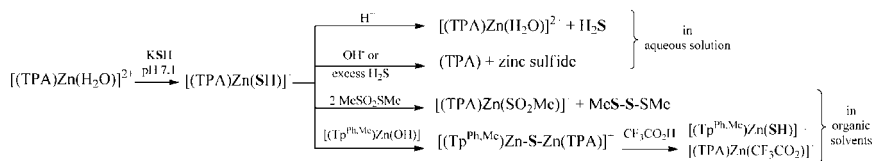


D. Bojer, B. Neumann, H.-G. Stammler, N. W. Mitzel\* ..... 3791–3796

Subtle Size Effects in C–H Activation Reactions of Lanthanum and Praseodymium Tetramethylaluminates by Neutral Trinitrogen Bases

**Keywords:** Triazacyclohexanes / C-H activation / Rare earths / Lanthanum / Praseodymium

## Zinc Complexes



In regard to the growing importance of hydrogen sulfide in biology, the reactivity of the aqua complex  $[(TPA)Zn(H_2O)]^{2+}$  [TPA = tris(2-pyridylmethyl)amine] towards hydrogen sulfide was studied in buffered

aqueous solution by  $^1H$  NMR spectroscopy. The stability and reactivity of the resulting monomeric hydrogensulfido complex  $[(TPA)Zn(SH)]^+$  are discussed.

E. Galardon,\* A. Tomas, P. Roussel, I. Artaud ..... 3797–3801

Synthesis, Stability, and Reactivity of  $[(TPA)Zn(SH)]^+$  in Aqueous and Organic Solutions

**Keywords:** Zinc / Sulfur / N ligands / Hydrogen sulfido ligand

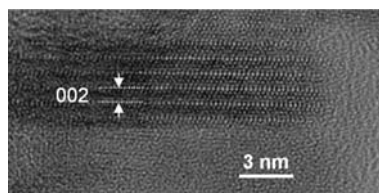
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## Strontium Hexaferrite Nanoparticles

D. Primc,\* M. Drofenik,  
D. Makovec ..... 3802–3809

Low-Temperature Hydrothermal Synthesis  
of Ultrafine Strontium Hexaferrite Nano-  
particles


**Keywords:** Strontium / Iron / Nanopar-  
ticles / Hydrothermal synthesis / Magnetic  
properties



Ultrafine strontium hexaferrite ( $\text{SrFe}_{12}\text{O}_{19}$ ) nanoparticles have been synthesized by the hydrothermal treatment of an appropriate suspension of Sr and Fe hydroxides at temperatures between 130 and 170 °C. The nanoparticles have a disc-like shape, 12 nm wide and 4 nm thick. This thinness is reflected in their unusual XRD patterns and magnetic properties.

\* Author to whom correspondence should be addressed.

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