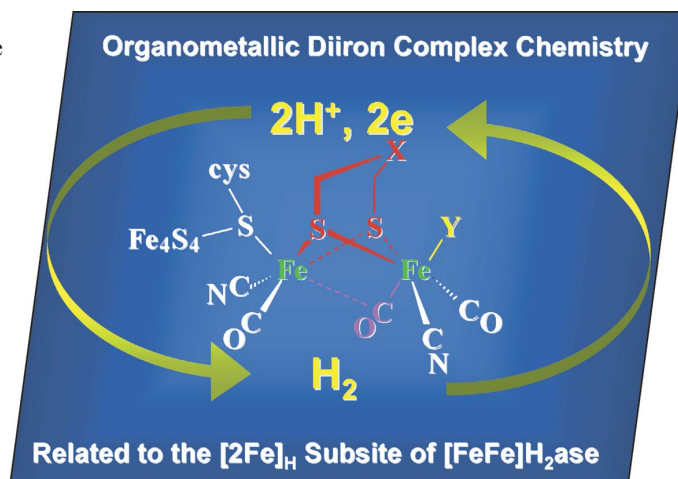


A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

## COVER PICTURE

The cover picture shows a schematic view of the diiron active site of [FeFe] hydrogenases that catalyze the reversible  $\text{H}^+/\text{H}_2$  conversion. Attempts to have a better understanding of the activity of this natural system and to design new organometallic electrocatalysts for the production of  $\text{H}_2$  have allowed new insight into the chemistry of sulfur-rich diiron carbonyls. Details are presented in the Microreview by P. Schollhammer et al. on p. 4671ff.



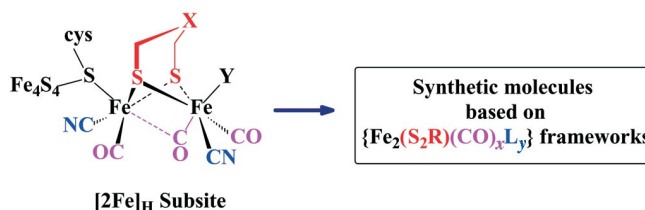
## MICROREVIEW

### Hydrogenase Models

J.-F. Capon, F. Gloaguen,  
F. Y. Pétillon, P. Schollhammer,\*  
J. Talarmin ..... 4671–4681

Organometallic Diiron Complex Chemistry  
Related to the  $[2\text{Fe}]_{\text{H}}$  Subsite of  $[\text{FeFe}]_{\text{H}_2\text{ase}}$

**Keywords:** Dihydrogen / Hydrogenase / Di-iron complexes / Diphosphane / Dithiolate / Hydride / Proton



The design of new molecules inspired by the active site of  $[\text{FeFe}]$  hydrogenases is currently a challenging and exciting field of research whose purpose is to achieve ef-

ficient bio-inspired catalysts for the production or oxidation of hydrogen through a better understanding of the mechanisms implied at the molecular level.

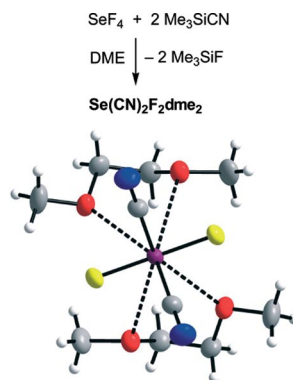
## SHORT COMMUNICATIONS

### Chalcogene Cyanides

S. Fritz, D. Lentz,\*  
M. Szwak ..... 4683–4686

Synthesis and Structure Determination of  
Selenium(IV) Cyanides

**Keywords:** Selenium / Tellurium / Cyanide / Solvation



NMR spectroscopic data and crystal structures of selenium cyanides with selenium in the oxidation state IV are presented and compared with tellurium(IV) cyanides. Quite unexpected the DME solvates of  $\text{Se}(\text{CN})_2\text{F}_2$  and  $\text{Te}(\text{CN})_2\text{F}_2$  crystallize isomorphous. The selenium(II) cyanide DME solvate was obtained as decomposition product and characterized by X-ray diffraction.

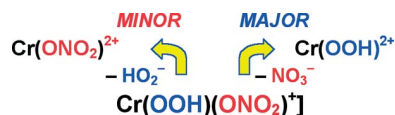
### Metal Hydroperoxides

M. Cheng, W. Song,  
A. Bakac\* ..... 4687–4689



Generation of a Hydroperoxidochromium  
Complex from Nitratochromium(III) Ions  
and Hydrogen Peroxide

**Keywords:** Chromium / Hydroperoxide / Kinetics / Nitrate / Substitution reactions

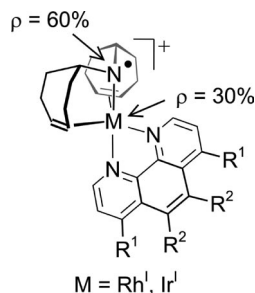


The reaction of a nitrate complex of chromium(III) with millimolar concentrations of hydrogen peroxide in acidic aqueous solutions generates the corresponding hydroperoxido complex in  $>60\%$  yield.

## FULL PAPERS

### Aminyl Radical Complexes

Trigonal bipyramidal bis(olefin) amido 18-electron complexes of  $Rh^I$  or  $Ir^I$  are easily oxidized ( $E_{1/2}^o \approx -0.55$  V vs.  $Fc^+/Fc$ ) to give aminyl radical complexes. High-resolution pulse EPR spectroscopy was used to demonstrate that both the  $Rh^I$  and  $Ir^I$  aminyl complexes have remarkably similar electronic structures (60% of the spin density at the N center, 30% at the metal).



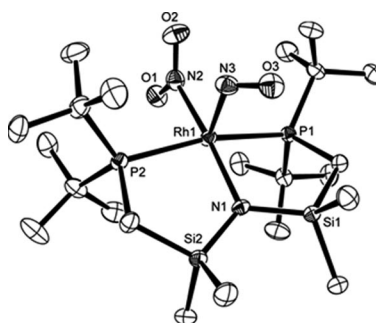
**N. Donati, D. Stein, T. Büttner,  
H. Schönberg, J. Harmer, S. Anadaram,  
H. Grützmacher\*** ..... 4691–4703

Rhodium and Iridium Amino, Amido, and Aminyl Radical Complexes

**Keywords:** Cyclic voltammetry / Iridium / Organometallic compounds / Phosphanes / Reaction mechanisms / Rhodium

### Fate of Radicals

This work establishes the fate of binding one radical (NO) to an even-electron rhodium, and shows the primary product of a 1:1 collision to be a member of the growing class of “half-bent” MNO complexes.



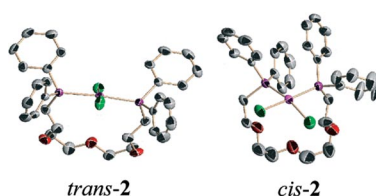
**A. Y. Verat, M. Pink, H. Fan,  
B. C. Fullmer, J. Telser,  
K. G. Caulton\*** ..... 4704–4709

Reactivity of the Radical NO with a Masked Form of 14 Valence Electron (PNP)Rh: Forming Rh(0, I or II)?

**Keywords:** Homogeneous catalysis / Nitrogen oxides / Pincer ligand / Radical reactions / Redox chemistry

### cis–trans Isomerization

An Eyring analysis was carried out on the isomerization of *cis*-[PdCl<sub>2</sub>{Ph<sub>2</sub>P(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>-P,P'}] (*cis*-1). Crystal structures of *cis*-1, *cis*-2, and *trans*-2, supported our conclusions as to the nature of the isomerization mechanism of the two square-planar metallacrown ethers.



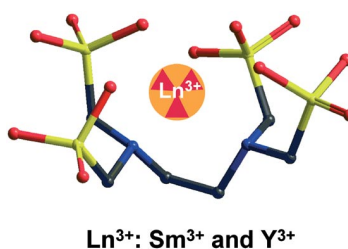
**S. B. Owens Jr., D. C. Smith Jr.,  
C. H. Lake, G. M. Gray\*** ..... 4710–4718

Synthesis, Characterization, and *cis*–*trans* Isomerization Studies of *cis*-[PdCl<sub>2</sub>{Ph<sub>2</sub>P(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>-P,P'}] and *trans*-[PtCl<sub>2</sub>{Ph<sub>2</sub>P(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>-P,P'}] Metallacrown Ethers

**Keywords:** Isomerization / Platinum / Palladium / Crown ethers

### Therapeutic Radiopharmaceuticals

<sup>153</sup>Sm(EDTMP) and <sup>90</sup>Y(EDTMP) are used as bone therapeutic radiopharmaceuticals. The stability and protonation constants of the complexes indicate the presence of the [Sm(HEDTMP)Ca]<sup>2–</sup> species in a simple plasma model. In the pH range 7–9, Sm(EDTMP) and Y(EDTMP) dissociate much faster than the Sm(EDTA) and Y(EDTA) complexes.



**F. K. Kálmán, R. Király,\*  
E. Brücher** ..... 4719–4727

Stability Constants and Dissociation Rates of the EDTMP Complexes of Samarium(III) and Yttrium(III)

**Keywords:** Chelates / Kinetics / Lanthanides / Radiopharmaceuticals / Yttrium

# CONTENTS

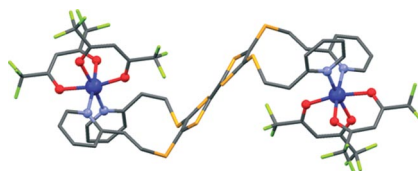
## Bimetallic Cobalt Complexes

S. I. G. Dias, A. I. S. Neves,  
S. Rabaça, I. C. Santos,  
M. Almeida\* ..... 4728–4734



Tetrapyridine and Tetrapyrazine TTF Derivatives: Synthesis, Characterization and Preparation of a Bimetallic Co<sup>II</sup> Complex

**Keywords:** Electron donors / Tetrathiafulvalene / Nitrogen ligands / Cobalt / Magnetic studies



A new series of tetrapyridine- and tetrapyrazine-substituted TTF donors were prepared. The synthesis of a new dinuclear Co<sup>II</sup>-coordination complex with the tetrapyridine TTF donor acting as a bridging ligand demonstrates their potential use in preparing polynuclear complexes and higher hierarchy structures.

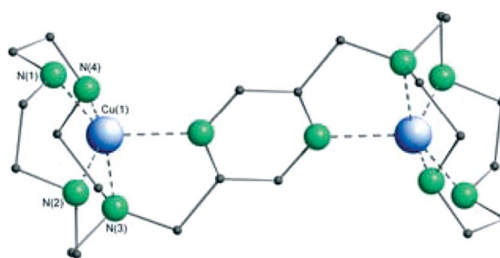
## Intermetallic Interactions

S. El Ghachtouli, C. Cadiou,  
I. Déchamps-Olivier, F. Chuburu,\*  
M. Aplincourt, T. Roisnel, V. Turcry,  
V. Patinec, M. Le Baccon,  
H. Handel ..... 4735–4744



Influence of a Pyrazyl Linker on the Physicochemical Properties of Homodinuclear Bis(cyclen) and Bis(cyclam) Complexes

**Keywords:** Copper / Nickel / Bis(cyclen) ligands / Bis(cyclam) ligands / Electrochemistry



Copper (II) and nickel(II) complexes of bis(cyclen)pyrazine and bis(cyclam)pyrazine have been prepared and character-

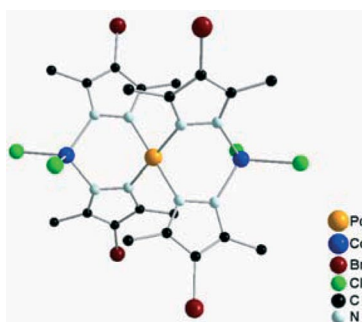
ized. A study of their electronic properties has shown that the two macrocyclic subunits behave independently.

## Linear Pyrazolate Compounds

H. N. Miras, H. Zhao, R. Herchel,  
C. Rinaldi, S. Pérez,  
R. G. Raptis\* ..... 4745–4755

Synthesis and Characterization of Linear Trinuclear Pd, Co, and Pd/Co Pyrazolate Complexes

**Keywords:** Heterometallic compounds / Nitrogen heterocycles / Magnetic properties / Palladium / Cobalt



A new family of dinuclear and linear trinuclear Co/Pd pyrazolate compounds has been characterized and a magnetostructural comparison to the corresponding carboxylate analogues is reported.

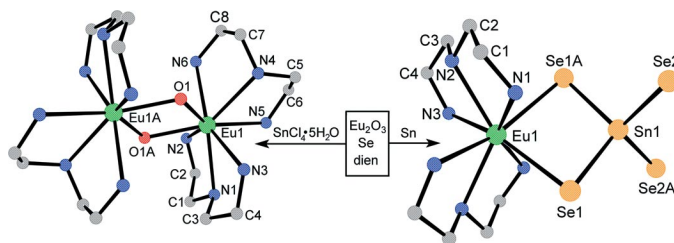
## Lanthanoid Selenidostannates

A.-M. Zhu, Q.-Y. Jin, D.-X. Jia,\*  
J.-S. Gu, Y. Zhang ..... 4756–4761



The First Example of the Tetraselenidostannate Anion [SnSe<sub>4</sub>]<sup>4-</sup> as a Chelating Li-gand to a Lanthanide Complex Ion: Solvothermal Synthesis and Characterization of Lanthanoid Selenidostannates [Hdien]-[Ln(dien)<sub>2</sub>(μ-SnSe<sub>4</sub>)] (Ln = Sm, Eu) and [Eu<sub>2</sub>(dien)<sub>4</sub>(μ-OH)<sub>2</sub>]Sn<sub>2</sub>Se<sub>6</sub>

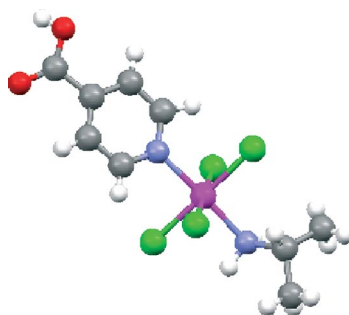
**Keywords:** Selenium / Lanthanides / Tin / Solvothermal synthesis / Crystal structure / Thermal stability



The structures of lanthanoid selenidostannates [Hdien][Ln(dien)<sub>2</sub>(SnSe<sub>4</sub>)] [Ln = Sm (1), Eu (2)] consist of a tetraselenidostannate anion [SnSe<sub>4</sub>]<sup>4-</sup> coordinated to a [Ln(dien)<sub>2</sub>]<sup>3+</sup> fragment as a chelating li-

gand. A water molecule, which leads to the formation of dimeric selenidostannate [Eu<sub>2</sub>(dien)<sub>4</sub>(μ-OH)<sub>2</sub>]Sn<sub>2</sub>Se<sub>6</sub> (3), prevents the [SnSe<sub>4</sub>]<sup>4-</sup> anion from coordinating to the lanthanide center.

New platinum(IV) complexes were synthesized and characterized by single-crystal X-ray diffraction. Their antitumor activity was studied against cell lines that included adenocarcinoma from the human mammary gland (MCF7), human large-cell lung cancer (NCI H460), and central nervous system epithelial cancer (SF268).



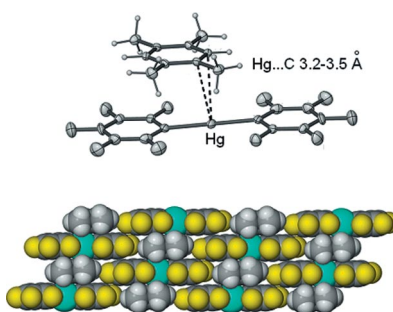
**M. J. Macazaga, J. Rodríguez,**  
**A. G. Quiroga, S. Peregrina, A. Carnero,**  
**C. Navarro-Ranninger,\***  
**R. M. Medina\* ..... 4762–4769**

Platinum(IV) Complexes of 3- and 4-Picolinic Acids Containing Ammine or Isopropylamine Ligands – Synthesis, Characterization, X-ray Structures, and Evaluation of Their Cytotoxic Activity against Cancer Cell Lines

**Keywords:** Platinum(IV) complexes / Platinum / Cytotoxic activity / Picolinic acids / Antitumor agents

### Sandwiched Organomercurials

Mononuclear Lewis acids, HgR<sub>2</sub> (e.g. R = C<sub>6</sub>F<sub>4</sub>-*o*-X, X = H, F, NO<sub>2</sub>) readily form 1:1 or 1:2 adducts, [HgR<sub>2</sub>(arene)] or [HgR<sub>2</sub>-(arene)<sub>2</sub>] with suitable arenes [e.g. 1,2,4,5-tetramethylbenzene, (TMB) or 1,2,4-trimethoxybenzene (TMO)], characterised by long (weak) Hg...C or Hg...O contacts. Crystal packing of these molecules exhibits stabilising supramolecular synthons such as aligned fluoroarene and/or arene rings and weak C–H...X contacts.

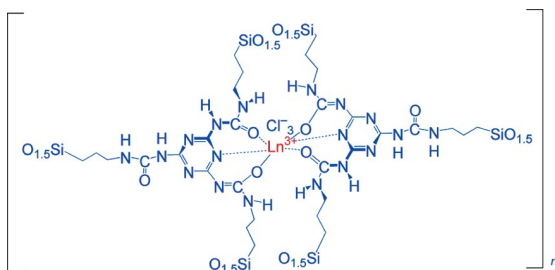


**G. B. Deacon,\* C. M. Forsyth, P. C. Junk,**  
**T. J. Ness, E. Izgorodina, J. Baldamus,**  
**G. Meyer, I. Pantenburg, J. Hitzbleck,**  
**K. Ruhlandt-Senge ..... 4770–4780**

The Supramolecular Architecture of Arene Complexes of Bis(polyfluorophenyl)mercurials

**Keywords:** Supramolecular / Mercury / Arene / Fluorocarbon

### Luminescent Polysilsesquioxanes



Luminescent lanthanide-complex-bridged polysilsesquioxanes were prepared by sol-gel processing of a monomer with a large heterocyclic bridging group. The <sup>5</sup>D<sub>0</sub> quan-

tum efficiency and the number of water molecules coordinated to the Eu<sup>3+</sup> ion were theoretically estimated.

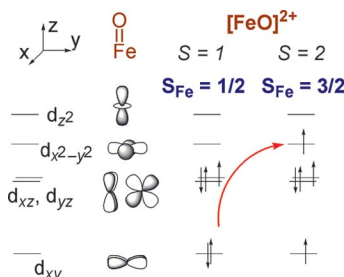
**N. Lin, H. Li,\* Y. Wang, Y. Feng, D. Qin,**  
**Q. Gan, S. Chen ..... 4781–4785**

Luminescent Triazine-Containing Bridged Polysilsesquioxanes Activated by Lanthanide Ions

**Keywords:** Luminescence / Organic–inorganic hybrid composites / Lanthanides / Sol–gel processes / Nitrogen heterocycles

### Spin-Dependent [FeO]<sup>2+</sup> Motifs

The low-energy *S* = 1 and *S* = 2 spin states in [FeO]<sup>2+</sup> can be seen as resulting from an *S*<sub>Fe</sub> = 1/2 → *S*<sub>Fe</sub> = 3/2 transition.



**F. Banse,\* J.-J. Girerd,**  
**V. Robert\* ..... 4786–4791**

Nonheme “Fe<sup>IV</sup>O” Models: Ab Initio Analysis of the Low-Energy Spin State Electronic Structures

**Keywords:** Metalloenzymes / Spin states / Ab initio calculations / Spin crossover / Iron

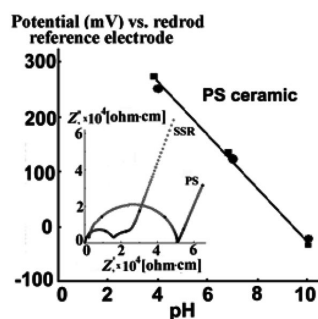
# CONTENTS

## Lithium-Conducting Niobate

A. Belous,\* O. Gavrilenko, O. Pashkova,  
O. Bohnké, C. Bohnké ..... 4792–4796

Structural Peculiarities and Electrophysical Properties of Lithium Ion Conducting Lanthanum Niobate Prepared by Solid-State Reaction and Precipitation from Solution

**Keywords:** Niobate / Solid-state reactions / Conducting materials / Sensors



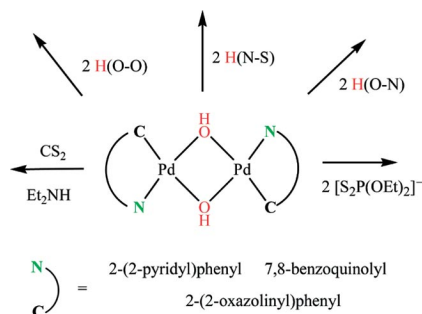
The resistance of grain boundary niobate ceramic is affected by the method of synthesis used. The niobate ceramic obtained by precipitation from solution can be used as a pH sensor with good sensitivity (48 mV/upH) in the pH range from 4 to 10.

## Hydroxo Complexes as Precursors

J. L. Serrano,\* L. García, J. Pérez,  
E. Pérez, J. García, G. Sánchez,  
G. López, M. Liu ..... 4797–4806

Reactivity Towards Acidic Protic Ligands of Cyclopalladated Di- $\mu$ -hydroxo Complexes

**Keywords:** Cyclometalated palladium(II) complexes / Hydroxo complexes / X-ray studies



The advantageous use of three Pd<sup>II</sup> di- $\mu$ -hydroxo complexes as precursors containing a cyclometalated backbone is presented. Strong basic treatments were avoided supporting the unique characteristics of such complexes as starting materials in simple acid–base reactions with protic electrophiles or related ligands.

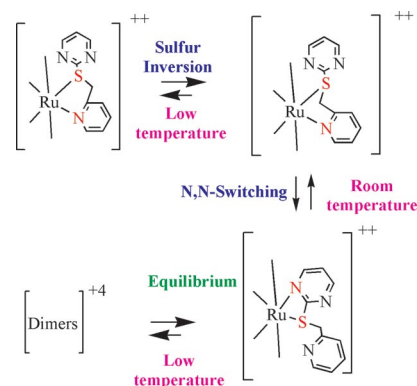
## Temperature-Switchable Ligands

G. Tresoldi,\* S. Lanza, S. Di Pietro,  
D. Drommi ..... 4807–4815



Dynamic Stereochemical Behaviour of Congested Ruthenium(II) Complexes Containing Asymmetric Thioether Ligands Based on Pyridine and Pyrimidine

**Keywords:** Ruthenium / Nitrogen heterocycles / Sulfur / N,S ligands / Bridging ligands



The temperature effect on inversion of the sulfur centre, N,N-switching and dimer–monomer equilibria in the congested octahedral ruthenium(II) complexes [Ru(N,N-L')<sub>2</sub>(L)]<sup>++</sup> [L' = 2-dipyridyl sulfide, 2,2'-bis(4-methylpyridyl) sulfide, 2,2'-bis(5-methylpyridyl) sulfide; L = 2-pyridylmethyl 2'-pyrimidyl sulfide, 2-(4-methylpyrimidyl) 2'-pyridylmethyl sulfide] was studied by <sup>1</sup>H NMR spectroscopy.

## CORRECTION

P. C. Andrews,\* M. Minopoulos,  
E. G. Robertson ..... 4816

Coordination and Reduction of HMPA in the Lithiation of (*S*)-*N*-( $\alpha$ -Methylbenzyl)-allylamine: Crystal Structures of {(*S*)- $\alpha$ -[PhC(H)CH<sub>3</sub>](CH<sub>2</sub>CH=C<sub>2</sub>)NLi·HMPA}<sub>2</sub> and [(Me<sub>2</sub>N)<sub>2</sub>POLi]<sub>6</sub>

**Keywords:** Lithium / Chiral metal amides

\* Author to whom correspondence should be addressed.

Supporting information on the WWW (see article for access details).

If not otherwise indicated in the article, papers in issue 29 were published online on October 6, 2008