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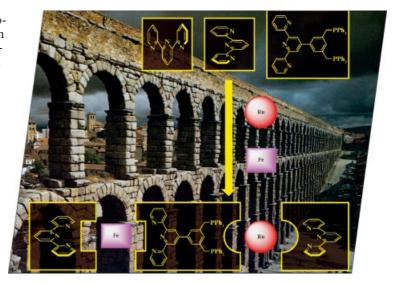


have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic and Sweden) are Associates of the two journals.

The EUChemSoc Societies

## **COVER PICTURE**

The cover picture shows, with the help of a heteroditopic tpy-pincer building block, the preparation of heterodimetallic complexes through the "complex as ligand" approach. Even with such small building blocks the construction of large molecular assemblies will eventually be possible. A beautiful example of small building blocks leading to large constructions is the Aquaduct Segovia, a masterpiece of classical Roman architecture. Details of the synthesis and structures of the heterodimetallic complexes are described in the article by G. van Koten et al. on p. 2111 ff.

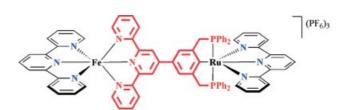


# **FULL PAPERS**

### **Pincer Ligands**

Mono- and Heterodimetallic Fe<sup>II</sup> and Ru<sup>II</sup> Complexes Based on a Novel Heteroditopic 4'-{Bis(phosphanyl)aryl}-2,2':6',2''-terpyridine Ligand

**Keywords:** Ruthenium / Iron / Terpyridine ligands / Pincer ligands / Spectroelectrochemistry



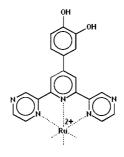
The redox and spectroscopic properties of the mono- and dimetallic complexes of the heteroditopic ligand 4'-{C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-3,5}-2,2':6',2''-terpyridine have been investigated in detail. The degree of electronic

communication between the Ru<sup>II</sup> and Fe<sup>II</sup> centres in the heterodimetallic complex was probed. The electronic interaction between the metal centres appears to be very limited

#### **Photosensitizers**

Catechol-Bearing Dipyrazinylpyridine Complexes of Ruthenium(II)

**Keywords:** Ruthenium / Tridentate ligands / Photosensitizers / Electron transfer / Energy conversion

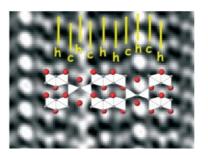


Homoleptic and heteroleptic dipyrazinylpyridine complexes of Ru<sup>II</sup> with one or two peripheral catechol groups were prepared via protected forms. They were characterized by electronic spectra and cyclic voltammetry, then assessed as photosensitizers in homogeneous solutions and in photovoltaic devices.

### **Hexagonal Perovskite Oxides**

Structural Chemistry of a New 10H Hexagonal Perovskite:  $BaMn_{0.4}Fe_{0.6}O_{2.73}$ 

**Keywords:** Hexagonal perovskites / Magnetic properties / Mn polytypes / Highresolution electron microscopy



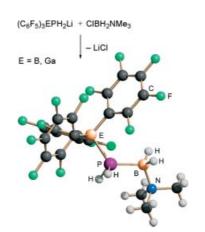
A new 10H polytype has been stabilized in the  $BaMn_{1-x}Fe_xO_{3-y}$  system with the composition  $BaMn_{0.4}Fe_{0.6}O_{2.73}$ . The anionic composition has been established by a reduction and re-oxidation cycle in the stability range of this phase. The structure can be described by the stacking of cubic (c) and hexagonal (h)  $BaO_3$  layers with oxygen-deficient hexagonal (h')  $BaO_{2-y}$  layers according to the sequence (hch'ch)<sub>2</sub>.

#### **Phosphanylboranes**

A. Adolf, M. Zabel, M. Scheer\* ...... 2136-2143

Main Group Lewis Acid/Base-Stabilised Phosphanylboranes

**Keywords:** Boron / Phosphorus / Hydrides / Lewis acids / Lewis bases

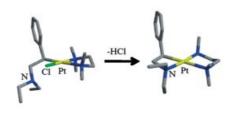


The synthesis of the novel parent compounds of the phosphanylboranes stabilised by Lewis acid/Lewis base is described, where the perfluorinated main group moieties B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and Ga(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, respectively, were used as Lewis acids for the first time. These are stable compounds which do not show any tendency of dehydrocoupling to form polymerisation products.



### **Markovnikov Addition**

A simple but efficient method for synthesizing stable azaplatinacyclobutanes containing platinum(II) is reported together with two crystal structures. The influence of the substituents on the parent complexes on the molar ratios of the anti-Markovnikov/Markovnikov isomers formed is highlighted and interpreted in terms of electronic and steric factors. These reactions can serve as models for metal-catalyzed amination of alkenes.



G. Lorusso, C. R. Barone, N. G. Di Masi, C. Pacifico, L. Maresca,\* G. Natile ....... 2144-2150

Aiding Factors in the Formation of Azaplatinacyclobutane Rings — X-ray and Crystal Structure of [Pt{CH(Ph)CH<sub>2</sub>NEt<sub>2</sub>- $\kappa$ C, $\kappa$ N}(N,N,N',N'-tetramethylethylenediamine)]<sup>+</sup> and of Its Open-Chain Precursor

**Keywords:** Chelates / Metallacycles / N ligands / Nucleophilic addition / Platinum

## **Aromatization of C<sub>5</sub> Rings**

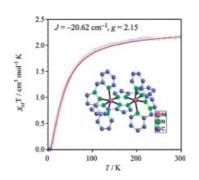
The reaction of  $RuOs_3(\mu-H)_2(CO)_{13}$  with saturated and unsaturated  $C_5$  rings led to the aromatization of the rings to afford the clusters  $RuOs_3(\mu-H)(CO)_9(\mu-CO)_2(\eta^5-C_5R_4R')$ . However, the reaction with cyclopentene gave the cluster  $RuOs_3(\mu-H)_3(CO)_{11}(\mu,\eta^1:\eta^2-C_5H_7)$  via C-H activation of an  $sp^2$  carbon instead. Thermolysis of two of the products led to their isomerization to butterfly clusters.

Y. L. K. Tan, W. K. Leong\* ...... 2151-2160

The Aromatization of  $C_5$  Rings on a Heteronuclear Cluster

**Keywords:** Heterometallic complexes / Ruthenium / Osmium / Carbocyclic rings / Cyclopentadienyl ligands

The dinuclear  $\mathrm{M^{II}}_2$  complexes (M = Ni, Cu) show steroelectronic preference of metal ions. Magnetic measurments reveal the existence of strong antiferromagnetic coupling for both complexes. Coulometric oxidation of the dinickel(II) complex generates mixed-valence  $\mathrm{Ni^{II}}$ - $\mathrm{Ni^{III}}$  species with interesting redox properties.



### **Magnetic Dinuclear Complexes**

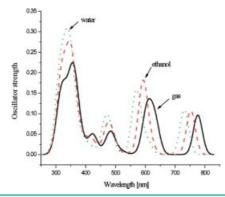
V. Mishra, F. Lloret, R. Mukherjee\* ...... 2161-2170

Bis-µ-pyrazolate-Bridged Dinickel(II) and Dicopper(II) Complexes: An Example of Stereoelectronic Preference of Metal Ions and Stabilization of Mixed-Valence Ni<sup>III</sup>-Ni<sup>II</sup> Species

**Keywords:** Nickel / Copper / Dinuclear complexes / Pyrazolate bridge / Ni<sup>III</sup>-Ni<sup>II</sup> species

**Black Dye** 

Ruthenium(II) "black dye" complexes are investigated by DFT and TD-DFT methods. In the calculated absorption spectra, the first four bands have MLCT/LLCT nature, whereas the fifth band, the one with the strongest intensity, arises from an intraligand tricarboxyterpyridine  $\pi \to \pi^*$  charge transfer (ILCT) with some LLCT character.



Theoretical Studies of the Electronic Structure and Spectroscopic Properties of [Ru(Htcterpy)(NCS)<sub>3</sub>]<sup>3-</sup>

**Keywords:** Black dyes / Electronic structure / Spectroscopic properties / Solvent effects

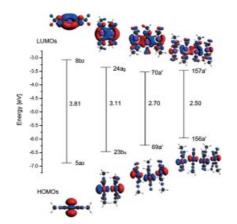
# **CONTENTS**

#### **Weak Transition-Metal Interactions**

X. Zhou, H.-X. Zhang,\* Q.-J. Pan, M.-X. Li, Y. Wang, C.-M. Che ....... 2181–2188

Electronic Structures and Spectroscopic Properties of  $[Pt(CNMe)_2(CN)_2]_n$  (n = 1-4): A Theoretical Exploration of Promising Phosphorescent Materials

**Keywords:** Ab initio calculations / DFT calculations / Luminescence / Excited states / Platinum(II) oligomer

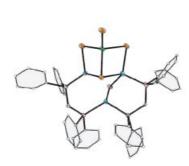


Platinum(II) oligomers were investigated by ab initio and DFT methods. The  ${}^3B_u \rightarrow {}^1A_g$  transition in the dimer corresponds to the experimental higher-energy emission at 530 nm in CH<sub>3</sub>CN solution, while the  ${}^3A' \rightarrow {}^1A'$  transitions in the trimer and tetramer at 557 and 650 nm, respectively, are responsible for the low-energy emission at 584 nm.

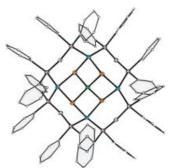
#### **Heterometallic Selenium Clusters**

Syntheses, Structures and Optical Nonlinearities of Heteroselenometallic W-Se-Cu Cluster Compounds Containing Bridging Phosphane Ligands

**Keywords:** Heterometallic complexes / Copper / Selenium / Nonlinear optical properties / Cluster compounds



Two types of heterometallic selenium cluster compounds with bridging phosphane ligands have been synthesized and structu-

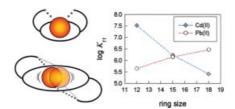


rally characterized and their nonlinear optical properties investigated [W (green, Se (gold), Cu (blue), P (purple), C (grey)].

### **Metal Ion Complementarity**

M. Regueiro-Figueroa, D. Esteban-Gómez,C. Platas-Iglesias, A. de Blas,\*

**Keywords:** Lead / Cadmium / Macrocycles / N,O ligands / Density functional calculations



A detailed structural and stability study of series of  $Cd^{II}$  and  $Pb^{II}$  complexes with N,N'-bis(benzimidazol-2-ylmethyl)-diazacrowns, where the crown ether ring size is systematically varied, shows that increasing the crown size induces a conformational change in the series of  $Cd^{II}$  complexes, whereas no such change was observed for the corresponding  $Pb^{II}$  complexes.

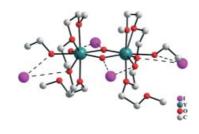
### **Dinuclear Yttrium Complexes**

S. Mishra,\* S. Daniele,\* L. G. Hubert-Pfalzgraf,

E. Jeanneau ...... 2208-2215

Hydrolysis of a (2-Propanol)yttrium Triiodide Complex in the Presence of Glymes: Synthesis and X-ray Structures of Hydroxo-Bridged Dinuclear Yttrium Complexes and Their Applications in Materials Science

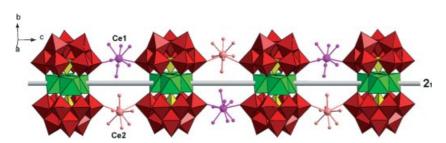
**Keywords:** Yttrium / Iodine / Glymes / Structure / Dinuclear complexes



The reactions of  $Y(iPrOH)_4I_3$  with stoichiometric amounts of water in the presence of di-, tri-, and tetraglyme yield a facile synthetic route to hydroxo-bridged, centrosymmetric dimeric yttrium complexes. The utility of these ionic derivatives as potential sources of yttrium oxide in high  $T_c$  superconductors is also evaluated.



### Polyoxometalates



K<sub>4</sub>Na<sub>2</sub>[{Ce(H<sub>2</sub>O)<sub>7</sub>}<sub>2</sub>Mn<sub>4</sub>Si<sub>2</sub>W<sub>18</sub>O<sub>68</sub>(H<sub>2</sub>O)<sub>2</sub>]· 21.5H<sub>2</sub>O (1) represents the first inorganic aggregate composed of sandwich-type polyanions and lanthanide cation linkers. Complex 1 comprises novel chiral ladder-

like chains based on sandwich-type polyanions and two different lanthanide linkers, which are further connected by K cations into a 3D open framework. An Inorganic Aggregate Based on a Sandwich-Type Polyoxometalate with Lanthanide and Potassium Cations: From 1D Chiral Ladder-Like Chains to a 3D Open Framework

**Keywords:** Polyoxometalates / Sandwich complexes / Lanthanides / Chirality / Open framework

### **Heterocyclic Carbenes**

A chiral imidazolinium salt with two bulky carbohydrate subunits and its corresponding NHC-coordinated Rh complex 5 were synthesized and characterized. A water adduct of the corresponding N-heterocyclic carbene was also isolated.

Synthesis of Chiral Imidazolinium Carbene from a Carbohydrate and Its Rhodium(I) Complex

**Keywords:** Nitrogen heterocycles / Carbenes / Rhodium / Carbohydrates / Chirality

If not otherwise indicated in the article, papers in issue 14 were published online on April 20, 2007