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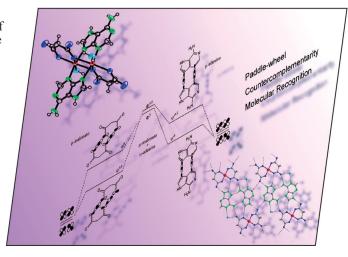




# **COVER PICTURE**

The cover picture shows the paddle-wheel motif adopted by the dinuclear complexes in which the metal centres are held together by bridging malonato and bridging neutral adenine ligands, the countercomplementarity of the bridging ligands responsible for their ferromagnetic behaviour, and the molecular recognition processes that take place between the protonated adeninium cations and the anionic copper-malonato fragments. Details are discussed in the article by O. Castillo, A. Luque et al. on p. 3889ff.

PORTUGAL



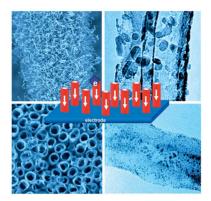
# **MICROREVIEW**

#### Nanoelectrodes

G. Centi,\* S. Perathoner ...... 3851-3878

The Role of Nanostructure in Improving the Performance of Electrodes for Energy Storage and Conversion

**Keywords:** Nanostructures / Electrode design / Hierarchical design / Lithium / Fuel cells / Solar cells



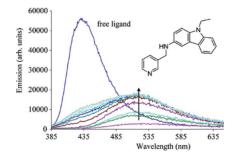
The role of nanoarchitecture of electrodes for applications ranging from energy storage (Li-ion batteries) to energy conversion (fuel cells, solar devices) is analyzed, with reference to metal oxides ( $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ), carbon nanotubes and nanofibres, and their hybrid materials, as well as their use to support noble metal particles.

# **SHORT COMMUNICATIONS**

### **Molecular Logic**

A Simple Fluorescent Ion-Pair Binding Host that Acts as an "If-Then" Logic Gate

**Keywords:** Fluorescence / Molecular logic / Supramolecular chemistry / Molecular devices / Anions / Nitrogen hetero cycles / Carbazole



A fluorescent molecular logic gate is quenched by  $\mathrm{Cu}^{2+}$  but recovers its emission on addition of  $\mathrm{NO_3}^-$  in accordance with the material conditional logic operation.

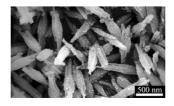
# **Shuttle-Shaped Ceria Nanoparticles**

C. Sun,\* L. Chen ...... 3883-3887



Controllable Synthesis of Shuttle-Shaped Ceria and Its Catalytic Properties for CO Oxidation

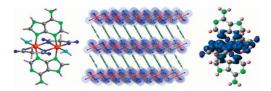
**Keywords:** Nanostructures / Nanoparticles / Solvothermal synthesis / Ceria / Catalytic properties



This paper describes a solvothermal method for the synthesis of shuttle-shaped ceria and its enhanced catalytic activity for CO oxidation reaction.



# **FULL PAPERS**



Metal-malonato frameworks act as receptors of the adenine nucleobase to give the five compounds whose crystal structures and magnetic properties are reported here-

in. DFT calculations have been performed to analyze unusual supramolecular interactions and to evaluate the magnetic behaviour of these compounds.

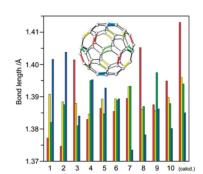
#### Metal-Nucleobase Complexes

Analysis of the Interaction between Adenine Nucleobase and Metal-Malonato Complexes

**Keywords:** Bioinorganic chemistry / Nucleobases / Supramolecular chemistry / Magnetic properties

### **Fullerene Chemistry**

The "break-and-seal" approach was applied to synthesize the new fulleride  $[K(DB24C8)(DME)]_2C_{60}$  DME. The  $C_{60}^{2-}$  anion is disordered assuming two orientations. The distribution of the bond lengths within the fullerene has been discussed with respect to a Jahn–Teller distortion.

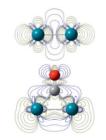


Synthesis and Crystal Structure of a New  ${C_{60}}^2$  Fulleride: [K(DB24C8)-(DME)] $_2$ C $_{60}$ \*DME

**Keywords:** Fullerenes / Fullerides / Crown compounds / Jahn-Teller distortion / X-ray diffraction

#### **Palladium Clusters**

A significant occupation of the 5s orbital explains the existence and cohesion of Pd-Pd bonds, which are described by sd hybrid orbitals and present triplet-state small clusters. The adsorption of a CO ligand goes through a back-bonding interaction favoured by a high 4d and a low 5s population that affects the Pd-Pd bond and restores a singlet ground state for the small clusters.

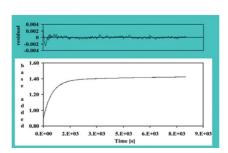


G. Zanti, D. Peeters\* ...... 3904-3911

DFT Study of Small Palladium Clusters  $Pd_n$  and Their Interaction with a CO Ligand (n = 1-9)

**Keywords:** Cluster compounds / Palladium / Carbonyl ligands / Density functional calculations

The  $[Pd(AEP)Cl_2]$  complex was synthesized and characterized [AEP = 2-(2-amino-ethyl)pyridine]. The stoichiometry and stability constants of the complexes formed with various biologically relevant ligands were studied. The kinetics of base hydrolysis of free and coordinated amino acid esters was investigated.



#### **Bio-Relevant Complex Formation**

Equilibrium Studies on Complex-Formation Reactions of  $Pd[(2-(2-aminoethyl)-pyridine)(H_2O)_2]^{2+}$  with Ligands of Biological Significance and Displacement Reactions of DNA Constituents

**Keywords:** Bioinorganic chemistry / Kinetics / Hydrolysis / N,O ligands / N ligands / S ligands / Structure—activity relationships / Palladium complexes

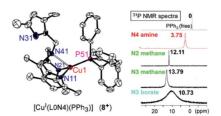
# **CONTENTS**

### **Cu-N4 Complexes**

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Copper Complexes with Neutral N4 Tripodal Ligands: Influence of the Number of Nitrogen Donors on Their Structures, Properties, and Reactivity

**Keywords:** Copper / N ligands / Ligand effects / Coordination modes / Structure elucidation / Electronic structure



Copper(II) chlorido, nitrato, and sulfato complexes of neutral tetradentate nitrogen-containing amine ligands and two related copper(I) complexes are synthesized in order to investigate the influence of the number of nitrogen donors on their structures, properties, and reactivity

### **Pyrazolylborate Copper Complexes**

H. V. R. Dias,\* G. G. Lobbia, G. Papini, M. Pellei, C. Santini\* .............. 3935–3941

Copper(I) Isocyanide and Phosphane Complexes of Fluorinated Mono- and Bis-(pyrazolyl)borates

**Keywords:** Copper / Phosphanes / Scorpionate ligands / Isocyanide ligands / Structure elucidation

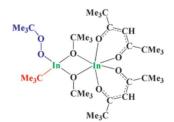
New copper(I) phosphane and isocyanide complexes supported by fluorinated monoand bis(pyrazolyl)borates have been synthesized and structurally characterized.

### **Alkylindium Peroxide**

W. Uhl,\* B. Jana ...... 3942-3947

Bridging and Terminal Arrangement of Alkylperoxo Groups in Organoindium Peroxides

**Keywords:** Indium / Peroxides / Organoelement compounds



Peroxoindium compounds were obtained by insertion of oxygen molecules into the In-C bonds of bis(tert-butyl)indium acetylacetonates. In one case, an oxygen-sensitive In-C bond remained intact despite the close proximity of a terminally arranged tert-butylperoxo group.

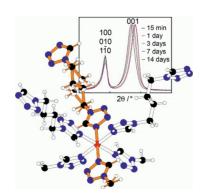
### **Spin-State Interactions**

G. N. L. Jameson,\* F. Werner, M. Bartel, A. Absmeier, M. Reissner, J. A. Kitchen, S. Brooker, A. Caneschi, C. Carbonera, J.-F. Létard, W. Linert\* ....... 3948–3959



Anion, Solvent and Time Dependence of High-Spin-Low-Spin Interactions in a 3D Coordination Polymer

**Keywords:** Spin crossover / Metal-organic frameworks / Anions / Solvent effects

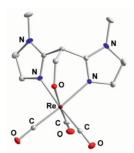


By using a specific spacer length between coordinating iron atoms, it is possible to form coordination polymers with interactions between iron atoms that can be changed subtly through the anion and the solvent.



## Ligand Design

The syntheses of two novel imidazolebased N,N,O and N,N,S ligands 2,2-bis(Nmethylimidazol-2-yl)ethanol (Hbmie) (6) and lithium bis(N-methylimidazol-2-yl)dithioacetate Lisbmidta (7) are described. The coordination properties of the two new ligands are studied by the synthesis of rhenium(I) and ruthenium(II) complexes.



N. V. Fischer, F. W. Heinemann, N. Burzlaff\* ...... 3960-3965

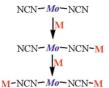
Two New Imidazole-Based Heteroscorpionate Ligands



Keywords: Ligand design / Rhenium / Ruthenium / Nitrogen heterocycles / Tripodal ligands / Heteroscorpionate

### **Cyanamide Metal Adducts**

Heterometallic di- and trinuclear complexes with the bridging cyanoimide NCN<sup>2-</sup> ligand are assembled upon addition of various transition-metal Lewis acids to the ligated cyanoimides in trans- $[Mo(NCN)_2(dppe)_2].$ 

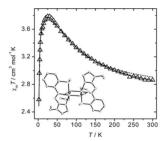


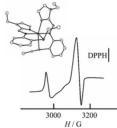
S. M. P. R. M. Cunha, M. F. C. Guedes da Silva,\* J. J. R. Fraústo da Silva. A. J. L. Pombeiro\* ...... 3966-3971

Cyanoimide-Bridged, Bi- and Trinuclear, Heterometallic Complexes with an NCN-Mo-NCN Phosphinic Core

Keywords: Bridging ligands / Molybdenum / Lewis acids / Lewis bases / Heterometallic complexes

### **Nickel Complexes**





1-Alkyl-2-[(o-thioalkyl)phenylazo]imidazole (SRaaiNR') acts as tridentate chelator in [Ni(SRaaiNR')2](ClO4)2. Ni<sup>II</sup>-azido-SRaaiNR' defines a  $\mu_{1,1}$ -N<sub>3</sub>-bridged Ni<sup>II</sup> dimer and [Ni(SRaaiNR')(N<sub>3</sub>)<sub>2</sub>]<sub>2</sub> shows in-

DFT indicates Cp<sub>2</sub>Mn<sub>2</sub>(NO)<sub>2</sub>(CO)<sub>2</sub> to have

six structures within ca. 3 kcal/mol of each

tramolecular ferromagnetic coupling. According to an EPR study, electrochemical oxidation of [Ni(SRaaiNR')2](ClO4)2 generates a Ni<sup>III</sup> species.

S. Nandi, D. Bannerjee, J. -S. Wu, T.-H. Lu, A. M. Z. Slawin, J. D. Woollins, J. Ribas, C. Sinha\* ...... 3972-3981

Thioether Bonded Nickel(II)-Azoimidazole Complexes: Structures, Spectra and Electrochemical Oxidation to the Nickel-(III) State

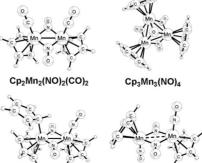
Keywords: Nickel / Electrochemistry / Magnetic properties / Ferromagnetic coupling / Density functional calculations

# DFT Studies on Cp(NO)Mn Compounds

B. Yan,\* Y. Xie, R. B. King,\* H. F. Schaefer III ...... 3982-3992

other with various combinations of bridging and terminal CO and NO groups. The triplet structures Cp<sub>2</sub>Mn<sub>2</sub>(μ-NO)<sub>2</sub>(μ-CO) and Cp<sub>2</sub>Mn<sub>2</sub>(μ-NO)<sub>2</sub> are global minima. The monomer CpMn(NO)2 is predicted to be unstable with respect to dimerization to  $Cp_2Mn_2(\mu-NO)_2(NO)_2$ . The latter molecule has two different structures of similar energies with very different Mn-Mn distances. Structures for  $Cp_2Mn_2(\mu-NO)_2(NO)X$  $(X = NO_2 \text{ and } \eta^5 - C_5H_5) \text{ and } Cp_3Mn_3(\mu - M_2)$ 

NO)<sub>3</sub>(μ<sub>3</sub>-NO) close to the experimental



 $Cp_2Mn_2(NO)_3(\eta^5-Cp)$ 

Cp<sub>2</sub>Mn<sub>2</sub>(NO)<sub>4</sub>

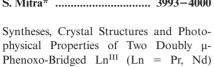
(Cyclopentadienyl)nitrosylmanganese Compounds: The Original Molecules Containing Bridging Nitrosyl Groups

Keywords: Manganese / Nitrosyl ligands / Cyclopentadienyl ligands / Density functional calculations / Bridging ligands / Carbonyl ligands / Structure elucidation

structures are predicted.

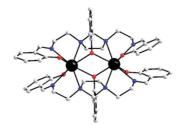
# **CONTENTS**

## **Photophysical Properties**



**Keywords:** Lanthanides / Schiff bases / Luminescence / Photophysics

Homodinuclear Schiff Base Complexes



Two new doubly  $\mu\text{-phenoxo-bridged}$  homodinuclear  $Pr^{III}$  and  $Nd^{III}$  complexes have been synthesized by using a heptadentate Schiff base ligand. In the complexes each  $Ln^{III}$  center adopts a distorted square antiprism geometry. Detailed photophysical investigations of the precursor ligand and interesting solid-state photoluminescence properties of the Ln complexes in the NIR region have been reported.

# **CORRECTION**

 Syntheses, Crystal Structures and Photophysical Properties of Two Doubly  $\mu$ -Phenoxo-Bridged Ln^{III} (Ln = Pr, Nd) Homodinuclear Schiff Base Complexes

**Keywords:** Lanthanides / Schiff bases / Luminescence / Photophysics

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

If not otherwise indicated in the article, papers in issue 25 were published online on August 19, 2009

<sup>\*</sup> Author to whom correspondence should be addressed.