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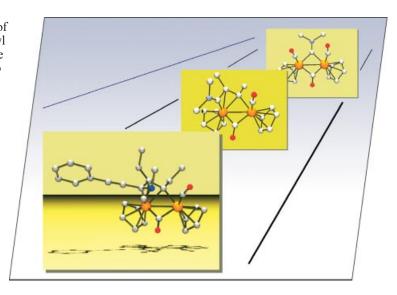




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

# **COVER PICTURE**

The cover picture shows the crystal structures of three diiron complexes with bridging hydrocarbyl ligands of increasing size and complexity: from the bridging aminocarbyne (at the back) through to the bridging vinyliminium (in the middle) to the allylidene complex (in the front). The complexes are the result of subsequent additions of alkynes and acetylides that take place at the bridging unit. For each step, the bridging coordination provides activation and also regio- and stereocontrol of the addition reactions. Thus, the nature and conformation of the growing bridging organic frame can be largely predicted and properly designed. Details are discussed in the article by V. Zanotti et al. on p. 1799 ff.



1785

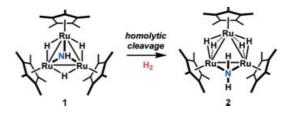
## SHORT COMMUNICATION

#### **Dihydrogen Activation**

H. Kameo, Y. Nakajima, H. Suzuki\* ...... 1793–1798

Hydrogenation of a Trinuclear  $\mu_3$ -Imido Complex of Ruthenium: Homolytic or Heterolytic H-H Bond Cleavage?

**Keywords:** Hydrido complexes / Ruthenium / Cleavage reactions / Imido complexes / Trinuclear complexes



To elucidate the mode of hydrogen—hydrogen bond cleavage at transition metal sites, the hydrogenation of  $(Cp*Ru)_3(\mu_3-NH)(\mu-H)_3$   $(Cp*=\eta 5-C_5Me_5)$  with deuterium was

carried out. The percentage of deuterium content in the amido ligand of  $(Cp*Ru)_3(\mu-NH_2)(\mu-H)_4$  proved the mode of cleavage of dihydrogen in the reaction.

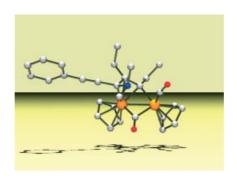
## **FULL PAPERS**

### **Growing Bridging Organic Frames**

L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti\* ...... 1799–1807

Acetylide Addition to Bridging Vinyliminium Ligands in Dinuclear Complexes

**Keywords:** Acetylides / Dinuclear complexes / Bridging ligands / C-C bond formation



Functionalized organic frameworks are built on diiron complexes by the addition of acetylides to bridging vinyliminium ligands under regio- and stereocontrolled conditions.

#### **Organoboron Complexes**

Boron Complexes with Chelating Anilido-Imine Ligands: Synthesis, Structures and Luminescent Properties

**Keywords:** Organoboron compounds / Schiff-base ligands / Luminescence

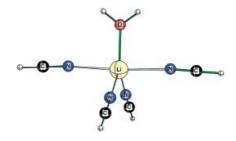
Three new organoboron complexes with anilido-imine ligands were synthesized. All complexes were characterized by <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C and <sup>19</sup>F NMR spectroscopy, X-ray crystallography, elemental analyses and mass spectrometry. These complexes show excellent luminescent properties.

### **Ligand-Exchange Mechanisms**

E. Pasgreta, R. Puchta, A. Zahl, R. van Eldik\* ...... 1815–1822

Ligand-Exchange Processes on Solvated Lithium Cations: Acetonitrile and Hydrogen Cyanide

**Keywords:** Lithium / Acetonitrile / Hydrogen cyanide / Solvation / Exchange mechanism



Experimental and theoretical studies indicate that  $Li^+$  is four coordinate in  $CH_3CN$  and in  $CH_3CN$ /water mixtures. Water coordinates strongly to  $Li^+$  such that addition of water immediately leads to the formation of  $[Li(H_2O)_4]^+$ . Ligand-exchange reactions on  $Li^+$  most probably follow an associative mechanism.



### **Luminescent Coordination Polymers**

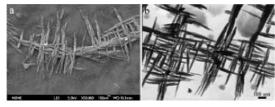
Treatment of CuI with PhS(CH<sub>2</sub>)<sub>n</sub>SPh (n=1, 2) affords the strongly luminescent 1D metal—organic coordination polymer, [Cu<sub>4</sub>I<sub>4</sub>{ $\mu$ -PhS<sub>2</sub>CH<sub>2</sub>SPh}<sub>2</sub>]<sub>n</sub>, and the 2D coordination polymer, [(CuI)<sub>2</sub>{ $\mu$ -PhS(CH<sub>2</sub>)<sub>2</sub>-SPh}<sub>2</sub>]<sub>n</sub>, respectively, by a self-assembly reaction.

H. N. Peindy, F. Guyon,\* A. Khatyr, M. Knorr,\* C. Strohmann ..... 1823–1828

Construction of 1D and 2D Copper(I) Coordination Polymers Assembled by  $PhS(CH_2)_nSPh$  (n=1, 2) Dithioether Ligands: Surprising Effect of the Spacer Length on the Dimensionality, Cluster Nuclearity and the Fluorescence Properties of the Metal-Organic Framework

**Keywords:** Dithioethers / Copper / Fluorescence / Coordination polymers / Metalmetal interactions

#### **Nanostructures**



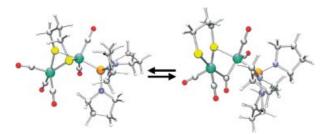
Network-like nanostructures made from the nonlinear optical material beta barium metaborate ( $\beta$ -BaB<sub>2</sub>O<sub>4</sub>,  $\beta$ -BBO) have been successfully synthesized from a BBO gel precursor using a sol-gel method. The

morphology of the synthesized  $\beta$ -BaB $_2$ O $_4$  materials exerts a significant influence on the second harmonic generation (SHG) efficiency.

Synthesis and Optical Properties of β-BaB<sub>2</sub>O<sub>4</sub> Network-Like Nanostructures

**Keywords:** Nonlinear optics / Materials science / Sol-gel processes / Borates

## **Biomimetic Dihydrogen Evolution**



The structural and electronic properties of  $(\mu\text{-pdt})[Fe_2(CO)_5P(NC_4H_8)_3]$ , a recently synthesized model of the active site of Fehydrogenase, have been studied by means of density functional theory. The unproto-

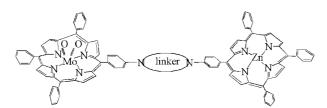
nated, mono-, and di-protonated forms of this compound were taken into account, in order to disclose the geometric features of the various intermediates involved in the electrocatalytic process of  $H_2$  evolution.

C. Greco, M. Bruschi, P. Fantucci, L. De Gioia\* ...... 1835–1843

Influence of a Large  $\sigma$ -Donor Ligand on Structural and Catalytic Properties of Di-Iron Compounds Related to the Active Site of Fe-Hydrogenase – A DFT Investigation

**Keywords:** Hydrogenases / Biomimetic chemistry / Catalytic H<sub>2</sub> evolution / Density functional calculations / Iron

#### **Porphyrinoids**



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Heterobinuclear porphyrin dimers are obtained by two different methods. They are characterized by UV/Vis, IR, XPS, <sup>1</sup>H

NMR, and luminescence spectroscopy and their TG-DTA and electrochemical properties determined. S.-N. Song, D.-M. Li,\* J.-F. Wu, C.-F. Zhuang, H. Ding, W.-B. Song, L.-F. Cui, G.-Z. Cao, G.-F. Liu .... 1844–1853

Syntheses and Characterization of Molybdenum/Zinc Porphyrin Dimers Bridged by Aromatic Linkers

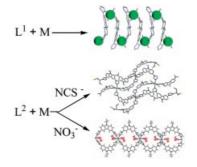
**Keywords:** Porphyrinoids / Heteronuclear complexes / Bridging ligands / Molybdenum / Zinc / Electrochemistry

## **CONTENTS**

## **Coordination Polymers**

Synthesis, Crystal Structures, and Photoluminescence of a Series of Coordination Polymers with Two Homologous Functional Flexible Ligands

**Keywords:** Coordination polymers / Flexible ligands / Supramolecular chemistry / Luminescence



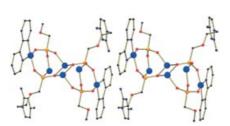
The functional flexible ligands 3,6-dipyrazolyl-9-ethylcarbazole and 3,6-diimidazolyl-9-ethylcarbazole are shown to be capable of coordinating to metal centers through their imidazolyl or pyrazolyl nitrogen atoms to form novel 2D or 3D polymers through different nonbonding and  $\pi-\pi$  interactions.

### Polynuclear Copper(II) Complexes

New Ternary Complexes of Copper(II) with 2,2'-Bipyridine (Bpy) and Phosphocholine (PCh<sup>-</sup>) or the Quaternary 1-(2-Phosphonomethoxy)ethyl Derivative of

2,4-Diaminopyrimidine (PMEDAPy<sup>-</sup>)

**Keywords:** Ternary complexes / Oxido bridges / Phosphonate bridges / Copper(II) / Magnetic properties



Ternary tetra- and hexanuclear copper(II) models of multicopper proteins were synthesised from the reaction of copper salts with bpy and phosphonate ligands which act as tri- or tetradentate bridges. Structural and magnetic properties were also studied.

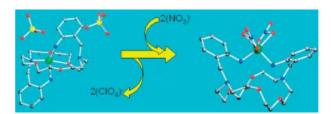
## **Crown Ether Complexation**

- L. Vaiana, C. Platas-Iglesias,D. Esteban-Gómez, F. Avecilla, A. de Blas,\*
- T. Rodríguez-Blas\* ...... 1874-1883



Receptor versus Counterion: Capability of N,N'-Bis(2-aminobenzyl)-diazacrowns for Giving Endo- and/or Exocyclic Coordination of  $\mathbf{Z}\mathbf{n}^{\mathrm{II}}$ 

**Keywords:** Zinc / Macrocyclic ligands / Crown compounds / Coordination modes / Density functional calculations



 $Zn^{II}$  binding by the lariat crown ethers  $L^1$  and  $L^2$  [ $L^1 = N,N'$ -bis(2-aminobenzyl)-1,10-diaza-15-crown-5 and  $L^2 = N,N'$ -bis(2-aminobenzyl)-4,13-diaza-18-crown-6] in the presence of different counterions has

been studied. The cavity of  $L^2$  is rather large for  $Zn^{II}$ , so that endo- or exocyclic coordinations are observed for the metal cation depending on the coordinative properties of the counterion.

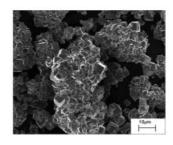
#### **Alkaline Niobates**

C. Sun, X. R. Xing,\* J. Chen, J. X. Deng, L. Li, R. B. Yu, L. J. Qiao,

G. R. Liu ...... 1884-1888

Hydrothermal Synthesis of Single Crystalline (K,Na)NbO<sub>3</sub> Powders

**Keywords:** Hydrothermal synthesis / Crystal growth / Crystal morphology / Niobates

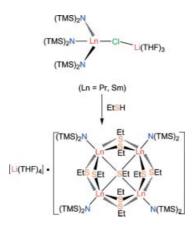


 $(K_{1-x}Na_x)NbO_3$  single crystalline powders with perovskite structure were synthesized by a hydrothermal method under moderate conditions. The mechanism of formation of  $(K_{1-x}Na_x)NbO_3$  was concluded. FE-SEM images showed that the morphological structures of niobates were cubes and nanofingers.



#### Amido-thiolato Ln Complexes

Protonolysis reactions of  $[(Me_3Si)_2N]_3$ - $Ln(\mu$ -Cl)Li(thf)<sub>3</sub> (Ln = Pr, Sm) with an equimolar amount of tBuSH or EtSH afforded four amidolanthanide alkylthiolate complexes  $[\{(Me_3Si)_2N\}_2Ln(\mu$ -StBu)]\_2 and  $[Li(thf)_4][\{(Me_3Si)_2N\}_4Ln_4(\mu_4$ -SEt)( $\mu$ -SEt)\_8] (Ln = Pr, Sm). These compounds show catalytic activity in ring-opening polymerization reactions.

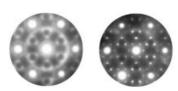


Protonolysis Reactions of [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>3</sub>-Ln( $\mu$ -Cl)Li(thf)<sub>3</sub> with tBuSH or EtSH: Isolation, Structures and Catalytic Properties of Dinuclear Complexes [{(Me<sub>3</sub>Si)<sub>2</sub>N}<sub>2</sub>-Ln( $\mu$ -StBu)]<sub>2</sub> and Tetranuclear Complexes [Li(thf)<sub>4</sub>][{(Me<sub>3</sub>Si)<sub>2</sub>N}<sub>4</sub>Ln<sub>4</sub>( $\mu$ <sub>4</sub>-SEt)( $\mu$ -SEt)<sub>8</sub>] (Ln = Pr, Sm)

**Keywords:** Amidolanthanides / Alkylthiolates / Synthesis / Crystal structure / Ringopening polymerization

### **Real Structure Analysis**

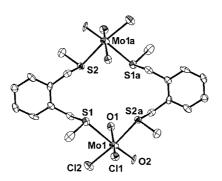
The real structure of a new partially ordered cluster phase of the ternary system La-Al-I was determined by a combined methodical approach of electron microscopy techniques and X-ray diffraction. The arrangement of neighboring clusters is comparable to chemically related, but strongly disordered cluster phases.



Order and Disorder in Cluster Phases – The Case of  $La_{\approx 0.7}(Al_{\approx 0.1}I_{\approx 0.9})$ 

**Keywords:** Electron microscopy / X-ray diffraction / Rare earth metal compounds / Clusters / Halides / Disorder

The first series of W<sup>VI</sup> dioxidodihalide complexes with soft thioether co-ligands are described, together with a range of new Mo<sup>VI</sup> thioether complexes; crystal structures of representative examples are described.

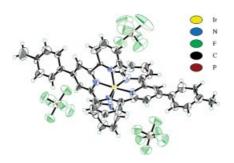


#### **Thioether Coordination Chemistry**

Tungsten(VI) and Molybdenum(VI) Complexes with Soft Thioether Ligand Coordination — Synthesis, Spectroscopic and Structural Studies

**Keywords:** Tungsten / Thioether / Molybdenum

Three new polypyridine iridium(III) complexes  $[Ir^{III}Cl(L)(tterpy)](PF_6)_2$  {L = phen (1), dpphen (2), and dmbpy (3)} were prepared. The calculated energies of the lowest singlet and triplet states in the  $[Ir^{III}(L)_2](PF_6)_3$  {L = tterpy (5) and terpy (6)} complexes are in good agreement with the experimental absorption and phosphorescence spectra.



## Iridium(III) Polypyridine Complexes

N. Yoshikawa,\* S. Yamabe, N. Kanehisa, Y. Kai, H. Takashima,

K. Tsukahara ...... 1911-1919

Synthesis, Characterization, and DFT Investigation of  $Ir^{\rm III}$  Tolylterpyridine Complexes

Complexes

Leywords: Iridium / Terpyridine / Absorp-

**Keywords:** Iridium / Terpyridine / Absorption / Emission / Density functional calculations

## **CONTENTS**

#### **Polynuclear Complexes**

V. Vertlib, J. Figueira, J. Mesquita,

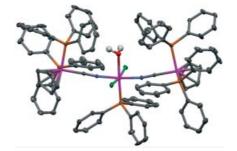
J. Rodrigues,\* K. Nättinen,

K. Rissanen\* ...... 1920-1924



A Trinuclear Aqua Cyano-Bridged Ruthenium Complex  $[\{(\eta^5-C_5H_5)(PPh_3)_2Ru(\mu-CN)\}_2RuCl_2(PPh_3)(H_2O)]PF_6$ : Synthesis, Characterization and Crystal Structure

**Keywords:** Ruthenium / Trinuclear complexes / Bridging ligands / X-ray structure / Metal-metal interactions / Chain structures



An unusual organometallic trinuclear aqua cyano-bridged complex  $[\{(\eta^5\text{-}C_5H_5)\text{-}(PPh_3)_2Ru(\mu\text{-}CN)\}_2RuCl_2(PPh_3)(H_2O)]PF_6$  was isolated and structurally characterized by FTIR,  $^1H$ ,  $^{13}C$ , and  $^{31}P$  NMR spectroscopy, mass spectrometry, elemental analysis, single-crystal X-ray diffraction, and cyclic voltammetry. The complex represents a rare example of a Ru-C=N-Ru'-N=C-Ru array with Ru-coordinated water.

#### **Water Chains**

Y. Jin, Y. Che, S. R. Batten, P. Chen, J. Zheng\* ...... 1925–1929



Unusual T4(1) Water Chain Stabilized in the One-Dimensional Chains of a Copper-(II) Coordination Polymer

**Keywords:** Water chain / Self assembly / One dimensional / Coordination polymers



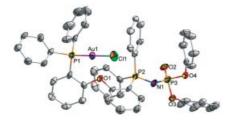
The water chain within the  $Cu^{II}$  coordination polymer lies about the  $3_2$  screw axes. The water tetramers are connected through the shared O(4) corners to form a chain with T4(1) symmetry.

#### **Suzuki Cross-Coupling**

R. Venkateswaran, M. S. Balakrishna,\* S. M. Mobin ...... 1930–1938

The Iminophosphorane-Phosphane Ph<sub>2</sub>P-C<sub>6</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>=NP(O)(OPh)<sub>2</sub>: Synthesis, Reactivity, and Catalytic Activity in Suzuki Cross-Coupling and the Homogeneous Hydrogenation of Olefins

**Keywords:** Monoimination / Monophosphane / Iminophosphorane-phosphane / Staudinger reaction / Suzuki cross-coupling



The synthesis of the iminophosphorane-phosphane ligand Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>= NP(O)(OPh)<sub>2</sub> (1) and its Pt, Pd, Au and Rh complexes is reported. Its catalytic utility in Suzuki cross-coupling reactions and the hydrogenation of olefins is also described.

If not otherwise indicated in the article, papers in issue 12 were published online on April 4, 2007