

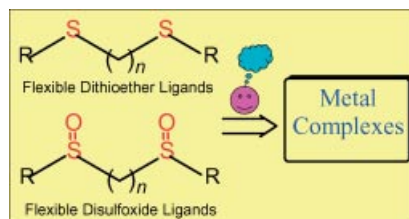
## MICROREVIEW

### Flexible Ligands

J.-R. Li, X.-H. Bu\* ..... 27–40

Structural Diversity and Modulation of Coordination Architectures with Flexible Dithioether or Disulfoxide Ligands

**Keywords:** Disulfoxide ligands / Dithioether ligands / Flexible ligands / Metal complexes / Structural modulation



Metal complexes of flexible dithioether and disulfoxide ligands are reviewed, with the aim of elucidating: (1) the coordination chemistry of the two types of ligands; (2) the structural diversity of their complexes; (3) structural modulation by fine-tuning the ligands, selecting metal ions, and controlling other factors including solvents, reagent ratios, counterions.

## SHORT COMMUNICATIONS

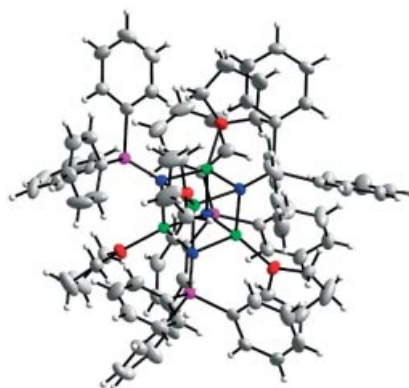
### Magnesium Imides

A. Fuchs, E. Kaifer,  
H.-J. Himmel\* ..... 41–43



Synthesis and Characterization of the New Tetrameric Magnesium Imide Compound  $[(thf)MgNSiPh_3]_4$

**Keywords:** Magnesium / Imides / Molecular main-group-element compounds



Reaction between  $Mg(n\text{-butyl})_2$  and  $H_2NSiPh_3$  in thf affords the new magnesium imide  $[(thf)MgNSiPh_3]_4$  featuring a distorted cubic  $Mg_4N_4$  unit.

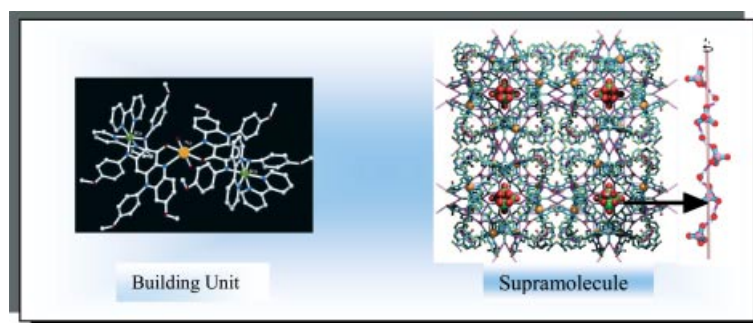
### Anion- $\pi$ Interactions

P. Banerjee, A. D. Jana, G. Mostafa,  
S. Goswami\* ..... 44–47



Organization of the  $RuNa$  Moiety of a Phenazine Ligand Into a New Coordination Network Promoted by  $ClO_4^-$ -Aromatic- $\pi$  Interactions

**Keywords:** Ruthenium / Solid-state structure / Self-assembly /  $\pi$  interactions / Optical properties

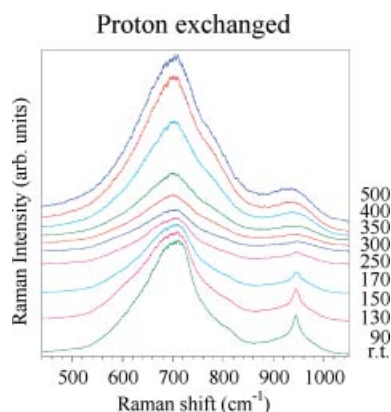


An example of a unique supramolecular network of an N-heterocyclic phenazine bridging ligand containing a  $Ru_2Na$  core is described. Several intermolecular inter-

actions including  $ClO_4^-$ - $\pi$ ,  $\pi$ - $\pi$ ,  $C-H\cdots\pi$  and hydrogen bonding are operative in the structure. Optical properties of the supramolecule are investigated.

## FULL PAPERS

The nature of the hydrogenated species contained in proton- and deuteron-exchanged TTB-like  $\text{Na}_{1.2}\text{Nb}_{1.2}\text{W}_{0.8}\text{O}_6$  is investigated by a combination of diffraction and spectroscopic methods. A model based on distortions and tilts of the  $\text{MO}_6$  framework connected to the presence of protons in the tunnels of the TTB structure is proposed as the origin of the superstructure observed in the ion-exchange products.



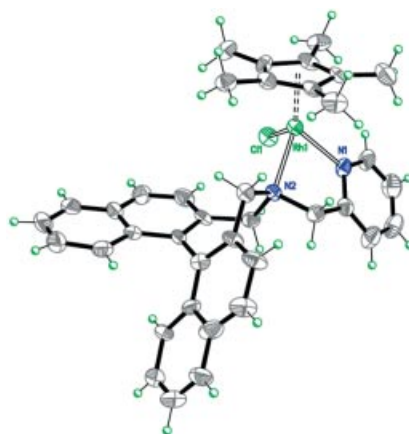
### Ion Exchange in TTB-Like Oxides

M. L. Sanjuán, A. Kuhn,\* M. T. Azcondo, F. García-Alvarado ..... 49–58

Proton and Deuteron Exchange in TTB-Like  $\text{Na}_{1.2}\text{Nb}_{1.2}\text{W}_{0.8}\text{O}_6$ : Structural Characterization and Spectroscopic Study

**Keywords:** Materials science / Ion exchange / Electron diffraction / IR spectroscopy / Raman spectroscopy

The ability of N-N\* chiral ligands to induce diastereoselectivity and configurational stability at the metal centre in the isoelectronic half-sandwich chelate complexes  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{N-N}^*)\text{Cl}]\text{X}$  ( $\text{X} = \text{Cl}, \text{PF}_6$ ) and  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{N-N}^*)\text{Cl}]\text{X}$  ( $\text{X} = \text{SbF}_6, \text{PF}_6$ ) is examined, and a rationalisation of the results is proposed on the basis of X-ray diffraction analysis and density functional calculations.



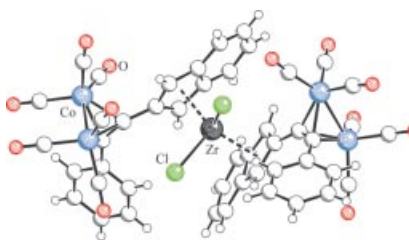
### Half-Sandwich Complexes

M. Saporita, G. Bottari, G. Brancatelli, D. Drommi, G. Bruno, F. Faraone\* ..... 59–72

Asymmetric Induction and Configurational Stability at the Metal Centre in Half-Sandwich  $(\eta^6\text{-}p\text{-Cymene})\text{ruthenium(II)}$  and  $(\eta^5\text{-C}_5\text{Me}_5)\text{rhodium(III)}$  Complexes Containing Chiral N-N\* Ligands with Different Rigidity and Flexibility

**Keywords:** Half-sandwich complexes / Bidentate N ligands / Diastereoselectivity / Ruthenium / Rhodium

The alkynyl substituents of bis(2-alkynylindenyl)dichlorozirconium complexes cleanly add a  $\text{Co}_2(\text{CO})_6$  unit and can also be hydroborated with  $\text{HB}(\text{C}_6\text{F}_5)_2$  to give a mixture of  $\alpha$ - and  $\beta$ -(borylalkenyl)metallocenes. Activation of these metallocenes with MAO gives active ethene and propene polymerization catalysts.



### Functionalized Zirconocenes

L. Chen, G. Kehr, R. Fröhlich, G. Erker\* ..... 73–83

Functional Group Chemistry at the Zirconocene Backbone: Addition Reactions to Pendant Alkynyl Substituents

**Keywords:** Zirconium / Cobalt / Boron / Hydroboration / Heterometallic complexes

A couple of aza-macrocyclic receptors containing penta- or hexamine bridges linked through methylene groups to the 5,5' positions of a terpyridine unit show interesting properties for  $\text{CO}_2$  fixation at neutral pH under electrochemical activation.



### $\text{CO}_2$ Fixation

B. Verdejo, S. Blasco, J. González, E. García-España,\* P. Gaviña, S. Tatay, A. Doménech, M. T. Doménech-Carbó, H. R. Jiménez, C. Soriano ..... 84–97

$\text{CO}$  Fixation and Activation by  $\text{Cu}^{\text{II}}$  Complexes of 5,5'-Terpyridinophane Macrocycles

**Keywords:** Macrocycles / N ligands / Copper / Carbon dioxide fixation / Electrochemistry

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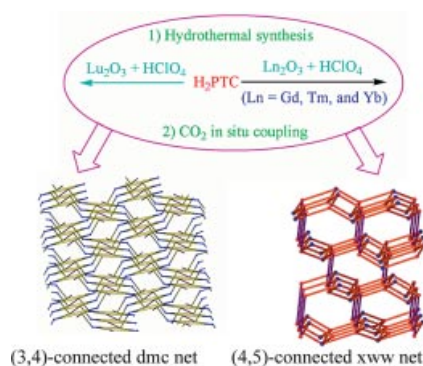
## Mixed-Node Topological MOFs

X.-W. Wang,\* X. Li, J.-Z. Chen,  
G. Zheng,\* H.-L. Hong ..... 98–105



Novel (3,4)- and (4,5)-Connected Lanthanide Metal–Organic Frameworks

**Keywords:** Mixed nodes / Lanthanides / Metal–organic frameworks



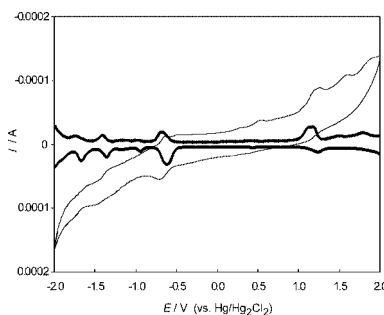
The (3,4)-connected (4.8<sup>2</sup>)(4.8<sup>5</sup>) dmc-type and (4,5)-connected (4<sup>4</sup>.6.8)(4<sup>4</sup>.6<sup>2</sup>.8<sup>4</sup>) xww-type topological lanthanide noninterpenetrating metal–organic frameworks formulated as [Ln(3,5-pdc)(C<sub>2</sub>O<sub>4</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O (Ln = Lu<sup>III</sup>, Gd<sup>III</sup>, Tm<sup>III</sup> and Yb<sup>III</sup>) were synthesized by hydrothermal reactions of 3,5-H<sub>2</sub>pdc with lanthanide oxide and perchloric acid.

## Gold Nanoparticles

F. Wen, U. Englert, B. Gutrath,  
U. Simon\* ..... 106–111

Crystal Structure, Electrochemical and Optical Properties of [Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>](NO<sub>3</sub>)<sub>3</sub>

**Keywords:** Gold clusters / Nanoparticles / Optical properties / Electrochemistry / Band gap



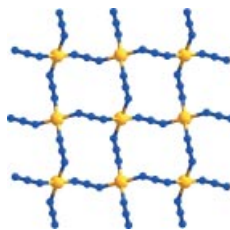
The single-crystal structure of the [Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>](NO<sub>3</sub>)<sub>3</sub> cluster was determined and the electrochemical and optical properties disclose molecule-like behaviour. As the electronic structure small gold nanoparticles evolve from the state of bulk continuum to discrete molecular orbital energy levels with decreasing size, such clusters may be attractive for application in nano-devices and molecular electronics.

## Molecular Magnetism

M. A. M. Abu-Youssef,\* V. Langer,  
D. Luneau, E. Shams, M. A. S. Goher,  
L. Öhrström\* ..... 112–118

1D and 2D Fe<sup>II</sup> Azide Coordination Polymers with Ferromagnetic Canting

**Keywords:** Crystal engineering / Bridging ligands / Azides / Magnetic properties / Network compounds / Topology



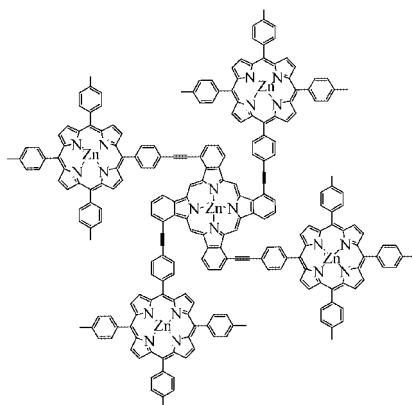
Two Fe<sup>II</sup> azides with 1D and 2D topologies, both displaying canted ferromagnetism in agreement with the structural features and other recent findings for Fe<sup>II</sup> and Mn<sup>II</sup> azides, were prepared. The new network topology **jsm** is assigned to some related six-connected 3D M<sup>II</sup> azides.

## Phthalocyanine–Porphyrin Oligomers

Z. Zhao, C.-T. Poon, W.-K. Wong,\*  
W.-Y. Wong, H.-L. Tam, K.-W. Cheah,  
T. Xie, D. Wang ..... 119–128

Synthesis, Photophysical Characterization, and Surface Photovoltage Spectra of Windmill-Shaped Phthalocyanine–Porphyrin Heterodimers and Heteropentamers

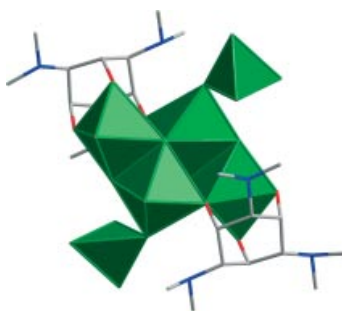
**Keywords:** Energy transfer / Photoluminescence / Photovoltage spectra / Phthalocyanines / Porphyrins



Mixed phthalocyanine–porphyrin zinc(II) dimeric and pentameric molecules were synthesized and photophysically characterized. They exhibit interesting optical-power-limiting and surface photovoltaic properties. They can behave as good light harvesters, and efficient energy transfer takes place from the porphyrin core to the phthalocyanine ring.

## Polynuclear Mo<sup>V</sup> Oxido Complexes

The reaction of MoCl<sub>5</sub> with the tripodal triol 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (tdci) in MeOH resulted in the formation of the dinuclear *syn*-[Mo<sub>2</sub>O<sub>4</sub>H(tdci)<sub>2</sub>]<sup>3+</sup>. Under aerobic conditions in the presence of H<sub>2</sub>O, this dinuclear species aggregated to a hexanuclear mixed-valence complex [Mo<sub>6</sub>O<sub>8</sub>(tdci)<sub>2</sub>-(MoO<sub>4</sub>)<sub>2</sub>].

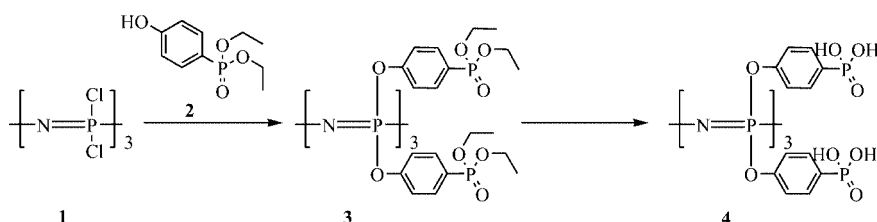


M. D. Meienberger, B. Morgenstern, S. Stucky, K. Hegetschweiler\* ... 129–137

Polymerization of Mo<sup>V</sup>: Synthesis and Characterization of a Dinuclear Mo<sup>V</sup> and a Hexanuclear Mixed-Valence Mo<sup>V</sup>/Mo<sup>VI</sup> Complex

**Keywords:** Molybdenum / Oxidation / O ligands / Tripodal ligands / Mixed-valence compounds

## Cyclotriphosphazenes



A convergent approach for the incorporation of arylphosphonate moieties into the cyclotriphosphazene unit is described. The products of the reactions are fully characterised, including a single X-ray diffraction

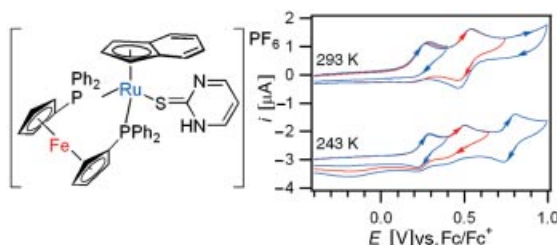
study for **3**. Finally, the thermal stability and degradation behaviour of these new compounds were investigated by thermogravimetric analysis.

N. Lejeune, I. Dez,\* P.-A. Jaffrès, J.-F. Lohier, P.-J. Madec, J. Sopkova-de Oliveira Santos .... 138–143

Synthesis, Crystal Structure and Thermal Properties of Phosphorylated Cyclotriphosphazenes

**Keywords:** Cyclotriphosphazenes / Phosphonates / Thermal properties

## Electrochemistry of Ru Complexes



Variable-temperature cyclic voltammetry experiments on the heterodimetallic [Ru(dppf)(ind)(Shet)] compounds support

the assignment of two noncommunicating metal centers (Ru<sup>II/III/IV</sup> and Fe<sup>II/III</sup>) that are involved in oxidative electron transfer.

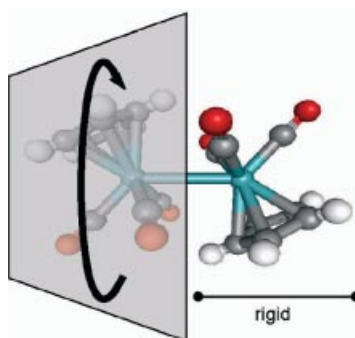
S. Y. Ng, W. K. Leong, L. Y. Goh,\* R. D. Webster\* ..... 144–151

Synthesis, X-ray Crystal Structures and Electrochemistry of (Indenyl)ruthenium Complexes Containing dppf and Heterocyclic Thiolato/Thione Ligands

**Keywords:** Cyclic voltammetry / Electron localization / Ruthenium / Heterocyclic thiolates/thiones / X-ray crystal structures

## Mobility in Cyclodextrins

The motion of FeCp(CO)<sub>2</sub>X (where X = I, CH<sub>3</sub>) and Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>6</sub> complexes included in β- or γ-cyclodextrin was studied by comparing the <sup>13</sup>C CPMAS NMR spectra of the adducts with that of FeCp(CO)<sub>2</sub>X and Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>6</sub>, respectively. The nature of the motion was shown to be dependent on the symmetry, size and orientation of the guest molecule within the host cavity.



S. Aime, M. R. Chierotti, R. Gobetto,\* A. Masic, F. Napolitano, H. C. Canuto, S. J. Heyes ..... 152–157

Intramolecular Host–Guest Dynamics of FeCp(CO)<sub>2</sub>X (X = I and CH<sub>3</sub>) and MoCp(CO)<sub>6</sub> Included in β- or γ-Cyclodextrin

**Keywords:** Solid-state NMR spectroscopy / Anisotropy / Inclusion compounds / Cyclodextrins / Metal–carbonyl complexes / Molecular dynamics



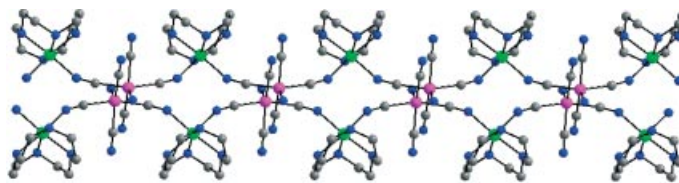
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## (Nitrido)manganese Polymers

J.-F. Guo, W.-F. Yeung, S. Gao,\*  
G.-H. Lee, S.-M. Peng, M. H.-W. Lam,  
T.-C. Lau\* ..... 158–163

Coordination Polymers Constructed from  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$ : Synthesis, Structures, and Magnetic Properties

**Keywords:** Heterometallic complexes / Coordination polymers / Cyanido ligands / Manganese / Magnetic properties



Three new compounds constructed from  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  have been synthesized and structurally and magnetically characterized. Compounds **1** and **2** have one-dimensional chain structures, while com-

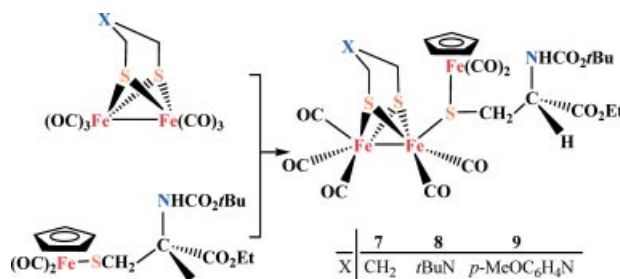
pound **3** has a two-dimensional sheet-like structure. Magnetic studies show that there is no significant magnetic coupling between the paramagnetic metal centers in **1** and **3**.

## The L-Cysteinyll-S Linkage

L.-C. Song,\* J.-H. Ge, J. Yan,  
H.-T. Wang, X. Luo, Q.-M. Hu .... 164–171

Iron-Only Hydrogenase Active Site Models Containing a Cysteinyll Group Coordinated through Its Sulfur Atom to One Iron Atom of the Diiron Subsite

**Keywords:** Bioinorganic chemistry / Cysteinyll ligand / Electrocatalysis / Dihydrogen evolution / Iron-only hydrogenase



H-cluster model compounds **7–9** have been synthesized and structurally characterized. These models contain a linkage,  $[\text{Fe}_{\text{Cp}}-(\mu\text{-cysteinyll-S})\text{-Fe}_{\text{subsite}}]$ , which resembles the linkage  $[\text{Fe}_{\text{cubane}}-(\mu\text{-cysteinyll-S})\text{-Fe}_{\text{subsite}}]$

found in natural enzymes and provides substantial electronic communication between the diiron subsite and the  $[\text{Cp}(\text{CO})_2\text{Fe}]$  unit through the L-cysteinyll-S bridge.

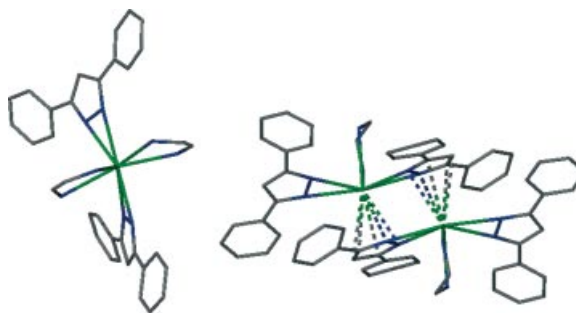
## Barium Pyrazolates

A. Y. O'Brien, J. Hitzbleck, A. Torvisco,  
G. B. Deacon,  
K. Ruhlandt-Senge\* ..... 172–182



More than Steric Effects: Unlocking the Coordination Chemistry of Barium Pyrazolates

**Keywords:** Pyrazolates / Barium / N ligands / Coordination modes / Structure elucidation / CVD precursors / Synthetic methods



In addition to ligand size and hapticity, secondary interactions including  $\pi$ -bonding, hydrogen bonding, and agostic interactions

are found to play a significant role in controlling the coordination chemistry of a family of barium pyrazolate compounds.

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