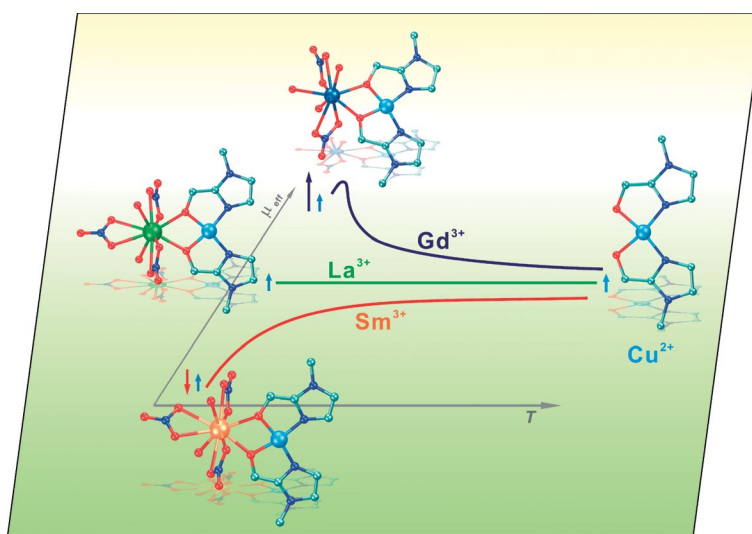


The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic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

## COVER PICTURE

The cover picture shows a cupric metalloligand, formed by the mixed O- and N-atom donor ligand 2-hydroxymethyl-1-methylimidazole, that further ligates to lanthanide ions, which results in dinuclear CuLn complexes. With different lanthanide ions ( $\text{Gd}^{3+}$ ,  $\text{La}^{3+}$ , and  $\text{Sm}^{3+}$ ), the  $\text{CuLn}$  complexes have different structural features and exhibit ferromagnetic, paramagnetic and antiferromagnetic behavior, respectively. Details are discussed in the article by Y.-Y. Yang, X.-M. Chen et al. on p. 679ff.



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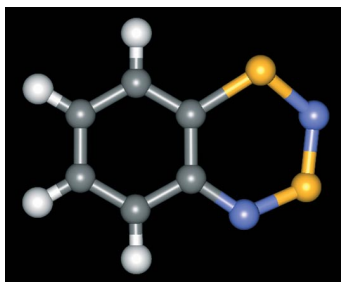
## MICROREVIEW

### Benzodithiadiazines

F. Blockhuys,\* N. P. Gritsan,  
A. Yu. Makarov, K. Tersago,  
A. V. Zibarev\* ..... 655–672

A Brave New World: The Heteroatom Chemistry of 1,3,2,4-Benzodithiadiazines and Related Compounds

**Keywords:** Antiaromaticity / Fluorine / Heteroatom chemistry / Sulfur–nitrogen heterocycles / Molecular structures / Persistent radicals / Reactivity Synthesis



The most important advances in the heteroatom chemistry of 1,3,2,4-benzodithiadiazines are highlighted: synthetic methods, features of the molecular and  $\pi$ -electronic structure, spectral properties, and reactivity, in particular the transformations into  $\pi$ -radicals. The chemistry of the benzodithiadiazines is compared to that of related chalcogen–nitrogen compounds, both cyclic and acyclic.

## SHORT COMMUNICATION

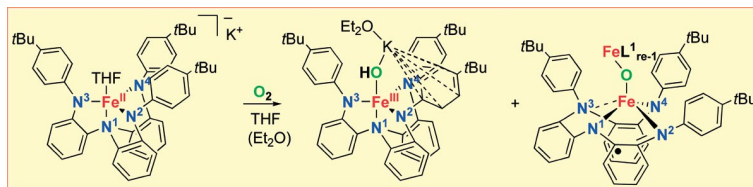
### Generation of Metalloradicals

R. Çelenligil-Çetin, P. Paraskevopoulou,  
R. Dinda, N. Lalioti, Y. Sanakis,  
A. M. Rawashdeh, R. J. Staples,  
E. Sinn, P. Stavropoulos\* ..... 673–677



Oxidative Ligand Rearrangement Due to Incipient Aminyl Radicals in the Oxidation of Iron(II) Species with Dioxygen

**Keywords:** Iron / N ligands / Radicals / Rearrangement / Tripodal ligands



Metalloradical systems that combine redox-active metals and non-innocent ligands are no longer rare chemical oddities; they are instead emerging as significant components of catalytic and enzymatic reactions. The present work examines the

synthetic and functional aspects of iron compounds featuring a new trisamido-amine ligand that can undergo one-electron oxidative rearrangement and store the oxidizing equivalent as a  $\pi$  radical.

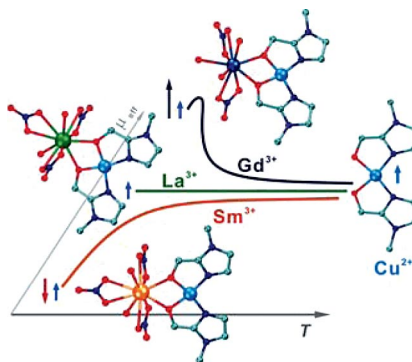
## FULL PAPERS

### Heterometallic 3d–4f Metal Clusters

W.-X. Zhang, Y.-Y. Yang,\* S.-B. Zai,  
S. Weng Ng, X.-M. Chen\* ..... 679–685

Syntheses, Structures and Magnetic Properties of Dinuclear Copper(II)–Lanthanide(III) Complexes Bridged by 2-Hydroxymethyl-1-methylimidazole

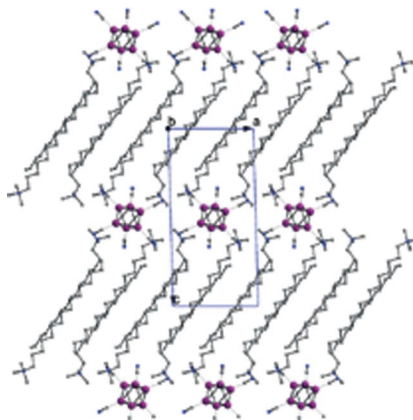
**Keywords:** Lanthanides / Copper / Nitrogen heterocycles / Magnetic properties



Three discrete dinuclear copper(II)–lanthanide(III) complexes, namely,  $[\text{CuLn}(\text{mmi})_2(\text{NO}_3)_3(\text{H}_2\text{O})_2]$  [ $\text{Ln} = \text{La}, \text{Sm}$ ] and  $[\text{CuGd}(\text{mmi})_2(\text{NO}_3)_2(\text{H}_2\text{O})_3][\text{NO}_3]$ , were assembled with the cupric metalloligand  $[\text{Cu}(\text{mmi})_2]$  and characterized by X-ray crystallography. They exhibit paramagnetic, antiferromagnetic and ferromagnetic behaviours, respectively.

## Lamellar Phases of Rhenium Clusters

The mesostructured lamellar phases with the general formula  $[\text{C}_n\text{H}_{2n+1}\text{N}(\text{CH}_3)_3]_4-[\text{Re}_6\text{Q}_8(\text{CN})_6]$  ( $n = 14, 16, 18$ ;  $\text{Q} = \text{Te, Se, S}$ ; 1:  $n = 14$ ,  $\text{Q} = \text{Te}$ ; 2:  $n = 16$ ,  $\text{Q} = \text{Te}$ ; 3:  $n = 18$ ,  $\text{Q} = \text{Te}$ ; 4:  $n = 16$ ,  $\text{Q} = \text{Se}$ ; 5:  $n = 16$ ,  $\text{Q} = \text{S}$ ) were prepared by an ion exchange/precipitation reaction of alkyltrimethylammonium surfactants and the corresponding cluster  $\text{K}_4[\text{Re}_6\text{Q}_8(\text{CN})_6]$  in an  $\text{H}_2\text{O}$ /acetone medium at room temperature. In the structure, the rhenium clusters form layers with a pseudo-hexagonal arrangement, and these inorganic layers are separated by a bi-layer of interdigitated surfactant cations.



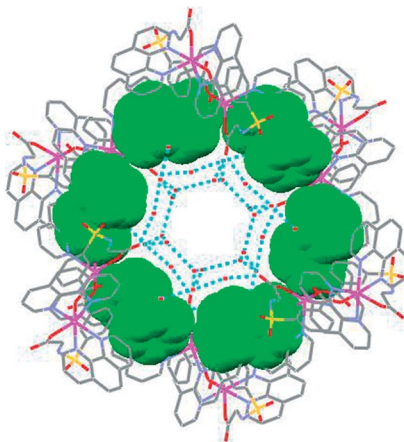
M.-J. Suh, V. Vien, S. Huh, Y. Kim,  
S.-J. Kim\* ..... 686–692

Mesolamellar Phases Containing  $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$  ( $\text{Q} = \text{Te, Se, S}$ ) Cluster Anions

**Keywords:** Mesolamellar phases / Meso-scale materials / Surfactant-template assembly / Octahedral rhenium clusters

## A New $(\text{H}_2\text{O})_{30}$ Cluster

Two novel versatile glycine derivatives,  $N$ -[(3-carboxyphenyl)sulfonyl]glycine and  $N,N'$ -(1,3-phenylenedisulfonyl)bis(glycine), were used for crystal engineering. Four  $\text{Cu}^{\text{II}}$  and  $\text{Mn}^{\text{II}}$  complexes were formed simply by changing the pH value or the base. A hitherto unknown discrete  $(\text{H}_2\text{O})_{30}$  cluster containing a puckered  $(\text{H}_2\text{O})_{12}$  ring core was found in **2**. Crystal structures and magnetic properties of the four complexes were also studied.



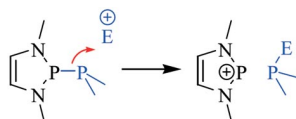
L.-F. Ma, Y.-Y. Wang,\* L.-Y. Wang,\*  
J.-Q. Liu, Y.-P. Wu, J.-G. Wang,  
Q.-Z. Shi, S.-M. Peng ..... 693–703

Two Novel Flexible Multidentate Ligands for Crystal Engineering: Syntheses, Structures, and Properties of  $\text{Cu}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$  Complexes with  $N$ -[(3-Carboxyphenyl)sulfonyl]glycine and  $N,N'$ -(1,3-Phenylenedisulfonyl)bis(glycine)

**Keywords:**  $N$ -[(3-Carboxyphenyl)sulfonyl]glycine /  $N,N'$ -(1,3-Phenylenedisulfonyl)bis(glycine) / Magnetic properties / Complexes / Crystal engineering

## P–P Bond Activation

$\text{N}$ -Heterocyclic diphosphanes react with Lewis acids ( $\text{E}^+ = \text{BH}_3$ ,  $\text{GaCl}_3$ ) or with elemental selenium by bond cleavage. Spectroscopic studies proved that the initial reaction with borane proceeds under preservation of the  $\text{P}-\text{P}$  bond to give a transient phosphane–borane which rearranged below ambient temperature. The results suggest that Lewis acid coordination decisively enhances the weakening of the polarised  $\text{P}-\text{P}$  bond.



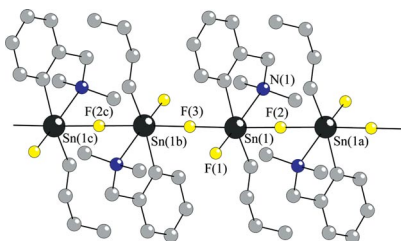
S. Burck, D. Gudat,\* M. Nieger,  
D. Vinduš ..... 704–707

Increasing the Lability of Polarised Phosphorus–Phosphorus Bonds

**Keywords:** Phosphorus / Phosphanes / Lewis acids / Bond polarisation / Substituent effects

## Hypervalent Tin Compounds

New hypervalent  $\text{R}_2\text{BuSnX}_2$  [ $\text{R} = 2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ ;  $\text{X} = \text{Cl}$  (**1**),  $\text{F}$  (**2**)] and  $\text{cyclo}-(\text{RR}^1\text{SnS})_2$  [ $\text{R}^1 = \text{Bu}$  (**3**) and  $2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$  (**4** and **4·2CHCl}\_3**)] were prepared. In the solid state a “zig-zag” polymeric chain is formed through  $\text{Sn}\cdots\text{Cl}$  interactions for **1**, while **2** is a linear  $-\text{Sn}-\text{F}-\text{Sn}-$  polymer. The thio derivatives are monomeric with distorted trigonal bipyramidal ( $\text{C},\text{N})\text{CSnS}_2$  (**3**) or octahedral ( $\text{C},\text{N})_2\text{SnS}_2$  (**4** and **4·2CHCl}\_3**) cores.



R. A. Varga, K. Jurkschat,  
C. Silvestru\* ..... 708–716

Solid-State Structure and Behaviour in Solution of Hypervalent Organotin(IV) Derivatives Containing  $2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$  Moieties

**Keywords:** Tin / Hypervalent / Halides / X-ray diffraction / Supramolecular chemistry

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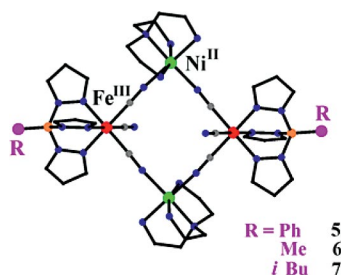
## Single-Molecule Magnets

C.-F. Wang, W. Liu, Y. Song, X.-H. Zhou,  
J.-L. Zuo,\* X.-Z. You ..... 717–727



Syntheses, Structures, and Electrochemical and Magnetic Properties of Rectangular Heterobimetallic Clusters Based on Tricyanometallic Building Blocks

**Keywords:** Cyanometalates / Crystal structures / Magnetic properties / Single-molecule magnets / Polynuclear complexes



Three tricyanometalate precursors and four rectangular clusters  $\text{Fe}^{\text{III}}_2\text{Cu}^{\text{II}}_2$  and  $\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}_2$  (5–7) were prepared and structurally characterized. Their electrochemical and magnetic properties were investigated. Clusters 5–7 show single-molecule magnet behavior with appreciable magnetic anisotropy.

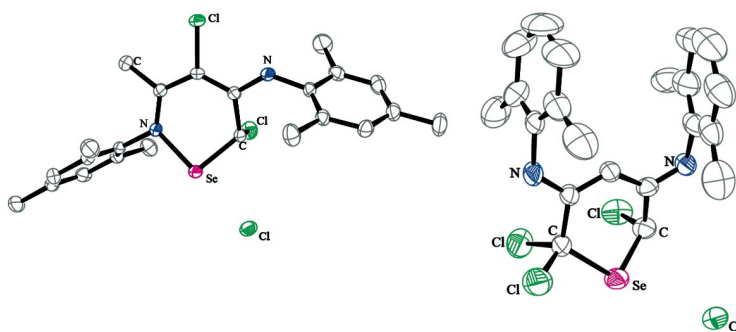
## Selenium Heterocycles

A. F. Gushwa, A. F. Richards\* ... 728–736



Selenium Heterocycles: Reactions of  $\text{SeX}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with the Enamine Form of  $\beta$ -Diketiminato Ligands

**Keywords:** Heterocycles /  $\beta$ -Diketiminato ligands / Enamines / Selenium



Four new selenium heterocycles are described that are formed by the rearrangement of  $\beta$ -diketiminato ligands,  $\text{H}\{\text{N}(\text{Ar})\text{C}(\text{Me})_2\text{CH}$ . These avoid usual  $\text{N}, \text{N}'$ -chelation and instead favor reaction at the for-

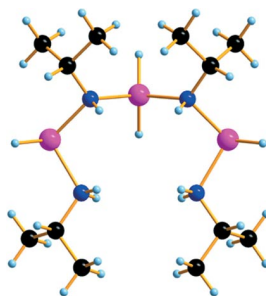
mer backbone methyl carbon atom and feature halide atom rearrangement to the ligand that can be controlled through reaction stoichiometry.

## Cationic Gallane Derivatives

C. Y. Tang, A. R. Cowley, A. J. Downs,\*  
S. Marchant, S. Parsons ..... 737–744

Formation and Characterization of the Cationic Gallane Derivatives  $[(\text{RH}_2\text{N})_2\text{GaH}_2]^+\text{Cl}^-$  ( $\text{R} = \text{Me}$  or  $i\text{Pr}$ ) and  $\{[(i\text{PrH}_2\text{N})\text{GaH}_2\text{NH}i\text{Pr}]_2\text{GaH}_2\}^+\text{Cl}^-$

**Keywords:** Gallane cations / Hydride ligands / N ligands / X-ray diffraction / Hydrogen bonds



$\text{LiGaH}_4$  can be made to react with a 50% molar excess of the amine hydrochloride  $[\text{RNH}_3]\text{Cl}$  to afford the cationic gallane derivative  $[(\text{RH}_2\text{N})_2\text{GaH}_2]^+\text{Cl}^-$ , with  $\text{R} = \text{Me}$  or  $i\text{Pr}$ , in 45–65% yield. A significant secondary product for  $\text{R} = i\text{Pr}$  is the trigallium compound  $\{[(i\text{PrH}_2\text{N})\text{GaH}_2\text{NH}i\text{Pr}]_2\text{GaH}_2\}^+\text{Cl}^-$ . The structures and other properties of such compounds give evidence of their mediating the formation of neutral amidogallanes, as well as having wider possible implications.

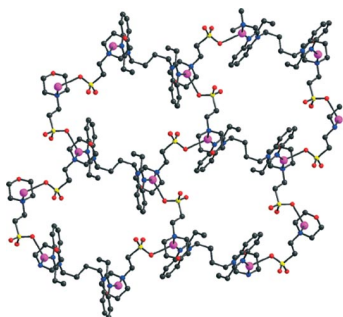
## Flexible Ligands in MOFs

H. Jiang, J.-F. Ma,\* W.-L. Zhang,  
Y.-Y. Liu, J. Yang, G.-J. Ping,  
Z.-M. Su ..... 745–755



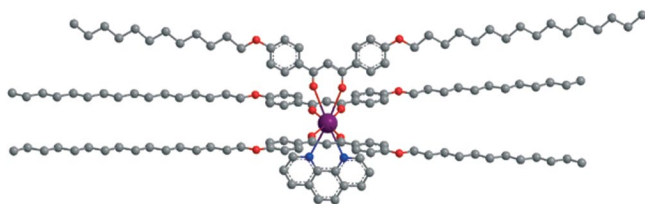
Metal–Organic Frameworks Containing Flexible Bis(benzimidazole) Ligands

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



The assembly reactions of metal ions and three kinds of flexible bis(benzimidazole) ligands afford 11 new coordination polymers with diversified frameworks.





Ternary rare-earth complexes of the type  $[\text{Ln}(\text{C}_{12}\text{C}_{16}\text{dbm})_3(\text{phen})]$  exhibit a monotropic smectic A phase for the heavy lanthanides. A model for the molecular or-

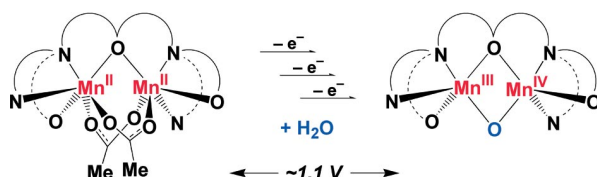
ganization within the smectic A layers is proposed and the luminescence properties of the complexes were investigated.

A. A. Knyazev, Y. G. Galyametdinov,\*  
B. Goderis, K. Driesen, K. Goossens,  
C. Görrler-Walrand, K. Binnemans,  
T. Cardinaels\* ..... 756–761

Liquid-Crystalline Ternary Rare-Earth Complexes



**Keywords:** Lanthanides / Lanthanidomesogens / Liquid crystals / Metallomesogens / Rare earths



Even small water concentrations were found to influence the redox properties of a dinuclear manganese complex significantly. As a consequence, the presence of water

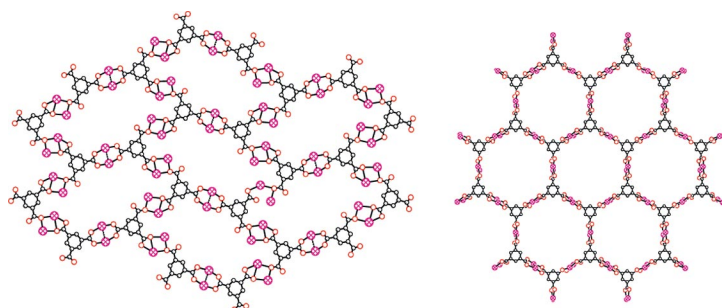
reduces the overall potential span needed to reach the  $\text{Mn}^{\text{III,IV}}_2$  oxidation state from the  $\text{Mn}^{\text{II,II}}_2$  state to only ca. 1.1 V.

P. Kurz, M. F. Anderlund, N. Shaikh,  
S. Styring, P. Huang\* ..... 762–770

Redox Reactions of a Dinuclear Manganese Complex – the Influence of Water



**Keywords:** Manganese / N,O ligands / Biomimetic synthesis / Redox chemistry / EPR spectroscopy



Two new coordination polymers containing 2D  $\text{Ag}_3(\text{btc})$  and  $\text{Ag}_3(\text{ctc})$  hexagonal motifs, respectively, are obtained from the reactions of freshly synthesized  $[\text{Ag}(\text{NH}_3)_2]$ -

(OH) with benzoselenadiazole (bsd) and benzene- or cyclohexane-1,3,5-tricarboxylic acid ( $\text{H}_3\text{btc}/\text{H}_3\text{ctc}$ ).

C.-K. Tan, J. Wang, J.-D. Leng,  
L.-L. Zheng, M.-L. Tong\* ..... 771–778

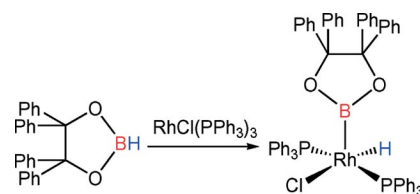
The Use of 2,1,3-Benzoselenadiazole as an Auxiliary Ligand for the Construction of New 2D Silver(I)/Benzene- or Cyclohexane-1,3,5-tricarboxylate Honeycomb Networks



**Keywords:** Silver / Selenium / Carboxylate ligands / Materials science / Organic-inorganic hybrid composites

## Metal-Catalysed Hydroboration

4,4,5,5-Tetraphenyl-1,3,2-dioxaborolane (HBBzpin) has been prepared in high yield and used in the catalysed hydroboration of alkenes to give air- and chromatography-stable organoboronate ester products. Reactions with metal complexes have also been investigated. Addition of HBBzpin to  $\text{RhCl}(\text{PPh}_3)_3$  gave the borylrhodium complex  $\text{Rh}(\text{H})\text{Cl}(\text{BzBpin})(\text{PPh}_3)_2$ .



C. B. Fritsch, S. M. Wernitz,  
C. M. Vogels, M. P. Shaver, A. Decken,  
A. Bell,\* S. A. Westcott\* ..... 779–785

4,4,5,5-Tetraphenyl-1,3,2-dioxaborolane: A Bulky Borane for the Transition Metal Catalysed Hydroboration of Alkenes



**Keywords:** Boranes / Catalysis / Hydroboration / Organoboronate esters / Borylrhodium complexes

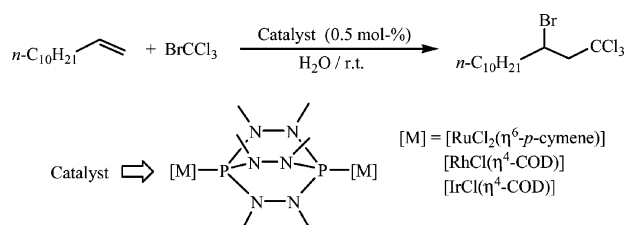
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## Kharasch Reaction

A. E. Díaz-Álvarez, P. Crochet,\*  
M. Zablocka,\* C. Duhayon, V. Cadierno,  
J.-P. Majoral\* ..... 786–794

Developing the Kharasch Reaction in Aqueous Media: Dinuclear Group 8 and 9 Catalysts Containing the Bridging Cage Ligand Tris(1,2-dimethylhydrazino)diphosphane

**Keywords:** Phosphane ligands / Ruthenium / Rhodium / Iridium / Radical reactions



The novel dinuclear complexes  $[\{\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-THDP})]$  and  $[\{\text{MCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$  ( $M = \text{Rh}, \text{Ir}$ ), containing the bridging ligand tris(1,2-dimethylhydrazino)diphosphane (THDP), have been

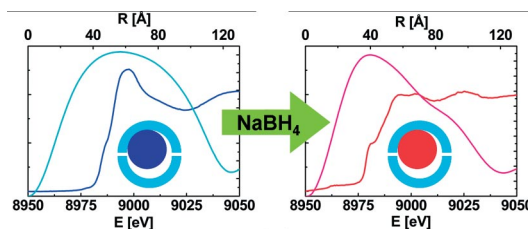
synthesized and used as catalysts in the atom-transfer radical addition of bromotrichloromethane to olefins (Kharasch reaction) in aqueous media.

## Apoferitin as a Nanoreactor

M. Ceolín,\* N. Gálvez,  
P. Sánchez, B. Fernández,  
J. M. Domínguez-Vera\* ..... 795–801

Structural Aspects of the Growth Mechanism of Copper Nanoparticles Inside Apoferritin

**Keywords:** Copper nanoparticles / Apoferritin / X-ray absorption spectroscopy / Small-angle X-ray scattering



Confined synthesis of inorganic materials provides an elegant route for size and shape control in nanostructures. The production of metallic copper nanoparticles, via chemical reduction, using the protein

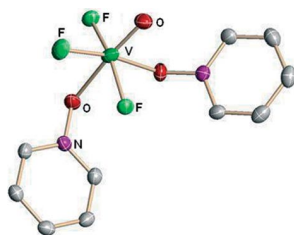
apoferritin as a nanoreactor is described. Further, a model for the atomic arrangement around copper in the metallic nanoparticle and its oxidized precursor is presented.

## Vanadium Oxide Fluoride Chemistry

M. F. Davis, W. Levason,\* J. Paterson,  
G. Reid, M. Webster ..... 802–811

Complexes of Vanadium(V) Oxide Trifluoride with Nitrogen and Oxygen Donor Ligands: Coordination Chemistry and Some Fluorination Reactions

**Keywords:** Vanadium complexes / Oxide-fluorides



Six-coordinate adducts of  $\text{VOF}_3$  with a variety of neutral N, O and S donor ligands have been prepared and spectroscopically and structurally characterised. The complexes are generally more stable than those of  $\text{VOCl}_3$ , but in some cases decomposition results in fluorination of the ligands.

## CORRECTIONS

A. El Majzoub, C. Cadiou,  
I. Déchamps-Olivier, F. Chuburu,\*  
M. Aplincourt ..... 813

(Benzimidazolymethyl)cyclen: A Potential Sensitive Fluorescent PET Chemosensor for Zinc

**Keywords:** Zinc / Macrocyclic ligands / X-ray diffraction / UV/Vis spectroscopy / Fluorescent probes / Fluorimetric titrations

E. Pardo, K. Bernot, F. Lloret,\* M. Julve,  
R. Ruiz-García, J. Pasán, C. Ruiz-Pérez,  
D. Cangussu, V. Costa, R. Lescouëzec,  
Y. Journaux\* ..... 814

Solid-State Anion–Guest Encapsulation by Metallosupramolecular Capsules Made from Two Tetranuclear Copper(II) Complexes

**Keywords:** Copper / Host–guest systems / Magnetic properties / Polynuclear complexes / Structure elucidation