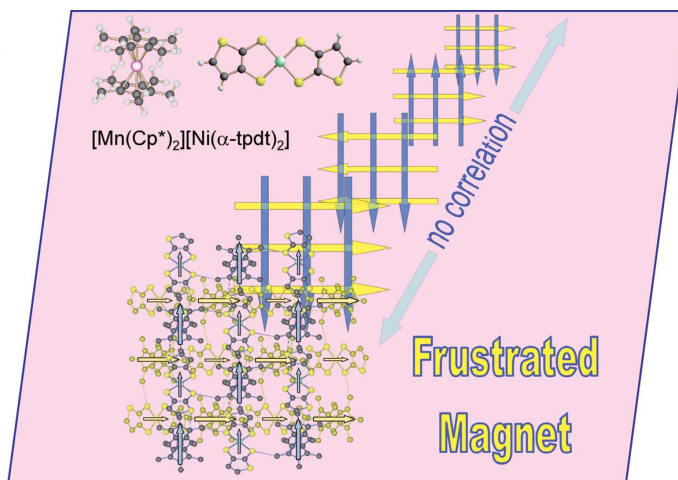


A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

## COVER PICTURE

The cover picture shows the multilayer spin arrangement in  $[\text{Mn}(\text{Cp}^*)_2][\text{Ni}(\alpha\text{-tpdt})_2]$  ( $\alpha\text{-tpdt}$  = 2,3-thiophenedithiolate). The crystal structures of the salts  $[\text{M}(\text{Cp}^*)_2][\text{Ni}(\alpha\text{-tpdt})_2]$  ( $\text{M} = \text{Fe}, \text{Mn}$  and  $\text{Cr}$ ) consist of alternating layers that are composed of arrangements of parallel mixed chains. The chains in neighboring layers are perpendicular. The arrangement between the chains and the magnetic anisotropy of the cations in case of the salt  $[\text{Mn}(\text{Cp}^*)_2][\text{Ni}(\alpha\text{-tpdt})_2]$  lead to a degenerate ground state and to a frustrated magnetic behavior, which can be associated with the absence of long-range order between the ferromagnetic layers. Details are discussed in the article by M. Almeida, V. Gama et al. on p. 5327ff.



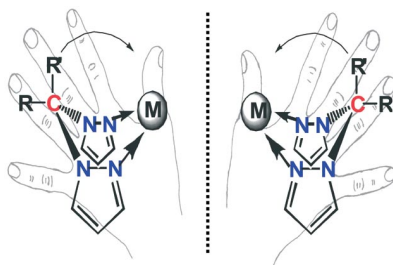
## MICROREVIEW

### Heteroscorpionate Ligands

A. Otero,\* J. Fernández-Baeza,  
A. Lara-Sánchez, J. Tejada,  
L. F. Sánchez-Barba ..... 5309–5326

Recent Advances in the Design and Coordination Chemistry of Heteroscorpionate Ligands Bearing Stereogenic Centres

**Keywords:** Bis(pyrazol-1-yl)methane / Heteroscorpionate / Chiral complexes



In this microreview an account of both the synthetic methodologies to prepare chiral heteroscorpionate ligands as well as their different classes of complexes from early to late transition metals is shown.

## FULL PAPERS

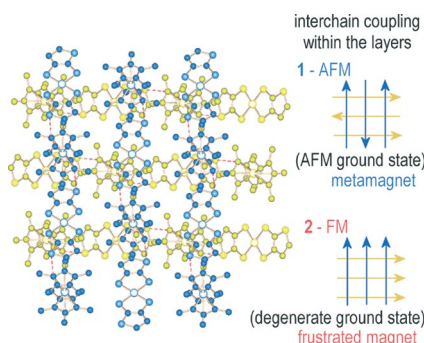
### Magnetic Anisotropy

D. Belo, J. Mendonça, I. C. Santos,  
L. C. J. Pereira, M. Almeida,\* J. J. Novoa,  
C. Rovira, J. Veciana,  
V. Gama\* ..... 5327–5337



Metalloccenium Salts of Nickel Bis( $\alpha$ -thiophenedithiolate)  $[M(Cp^*)_2][Ni(\alpha\text{-tpdt})_2]$  ( $M = Fe, Mn, Cr$ ) – Metamagnetism and Magnetic Frustration

**Keywords:** Donor–acceptor systems / Metallocenes / S ligands / Through-space interactions / Magnetic anisotropy



$[M(Cp^*)_2][Ni(\alpha\text{-tpdt})_2]$  [ $M = Fe$  (1),  $Mn$  (2),  $Cr$  (3)] show similar multilayer structural arrangements, but at low temperatures, 1 is a metamagnet, 2 is a frustrated magnet, and 3 is a paramagnet. The unusual behavior of 2 is due to a degenerate ground state resulting from interlayer chain arrangements and magnetic anisotropy.

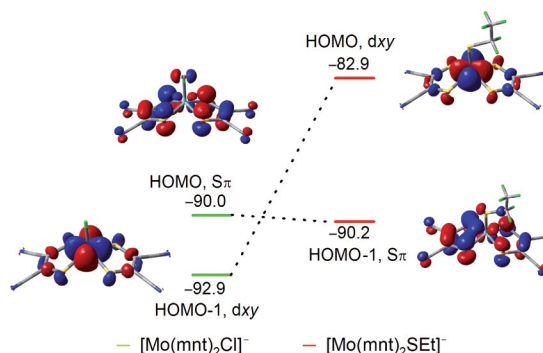
### Mechanism of Nitrate Reduction

K. Pal, S. Sarkar\* ..... 5338–5349



The Role of Axial Ligation in Nitrate Reductase: A Model Study by DFT Calculations on the Mechanism of Nitrate Reduction

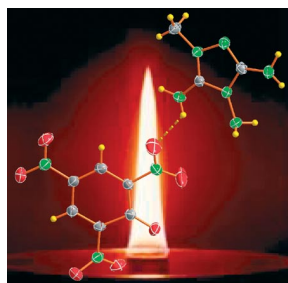
**Keywords:** Density functional calculations / Enzyme models / Oxidoreductases / Molybdenum



Computational studies on the binding of substrates to some functional models of nitrate reductase support the experimental findings concerning the formation of a

Michaelis-type complex. The calculated energy profile of this type of reaction shows the necessity of axial thiolate coordination in contrast to halide coordination.

The energetic properties of picrate salts with azolium cations were studied. The compounds combine the high thermal stabilities of classical nitroaromatic energetic materials with relatively high performances. All compounds also proved to be insensitive and higher performing than TNT or picric acid and were predicted to yield less decomposition residue, with potential for energetic applications.



T. M. Klapötke,\*

C. Miró Sabaté ..... 5350–5366

1,2,4-Triazolium and Tetrazolium Picrate Salts: “On the Way” from Nitroaromatic to Azole-Based Energetic Materials



**Keywords:** Azolium cations / Energetic materials / Explosives / Picrates

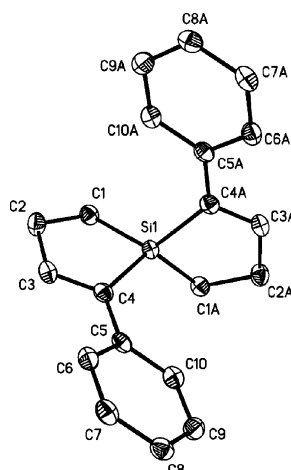
## Spirosilane Derivatives

E. Khan, B. Wrackmeyer,\*

R. Kempe ..... 5367–5372

Combination of 1,2-Hydroboration and 1,1-Organoboration: A Convenient Route to 5-Silaspiro[4.4]nona-1,6-diene Derivatives

**Keywords:** Silanes / Spiro compounds / Hydroboration / Organoboration / NMR spectroscopy



Dialkyn-1-yl(divinyl)silanes react with 9-borabicyclo[3.3.1]nonane (9-BBN) by 1,2-hydroboration followed by intramolecular 1,1-organoboration to give 5-silaspiro[4.4]nona-1,6-diene derivatives. Protodeborylation with excess acetic acid affords the respective spirosilanes bearing substituents only in 1,6-positions. Multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR) and X-ray structural analysis served for the characterization of the new spirosilanes.

## Vanadates in Ionic Liquids

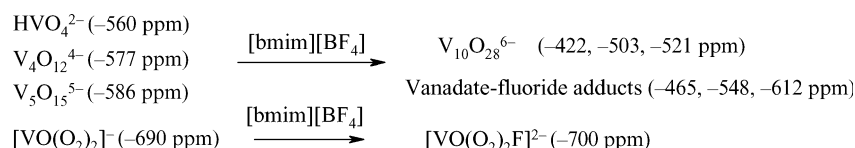
I. Bányai, V. Conte,\* L. Pettersson,

A. Silvagni ..... 5373–5381

On the Nature of  $\text{V}^{\text{V}}$  Species in Hydrophilic Ionic Liquids: A Spectroscopic Approach

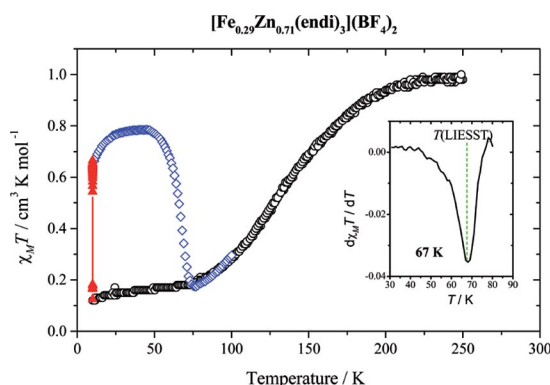


**Keywords:** Vanadates / Ionic liquids / NMR spectroscopy / Hydrogen peroxide



Heteronuclear NMR experiments, in particular  $^{51}\text{V}$ , were performed with the aim to elucidate the nature of vanadates and per-

oxovanadates in hydrophilic ionic liquids, that is,  $[\text{bmim}][\text{BF}_4]$ ,  $[\text{bmim}][\text{TfO}]$  and  $[\text{bdmim}][\text{BF}_4]$ .



Thermal spin transition and Light-Induced Excited Spin State Trapping (LIESST) studies have been undertaken on a series of zinc-diluted polymeric chain iron(II)

complexes. The relationship between  $T(\text{LIESST})$  and dilution by zinc(II) on these systems is discussed.

C. Baldé, C. Desplanches,

M. Grunert, Y. Wei, P. Gülich,

J.-F. Létard\* ..... 5382–5389

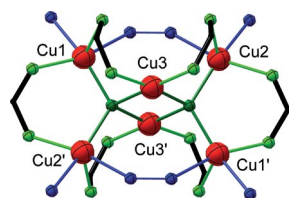
Influence of Metal Dilution on the Light-Induced Spin Transition in Two 1D Chain Compounds:  $[\text{Fe}_x\text{Zn}_{1-x}(\text{btzp})_3](\text{BF}_4)_2$  and  $[\text{Fe}_x\text{Zn}_{1-x}(\text{endi})_3](\text{BF}_4)_2$  {btzp = 1,2-Bis-(tetrazol-1-yl)propane and endi = 1,2-Bis-(tetrazol-1-yl)ethane}

**Keywords:** Iron / Magnetic properties / Spin crossover / Photomagnetism / Dilution effects

# CONTENTS

## Compartmental Ligand Scaffolds

A. Sachse, G. Noël, S. Dechert,  
S. Demeshko, A. Honecker, A. Alfonsov,  
V. Kataev, F. Meyer\* ..... 5390–5396



Using pyrazolate ligands with appended bulky imine donor side arms, novel hexanuclear Cu<sup>II</sup> complexes with an unusual {Cu<sub>6</sub>(μ<sub>4</sub>-O)<sub>2</sub>}-bitetrahedral core were obtained, and their structures determined by X-ray crystallography. Magnetic and high-field EPR data reveal an overall  $S = 0$  ground state with the first excited triplet at  $\Delta E \approx 95 \text{ cm}^{-1}$ .

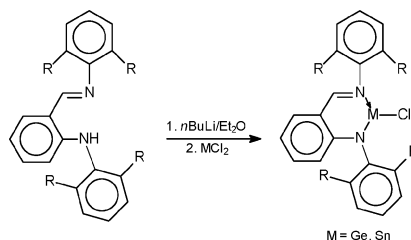


Bulky Pyrazolate-Based Compartmental Ligand Scaffolds: Encapsulation of an Edge-Sharing Cu<sub>6</sub>O<sub>2</sub> Bitetrahedral Core

**Keywords:** Oligonuclear complexes / N ligands / Copper / μ<sub>4</sub>-Oxo ligands / Magnetic properties

## Divalent Group 14 Species

A. Mcheik, N. Katir, A. Castel,\*  
H. Gornitzka, S. Massou, P. Rivière,\*  
T. Hamieh ..... 5397–5403



The anilido–imine ligand has proved to be particularly effective in the stabilization of divalent group 14 compounds into their monomeric form. NMR spectroscopy and X-ray analysis highlight the perfect chelation of the ligands and the formation of a three-coordinate metal. These complexes preserve their specific reactivity of low-coordinate group 14 species.



Germynes and Stannylenes with Chelating Anilido–Imine Ligands: Syntheses, Structures and Reactivity

**Keywords:** Germanium / Tin / N ligands / Chelates

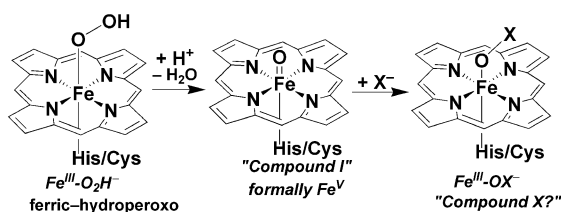
## Heme Peroxidases

R. Silaghi-Dumitrescu\* ..... 5404–5407



Halide Activation by Heme Peroxidases: Theoretical Predictions on Putative Adducts of Halides with Compound I

**Keywords:** Porphyrinoids / Density functional calculations / Enzyme models / Structure–activity relationships



DFT results on models of the Fe<sup>III</sup>–OX and Fe<sup>III</sup>–HOX (X = halogen) adducts of chloroperoxidase and myeloperoxidase are reported. The O–X bonds are very weak, and a ‘caged’ adduct, with a Fe<sup>III</sup> species

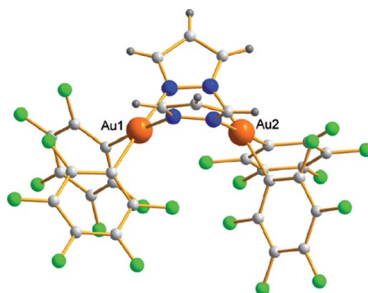
close to the oxidized halide, is a likely alternative for the intermediate in CPO and MPO. The presence of a *trans* axial thiolate or imidazole ligand appears to have an effect on halide activation.

## Pyrazolate Gold Complexes

O. Crespo, M. Concepción Gimeno,\*  
P. G. Jones, A. Laguna, M. Naranjo,  
M. D. Villacampa ..... 5408–5417

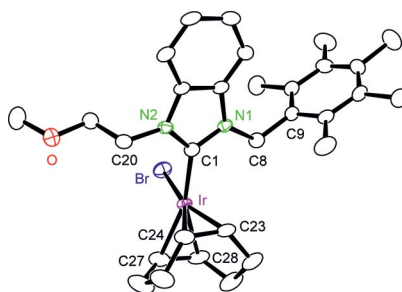
Coordination Behaviour of Gold and Silver Towards Pyrazole Ligands

**Keywords:** Gold / Silver / N ligands / Bridging ligands



Several gold(I), gold(III) and silver(I) complexes with pyrazole or pyrazolate ligands have been synthesized and structurally characterized.

Iridium and rhodium complexes with symmetrically and unsymmetrically substituted benzimidazolin-2-ylidene ligands like **3a** were prepared and studied in the catalytic transfer hydrogenation of acetophenone and cyclohexanone by using isopropyl alcohol as the hydrogen source.



**3a**

**H. Türkmen,\* T. Pape, F. E. Hahn,\***

**B. Çetinkaya ..... 5418–5423**

Efficient Transfer Hydrogenation Using Iridium and Rhodium Complexes of Benzannulated N-Heterocyclic Carbenes

**Keywords:** Carbenes / Rhodium / Iridium / Hydrogenation / Homogeneous catalysis

\* Author to whom correspondence should be addressed.

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

If not otherwise indicated in the article, papers in issue 33 were published online on November 12, 2008