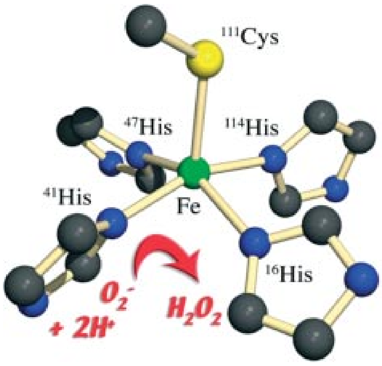
MICROREVIEW

Functional Metalloenzyme Models

Synthetic models of the iron enzyme superoxide reductase (SOR) are described that, in combination with biochemical studies, are beginning to generate a clearer picture of the biological mechanism of superoxide reduction. Iron–peroxo species, trapped at low temperatures, are shown to be viable SOR intermediates, and provide key spectroscopic parameters for their identification.



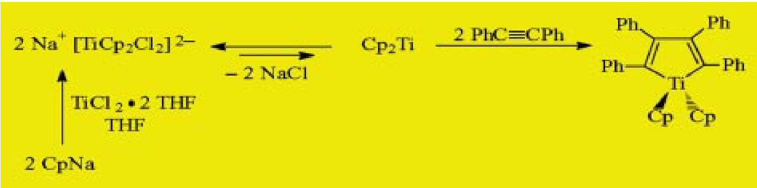
L. M. Brines, J. A. Kovacs* 29–38

Understanding the Mechanism of Superoxide Reductase Promoted Reduction of Superoxide

Keywords: Bioinorganic chemistry / Metalloenzymes / Thiolate-ligated nonheme iron / Superoxide

SHORT COMMUNICATIONS

Carbenoid Character of Titanocene(II)



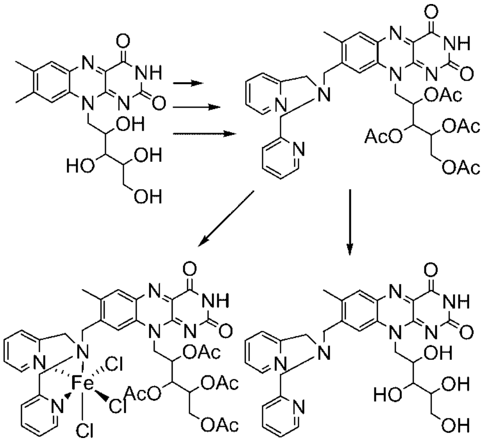
Titanocene(II) has been directly synthesized by the interaction of THF-soluble titanium(II) chloride with two equivalents of cyclopentadienylsodium in THF solution at 0°C. Because of the instability of titanocene(II), it was trapped in high yield as 1,1-bis(cyclopentadienyl)-2,3,4,5-tetraphenyltitanacyclopentadiene with diphenylacetylene.

J. J. Eisch,* A. A. Adeosun,
J. M. Birmingham 39–43

The Transient Titanocene(II): Direct Synthesis from Solvated Titanium(II) Chloride and Cyclopentadienylsodium and Ensuing Interception with Diphenylacetylene as 1,1-Bis-(cyclopentadienyl)-2,3,4,5-tetraphenyltitanacyclopentadiene

Keywords: Titanocene / Wilkinson metallocene synthesis / Epititanation

Chelates Linked to Vitamin B2



The preparation of the 8α-[bis(2-pyridylmethyl)amine]-*N*-Ac$_4$riboflavin ligand is reported. The trichloroferric complex has been prepared, and together with the low potential reduction wave of the flavin moiety, the presence of a reversible Fe^{III}/Fe^{II} couple at a higher potential is observed. The deacetylated ligand 8α-[bis-(2-pyridylmethyl)amine]-*N*-riboflavin can easily be obtained.

N. K. Thallaj, D. Mandon,*
K. A. White 44–47

The Design of Metal Chelates with a Biologically Related Redox-Active Part: Conjugation of Riboflavin to Bis(2-pyridylmethyl)amine Ligand and Preparation of a Ferric Complex

Keywords: N ligands / Iron complexes / Riboflavin / Electrochemistry / Electron mediators

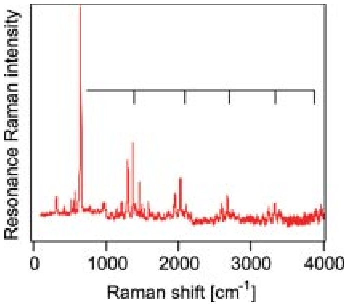
CONTENTS

Resonance Raman Overtones

R. Beaulac, A. B. P. Lever,* C. Reber* 48–52

Resonance Raman Spectroscopy with Overtones Involving Metal-Ligand and Ligand-Centered Modes in (*o*-Benzoquinonediimine)ruthenium(II) Complexes

Keywords: Raman spectroscopy / Ruthenium complexes / Charge transfer / Density functional calculations / Luminescence



Resonance Raman spectra with visible excitation wavelengths show distinct resonance enhancements and intense overtone and combination bands resulting from charge-transfer excitations. Assignments of fundamental bands are based on theoretical spectra obtained from DFT calculations.

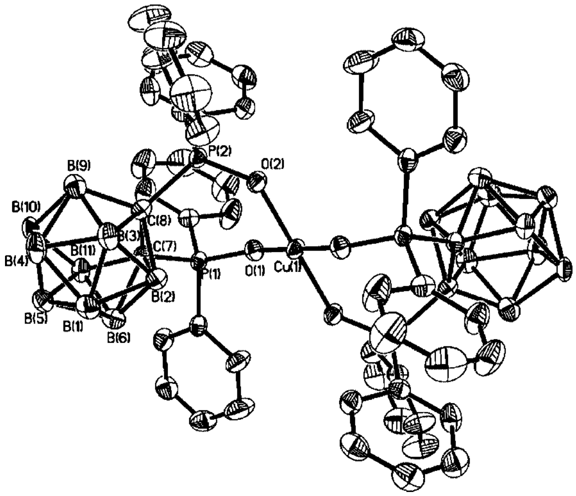
FULL PAPERS

Phosphorylcarborane Complexes

J. M. Dou,* D. P. Zhang, D. C. Li, D. Q. Wang 53–59

Synthesis and Crystal Structure of Three Carborane Complexes, [M{7,8-(OPPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}$_2$] (M = Cu, Zn) and [Ni(thf)-{7,8-(OPPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}$_2$]·thf, and Two Carborane Compounds, 1-(OPPh$_2$)-2-(PPh$_2$)-1,2-C$_2$B$_{10}$H$_{10}$ and H[7,8-(OPPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]·0.25C$_2$H$_5$OH

Keywords: Cu complexes / Zn complexes / Ni complexes / Carborane complexes / Oxidation / Degradation



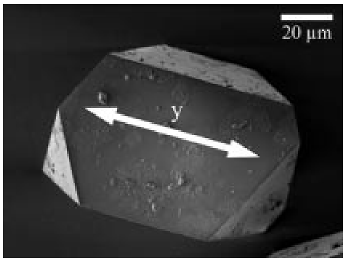
Three new carborane complexes containing a phosphoryl-*nido*-carborane ligand were synthesized by the reactions of 1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ with three inorgnic compounds in ethanol in air. Two other phosphoryl compounds were also obtained through the oxidation of the *closo* ligand in air.

Supported Membranes

M. Arnold,* P. Kortunov, D. J. Jones, Y. Nedellec, J. Kärger, J. Caro 60–64

Oriented Crystallisation on Supports and Anisotropic Mass Transport of the Metal-Organic Framework Manganese Formate

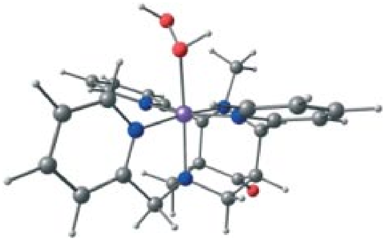
Keywords: Organic–inorganic hybrid composites / Membranes / Anisotropic mass transport / Oriented crystallisation / Manganese



The MOF manganese formate was examined regarding its ability to be applied in supported gas-separating membranes. For this purpose, the anisotropic mass transport of methanol in the MOF has been investigated by IFM, proving a 1D channel system. Additionally, the oriented crystallisation of the manganese formate on different supports has been investigated by XRD and SEM.

O–O Bond Cleavage

Density functional theory reveals two distinct pathways for the decomposition of an $LFe^{II}(H_2O_2)$ complex to $LFe^{IV}(O)$ and water. One pathway involves initial O–O bond homolysis followed by hydrogen-atom transfer while in the other proton transfer precedes O–O bond heterolysis. The barriers to the two processes are rather similar, suggesting that subtle changes in the identity of L or in the reaction conditions may cause a complete change in mechanism.



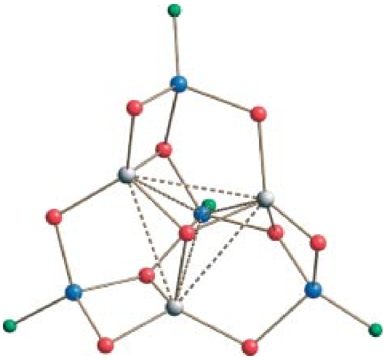
A. E. Anastasi, A. Lienke, P. Comba, H. Rohwer, J. E. McGrady* 65–73

Competing Radical and Non-Radical Pathways for the Decomposition of $LFe^{II}(H_2O_2)$ Complexes: a Density Functional Study

Keywords: Density functional calculations / Oxido ligands / O–O activation / Electronic structure / Transition states

Copper-Iron Chalcogenide Clusters

Reactions of mixtures of copper and iron salts with $PhSeSiMe_3$ led in the prescence of phosphanes or ammonium salts to the formation of mixed copper-iron selenolate cluster molecules. Heating of the clusters results in the formation of mixtures of binary Cu_2Se and ternary $CuFeSe_2$.



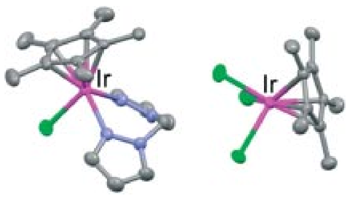
A. Eichhöfer,* D. Fenske, J. Olkowska-Oetzel 74–79

Synthesis and Structure of $[nPr_3N(CH_2)_6NnPr_3][CuFe_3Br_3(SePh)_6]$, $[Cu_5Fe(SePh)_7(PPh_3)_4]$ and $[Cu_4Fe_3(SePh)_{10}(PPh_3)_4]$

Keywords: Iron / Copper / Selenium / Cluster compounds

Bimetallic Ion Pairs

Complexes of the type [Cp*MCl(N–N)][X] (M = Rh and Ir) have been synthesised, where N–N is a series of bidentate ligands with sp^2 N-donors and X = $[Cp^*MCl_3]^-$, Cl^- or BF_4^-.

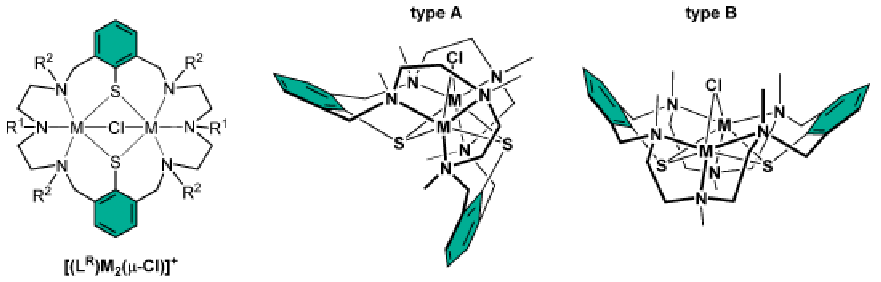


D. F. Kennedy, B. A. Messerle,* M. K. Smith 80–89

Synthesis of Cp* Iridium and Rhodium Complexes Containing Bidentate sp^2-N-Donor Ligands and Counter-Anions $[Cp^*MCl_3]^-$

Keywords: Iridium(III) / Rhodium(III) / N-donor ligands / Cyclopentadienyl ligands

Ligand Conformation



The effect of *N*-alkylation on the coordination properties of macrocyclic N_6S_2 ligands has been examined. The ligand conformation adopted depends on the type of the coligand, the metal ion radius, and the *N*-alkylation grade.

M. Gressenbuch, B. Kersting* 90–102

Synthesis and Characterisation of Dinuclear Nickel(II) and Cadmium(II) Complexes of *N*-Alkylated Derivatives of Hexaazadithiophenolate Macrocycles

Keywords: Macrocyclic ligands / N ligands / S ligands / Nickel / Cadmium

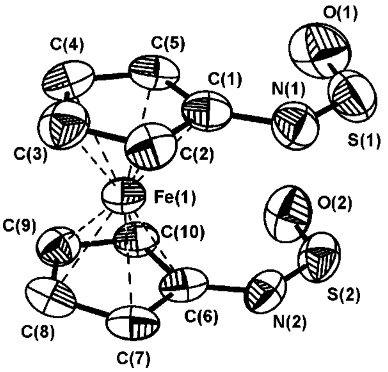
CONTENTS

(Sulfinylamino)ferrocenes

B. Wrackmeyer,* E. V. Klimkina, W. Milius, M. Siebenbürger, O. L. Tok, M. Herberhold 103–109

Ferrocenes Bearing Sulfinylamino Groups

Keywords: Ferrocenes / Sulfinylamine pendant groups / Electronic structure



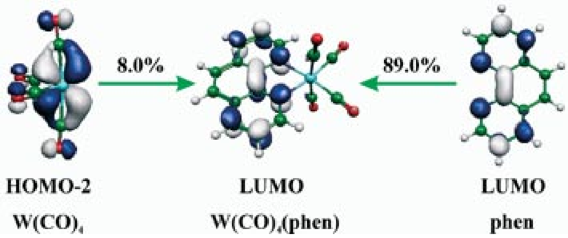
Three new (sulfinylamino)ferrocenes [1,1'-bis(sulfinylamino)ferrocene, 6-amino-1-sulfinylaminoferrocene, 1-sulfinylamino-6-(trimethylsilylamino)ferrocene] were prepared and characterised by X-ray structural analysis in the solid state, and by ^{1}H, ^{13}C, ^{14}N, ^{15}N, ^{29}Si and ^{57}Fe NMR spectroscopy in solution.

Structure–Back Bonding Correlation

C. Makedonas, C. A. Mitsopoulou* 110–119

W(CO)$_4$(diimine) Structure Revised – Correlating Structure to π* Back-Bonding

Keywords: Tungsten / Pi interactions / N ligands / Carbonyls / Ligand effects



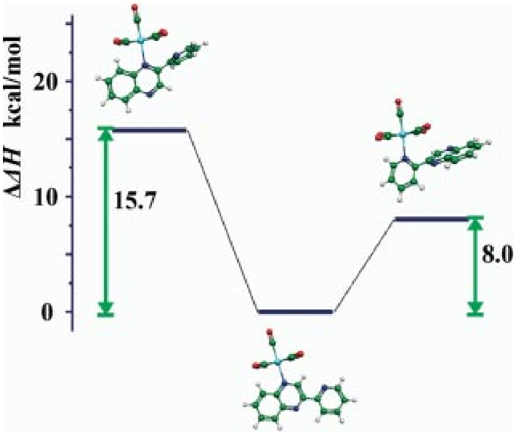
DFT calculations carried out on a series of W(CO)$_4$(diimine) compounds reveal that the best indices for the extent of back donation are both the deviation of C–W–C and O–C–W angles from orthogonality and linearity, respectively. This is quantitatively described by a structure–properties relation.

Conformation and Electronic Structure

C. Makedonas, I. Veroni, C. A. Mitsopoulou* 120–131

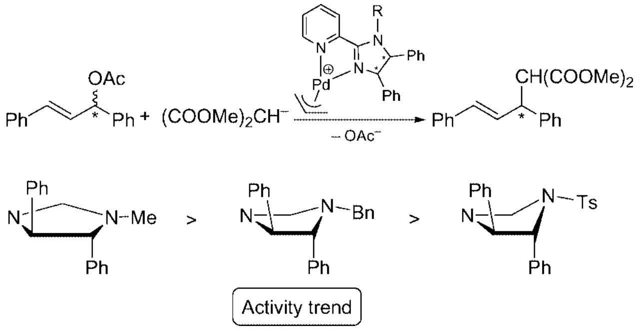
Pentacarbonyl[2-(2′-pyridyl)quinoxaline-κN^4]tungsten: A Combined Study of Its Conformational and Electronic Structure Based on Experimental and DFT-TDDFT Data

Keywords: Pentacarbonyl complexes / Monodantatepyridyl)quinoxaline / Tungsten / TD-DFT calculations / Pi stacking



The title compound is isolated en route to photolytic W(CO)$_4$pq chelate ring closure and it is the first example where the pq ligand is coordinated in a monodentate fashion. The preference of the coordinated nitrogen atom is elucidated both experimentally by spectroscopic and crystallographic methods and theoretically by means of DFT and TDDFT calculations.

Pd/Imidazolines in Allylic Alkylations



Palladium/chiral imidazolylpyridines systems were tested in allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene and 3-acetoxy-1-phenyl-1-propene, paying particular attention to the influence of the amine nitrogen hybridisation on their catalytic behaviour. Allylpalladium intermediates containing phenylallyl groups were synthesised and fully characterised both in solution (NMR) and the solid state (single-crystal X-ray diffraction).

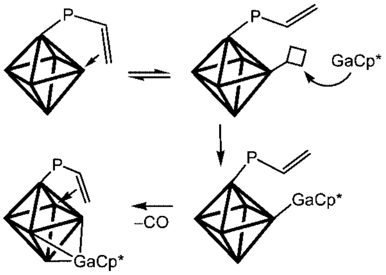
A. Bastero, A. F. Bella, F. Fernández,
S. Jansat, C. Claver,* M. Gómez,*
G. Muller, A. Ruiz, M. Font-Bardía,
X. Solans .... **132−139**

First Allylpalladium Systems Containing Chiral Imidazolylpyridine Ligands − Structural Studies and Catalytic Behaviour

Keywords: Palladium / Chiral imidazolines / Catalysis / Allylic alkylation / Intermediates / Heterocycles

Hemilabile Clusters

Reaction of the $Rh_6(CO)_{14}(Ph_2PCH{=}CH_2)$ cluster containing hemilabile diphenylvinylphosphane with GaCp* (Cp* = C_5Me_5) affords two novel heterometallic clusters, $Rh_6(CO)_{13}(\mu,\kappa^3\text{-}Ph_2PC_2H_3)(\mu_3\text{-}GaCp^*)$ and $Rh_6(CO)_{13}(\kappa^1\text{-}Ph_2PC_2H_3)(\mu_3\text{-}GaCp^*)_2$.

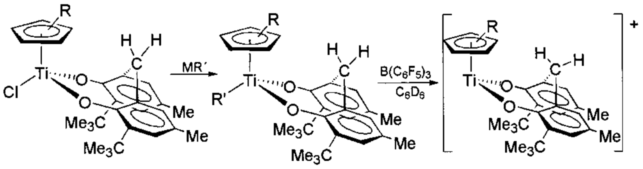


E. V. Grachova, G. Linti, H.-G. Stammler,
B. Neumann, S. P. Tunik,*
H. Wadepohl .... **140−146**

Reactions of GaCp* with a Hemilabile Derivative of $Rh_6(CO)_{16}$ − Synthesis and Structural Characterization of Two Novel Heterometallic Clusters: $Rh_6(CO)_{13}(\mu,\kappa^3\text{-}Ph_2PC_2H_3)(\mu_3\text{-}GaCp^*)$ and $Rh_6(CO)_{13}(\kappa^1\text{-}Ph_2PC_2H_3)(\mu_3\text{-}GaCp^*)_2$

Keywords: Cluster compounds / Heterometallic complexes / Phosphane ligands

Ti Complexes in Polymerisation



The synthesis of 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxido)titanium complexes is described. Structural data are derived from DFT methods and X-ray diffraction studies. The complexes polymerise α-olefins when activated with MAO or $[Ph_3C][B(C_6F_5)_4]$, while they are inactive in the presence of $B(C_6F_5)_3$. Stoichiometric reactions with Lewis acids were studied by NMR spectroscopy.

M. González-Maupoey, T. Cuenca,*
L. M. Frutos, O. Castaño, E. Herdtweck,
B. Rieger .... **147−161**

Alkylmono(cyclopentadienyl)titanium Complexes Containing the 2,2′-Methylenebis(6-*tert*-butyl-4-methylphenoxido) Ligand − Studies on the Nature of the Catalytic Species Present in α-Olefin Polymerisation Processes

Keywords: Titanium / Chelates / Olefin polymerisation / Density functional calculations

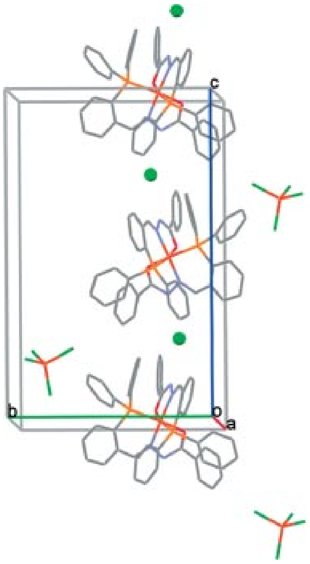
CONTENTS

Iron Complexes with Tridentate Ligands

**P. Pelagatti,* A. Bacchi, M. Balordi,
A. Caneschi, M. Giannetto, C. Pelizzi,
L. Gonsalvi, M. Peruzzini,
F. Ugozzoli 162–171**

A Ligand-Driven Geometry Switch in Octahedral and Trigonal-Bipyramidal Iron Complexes Containing (H)PNO and PNN Ligands

Keywords: Iron / N,P ligands / Ligand effects



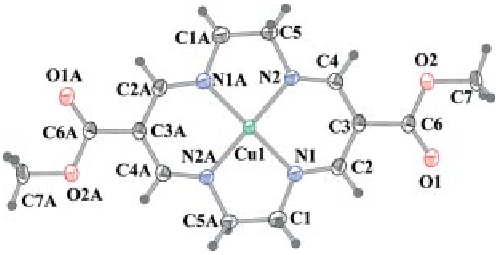
Complexation reactions of Fe^{II} and Fe^{III} salts with the tridentate ligands (H)PNO and PNN are reported. (H)PNO leads to the formation of the octahedral cation *fac*-$[Fe\{\kappa^3\text{-(H)PNO}\}_2]^{n+}$ ($n = 2$ or 3), while PNN leads to the formation of the trigonal-bipyramidal complex [*mer*-$Fe(\kappa^3\text{-PNN})Cl_2$].

Tetraazamacrocyclic Complexes

**A. Rybka, R. Koliński, J. Kowalski,
R. Szmigielski, S. Domagała, K. Woźniak,*
A. Więckowska, R. Bilewicz,*
B. Korybut-Daszkiewicz* 172–185**

Tuning the Properties of Neutral Tetraazamacrocyclic Complexes of Copper(II) and Nickel(II) for Use as Host–Guest Compounds with Bismacrocyclic Transition Metal Cations

Keywords: Macrocyclic ligands / Copper / Nickel / Cyclic voltammetry / Template synthesis



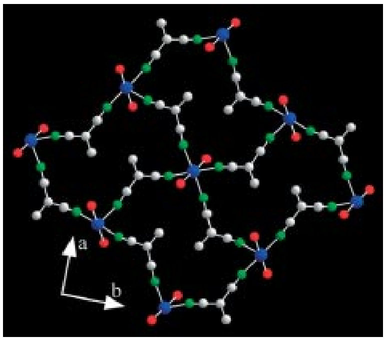
Deviations from planarity increase with increasing size of the tetraazamacrocyclic ligands and their neutral and protonated 14-, 15-, and 16-membered complexes of Cu^{II} and Ni^{II}. As a consequence, the donor properties are weaker, the redox potential is shifted towards more positive values, and contribution of chemical reactions can also be observed. The formation of host–guest complexes between the strongest metal-containing donors and transition-metal-containing bismacrocyclic acceptors of suitable size is proved in solution and the gas phase by voltammetric and ESI MS methods. The transition metal building blocks described in this contribution could be applied in the synthesis of new redox-active rotaxane and catenane systems.

Coordination Polymers

**S. Benmansour, F. Setifi, S. Triki,*
J.-Y. Salaün, F. Vandevelde, J. Sala-Pala,
C. J. Gómez-García,* T. Roisnel 186–194**

New Multidimensional Coordination Polymers with μ_2- and μ_3-dcno Cyano Carbanion Ligand $\{dcno^- = [(NC)_2CC(O)O(CH_2)_2OH]^-\}$

Keywords: Cyano carbanions / Bridging ligands / Coordination polymers / Multidimensional networks / Magnetic properties



This study involves the design of multidimensional transition metal compounds with the cyano carbanion $dcno^-$ acting as μ_2- and μ_3-bridging ligand. The bonding affinity and flexibility of the cyano carbanion ligand towards transition metal ions are clearly illustrated.