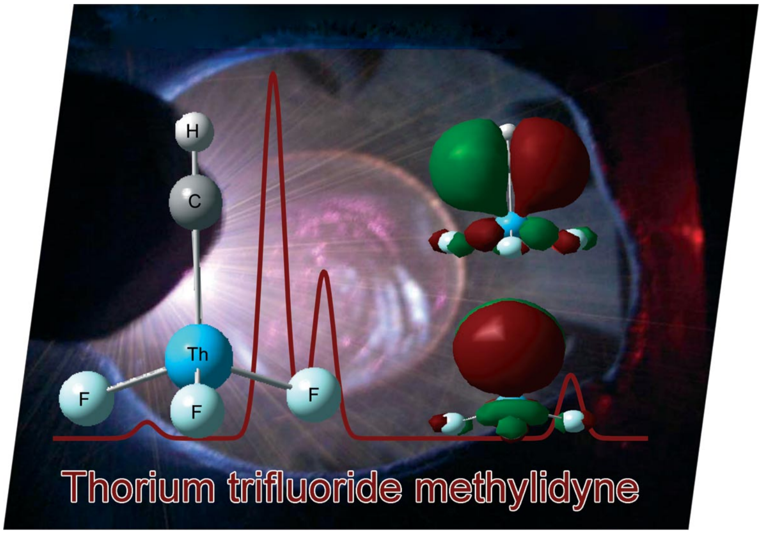
COVER PICTURE

The cover picture shows the $HC{\div}ThF_3$ complex product of the Th and CHF_3 reaction. The two singly occupied SOMO orbitals on the right reveal a strong overlap with the thorium center. A portion of the DFT-predicted infrared spectrum for this complex is illustrated over the background image of a typical laser-ablation experiment in progress in our vacuum chamber. Details are discussed in the article by J. T. Lyon and L. Andrews on p. 1047ff.



CONTENTS

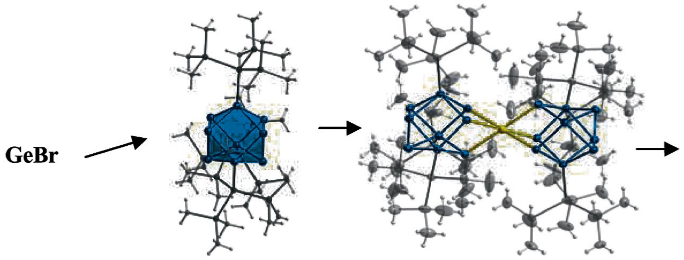
MICROREVIEW

Germanium Clusters

A. Schnepf* **1007–1018**

Metalloid Cluster Compounds of Germanium: Synthesis – Properties – Subsequent Reactions

Keywords: Germanium / Metalloid clusters / Metals / Intermediates



Metalloid cluster compounds represent ideal model compounds that provide an insight into the area between the molecular and the solid state. This review describes recent achievements in the synthesis of metalloid cluster compounds of germanium. Besides different ligand systems applied in synthesis, first examples of subsequent reactions of such cluster compounds are presented.

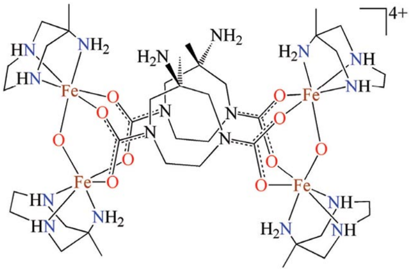
SHORT COMMUNICATIONS

Polynuclear Polycarbamate Complex

C. Neis, T. Weyhermüller, E. Bill, S. Stucky, K. Hegetschweiler* **1019–1021**

Carbamates of Polyamines – Versatile Building Blocks for the Construction of Polynuclear Metal Complexes

Keywords: Carbon dioxide / Chelates / Iron / Mössbauer spectroscopy / N ligands / O ligands



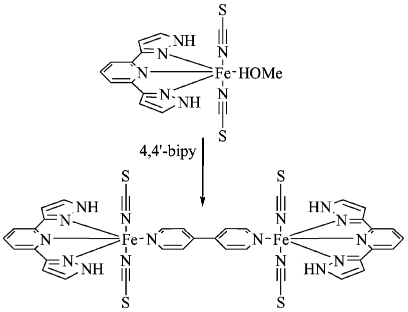
Polynuclear metal complexes can be readily prepared by the reaction of a transition metal cation with a polyamine which has been partially converted into a polycarbamate by aeration with CO_2. The complex shown is an illustrative example for this method.

Spin-Transition Dinuclear Complexes

D. Fedaoui, Y. Bouhadja, A. Kaiba, P. Guionneau, J.-F. Létard,* P. Rosa* **1022–1026**

Complexation of 2,6-Bis(3-pyrazolyl)pyridine–Bis(thiocyanato)iron(II) with a Bridging 4,4′-Bipyridine: A New Example of a Dinuclear Spin Crossover Complex

Keywords: Spin crossover / Magnetic properties / Iron / Dinuclear complexes

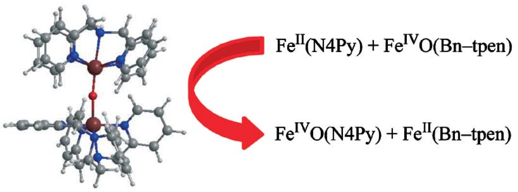


Investigation of the coordination behavior of 2,6-bis(3-pyrazolyl)pyridine–bis(thiocyanato)iron(II) towards bridging ligands led to the discovery of a novel dinuclear complex showing spin-crossover. Chemical and structural characterization and a first report of physical properties are presented.

Enzyme Models

S. P. de Visser,* Y.-M. Lee, W. Nam* 1027–1030

Theoretical Investigation on the Mechanism of Oxygen Atom Transfer between Two Non-Heme Iron Centres



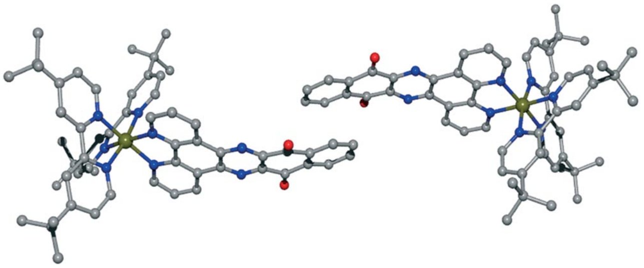
Density functional theory calculations on the oxygen transfer reaction between two non-heme iron centres revealed that an intermediate complex with the oxygen atom sandwiched between the two iron clusters is a stable entity with almost equal Fe–O bonds. The orbital occupation and group spin densities show that in the formation of the diiron complex, an electron transfer has taken place to form two Fe^{III} ions. Nevertheless, the complex can dissociate into two different oxidoiron complexes, but the most stable and exothermic process leads to $Fe^{IV}(O)(N4Py)$ and $Fe^{II}(Bn–tpen)$ products. Thus, the mechanism of oxygen atom transfer between two non-heme iron complexes takes place via this stable (μ-oxido)-diiron intermediate.

Keywords: Bioinorganic chemistry / Enzyme models / Non-heme iron enzymes / Density functional calculations / Oxygen

Photocatalysis

S. Rau,* M. Schwalbe, S. Losse, H. Görls, C. McAlister, F. M. MacDonnell, J. G. Vos 1031–1034

Photoinduced Ligand Transformation in a Ruthenium Polypyridophenazine Complex



Irradiation of a ruthenium polypyridyl complex in the presence of oxygen leads to the selective oxidation of a complex-bound benzodipyridophenazine ligand to a quinone. The corresponding tetraazatetrapyridopentacene complex is not oxidized under the same conditions.

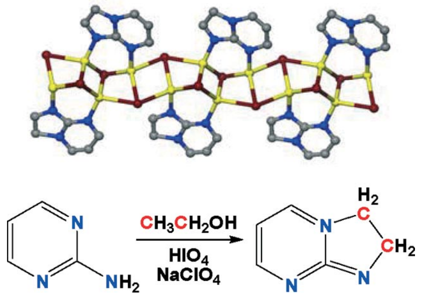
Keywords: Ruthenium compounds / Nitrogen heterocycles / Photooxidation / Photochemistry

Luminescent Cu Coordination Polymers

M. Bi, G. Li, J. Hua, Y. Lin, J. Cao, Z. Shi,* S. Feng 1035–1038

Synthesis of Copper Halide Coordination Polymers with Ligands Formed by In Situ Cyclization of 2-Aminopyrimidine and Ethanol

Two luminescent copper halide coordination polymers, $(CuCl)_3C_6H_7N_3$ and $(CuI)_2C_6H_7N_3$ ($C_6H_7N_3$ = 2,3-dihydroimidazo[1,2-*a*]pyrimidine), were assembled under solvothermal conditions starting with $CuCl_2·2H_2O$, $HIO_4·2H_2O$, $NaClO_4·H_2O$, $NaHCO_3$, 2-aminopyrimidine, and ethanol. The nitrogen heterocyclic 2,3-dihydroimidazo[1,2-*a*]pyrimidine ligand was synthesized by an in situ reaction.



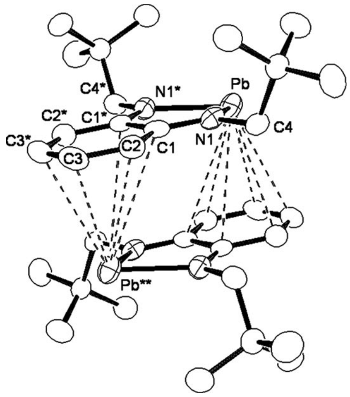
Keywords: Coordination polymers / Copper / Halides / In situ cyclization

N-Heterocyclic Plumbylenes

F. E. Hahn,* D. Heitmann, T. Pape 1039–1041

Synthesis and Characterization of Stable N-Heterocyclic Plumbylenes

Benzannulated N-heterocyclic plumbylenes have been prepared by the transamination reaction between *N*,*N'*-dialkyl-1,2-diaminobenzenes and bis[bis(trimethylsilyl)amido]lead(II). The N-heterocyclic plumbylenes exist in the solid state as dimers with intermolecular $[\eta^2-(C_6H_4)\cdots Pb]_2$ or $[\eta^6-(C_6H_4)\cdots Pb]_2$ contacts.



Keywords: Lead / N-Heterocyclic plumbylenes / Carbene analogues / X-ray structure determination

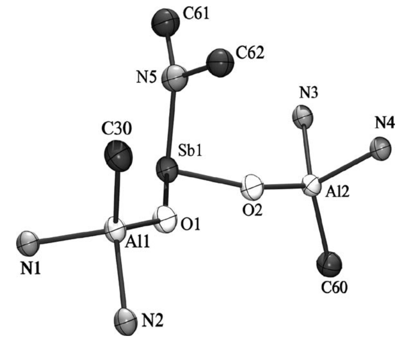
CONTENTS

Main Group Metal Oxides

S. Singh, S. Nembenna, V. Jancik, H. W. Roesky* 1042–1044

Antimony Amide Oxide and Antimony Chloride Oxide Wrapped in an Organoaluminum Framework

Keywords: Aluminum / Antimony / Chloride / Trimetallic compounds / Oxide



Syntheses and characterization of novel antimony amide oxide and antimony chloride oxide each surrounded by two organoaluminum units are reported. The adjacent figure shows the molecular structure the core of the antimony amide oxide compound.

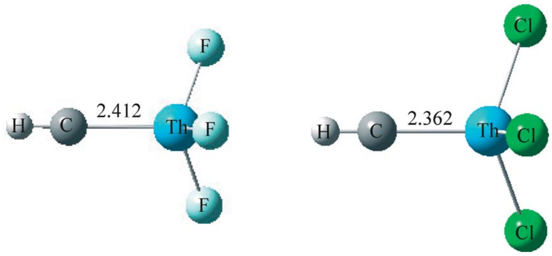
FULL PAPERS

(Methylidyne)thorium Trifluoride

J. T. Lyon, L. Andrews* 1047–1058

Reactions of Thorium Atoms with Polyhalomethanes: Infrared Spectra of the $CH_2{=}ThX_2$, $HC{\div}ThX_3$, and $XC{\div}ThX_3$ Molecules

Keywords: Thorium / Matrix infrared spectra / Density functional calculations / Methylidene / Methylidyne



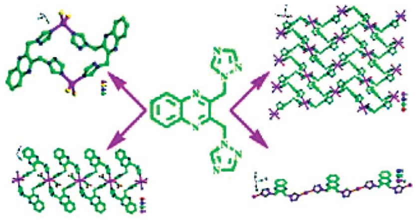
Thorium–carbon bonds: Laser-ablated Th atoms react with haloforms to produce triplet $HC{\div}ThX_3$ complexes that are analogous to those of the Group 4 metals. The electron-deficient C–Th multiple bond is shorter for the Cl than the F substituent.

Counterion Effects

J.-L. Du, T.-L. Hu, J.-R. Li, S.-M. Zhang, X.-H. Bu* 1059–1066

Metal Coordination Architectures of 2,3-Bis(triazol-1-ylmethyl)quinoxaline: Effect of Metal Ion and Counterion on Complex Structures

Keywords: Counterions / Crystal structure / Flexible ligands / Synthesis / Weak interactions / Ligand design



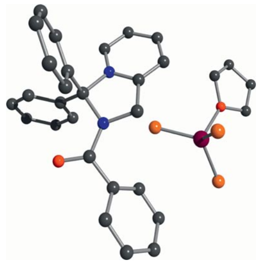
A triazole-based flexible ligand was synthesized and its treatment with Zn^{II}, Cd^{II}, Mn^{II}, and Ag^{I} salts afforded seven metal complexes with 0D, 1D, and 2D structures. The results indicate that metal ions and counteranions play important roles in crystal engineering. The properties of these complexes were also investigated.

Functionalized (2-Pyridylmethyl)amines

C. Koch, M. Kahnes, M. Schulz, H. Görls, M. Westerhausen* 1067–1077

Lithium and Zinc Complexes of *C*- and *N*-Functionalized (2-Pyridylmethyl)amines

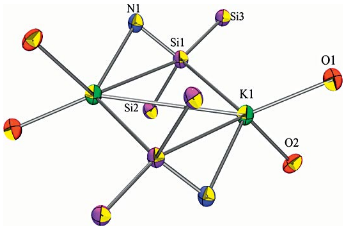
Keywords: Lithium / Zinc / Amines / Diketonates



(2-Pyridylmethyl)amines are substituted with oxygen-containing side arms thus offering a variety of coordination pockets. Alkylzinc and aminozinc fragments bind preferably to the N-donor bases whereas lithium cations show their oxophilicity. Blocking of the N donor atoms leads to solvent-separated ions as shown in the picture (N blue, O red, Cl orange, Zn violet, C black).

Aminooligosilyl Anions

$Et_2N(Me_3Si)_2SiK$ was used to synthesize larger aminooligosilanes. Its reaction with group-4 metallocene dichlorides gave the expected products which showed no strong interaction between the amino nitrogen atom and the group-4 metal.



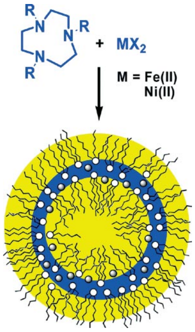
M. Zirngast, J. Baumgartner, C. Marschner* 1078–1087

Preparation, Structure and Reactivity of $Et_2N(Me_3Si)_2SiK$

Keywords: Silicon / Oligosilanes / Aminosilanes / Sandwich complexes

Metalloaggregates

The aggregation behaviour of Ni^{II} and Fe^{II} metalloamphiphiles with the macrocycles 1,4,7-triazacyclanonane (tacn) and 1-oxa-4,7-diazacyclononane (odacn) was studied by means of dynamic light scattering. We found dramatic differences between the resultant aggregates depending on the macrocycle employed and these differences were further examined with atomic force microscopy to substantiate the vesicular structures of the aggregates.



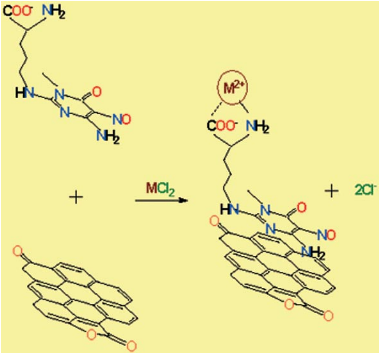
D. Domínguez-Gutiérrez, E. Eiser, C. J. Elsevier* 1088–1094

Amphiphilic Iron(II) and Nickel(II) Complexes Based on Alkylated Diazaoxa- and Triazacyclononane

Keywords: Iron complexes / Nickel complexes / Macrocyclic ligands / Self-assembly / Metalloaggregates

Functionalised Carbon Materials

Anchoring N^{ε}-(4-amino-1-methyl-5-nitroso-1,6-dihydro-6-oxopyrimidin-2-yl)-L-lysine to the graphitic surface of an activated carbon results in an enhancement of the latter's ability to adsorb Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} ions, in agreement with the reactivities of the metal ion/ligand systems.



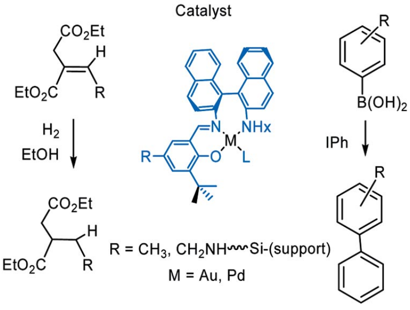
J. García-Martín, M. L. Godino-Salido, R. López-Garzón,* M. D. Gutiérrez-Valero, P. Arranz-Mascarós, H. Stoeckli-Evans 1095–1106

Adsorption of Metal Ions on an Activated Carbon/L-Lysine Derivative Hybrid Compound

Keywords: Adsorption / Ligand design / Transition metals / UV-Vis spectroscopy / Zinc

Heterogenized Au and Pd Complexes

Chiral Schiff base–gold and –palladium complexes were immobilized on ordered mesoporous silica supports (MCM-41), and their ability to catalyse hydrogenation, Suzuki and Sonogashira reactions are compared to that of their homogeneous counterparts. Gold(III) complexes catalyze the homocoupling of arylboronic acids or alkynes, whereas gold(I) and palladium(II) complexes catalyze the corresponding cross-coupling reactions.



C. González-Arellano, A. Corma, M. Iglesias,* F. Sánchez* 1107–1115

Soluble Gold and Palladium Complexes Heterogenized on MCM-41 Are Effective and Versatile Catalysts

Keywords: Gold / Palladium / Hydrogenation / C-C coupling / Supported catalysts / Schiff bases

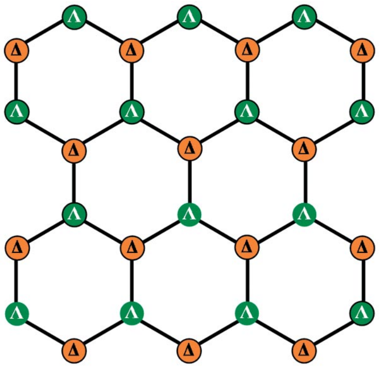
CONTENTS

Phosphorus-Supported Ligands

**V. Chandrasekhar,* R. Azhakar,
B. M. Pandian, J. F. Bickley,
A. Steiner 1116–1124**

A Tunable Coordination Response of the Phosphorus-Based Hexadentate Ligand (S)-P[N(Me)N=CHC$_6$H$_4$-*o*-OH]$_3$ (LH$_3$): Synthesis and Structure of LM (M = Sc, Cr, Mn, Fe, Co, Ga)

Keywords: Tripodal ligands / N,O ligands / Hydrogen bonds / Chiral recognition / Transition metals



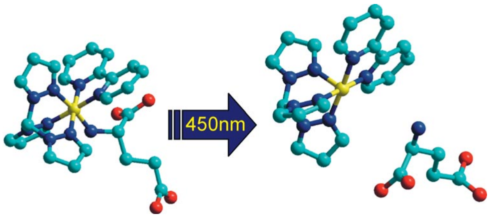
The multidentate ligand (S)P[N(Me)-N=CHC$_6$H$_4$-*o*-OH]$_3$ (LH$_3$) reacts with a number of M^{III} salts to afford neutral mononuclear complexes LM (M = Sc, Cr, Mn, Fe, Co and Ga). All these complexes crystallise as racemic compounds where both the clockwise (Δ) and anticlockwise (Λ) enantiomorphs are present in the crystal structure in an ordered arrangement. All the complexes show supramolecular chiral recognition in their crystal structures; the Δ form recognizes the Λ form by means of intermolecular C–H···O and C–H···S interactions.

Visible-Light Phototriggers

**M. Salierno, C. Fameli,
R. Etchenique* 1125–1128**

Caged Amino Acids for Visible-Light Photo-delivery

Keywords: Caged compounds / Phototriggers / Neurophysiology



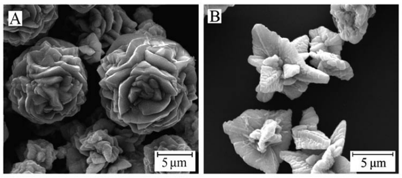
We designed and synthesized a family of caged α-amino acids based on ruthenium bipyridyl complexes that present visible-light photoactivity. Their quantum yield of photorelease at 450 nm is $f = 0.035$, which is about 17 times higher than that of other known phototriggers.

Controlled Growth of Nanocrystals

**D.-W. Deng, J.-S. Yu,*
Y. Pan 1129–1134**

Small Molecule-Controlled Spontaneous Growth of Rose-Like Se Crystals at Room Temperature

Keywords: Selenium / Rose-like / Small molecules / Spontaneous growth / Crystal growth



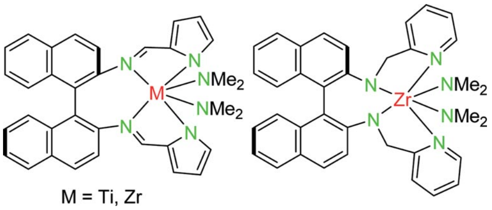
Rose- and orchid-like Se crystals were synthesized in Na$_2$Se aqueous solutions containing thioglycerol and mercaptamine, respectively, in the dark at room temperature. An interesting formation process for Se crystals from initial Se monomers to amorphous Se spheres, and to the final rose-like Se complex structures was observed.

Asymmetric Catalysis

L. Xiang, H. Song, G. Zi* 1135–1140

Synthesis, Structure, and Catalytic Activity of Ti^{IV} and Zr^{IV} Complexes Derived from (*R*)-2,2′-Diamino-1,1′-binaphthyl-Based N$_4$-Donor Ligands

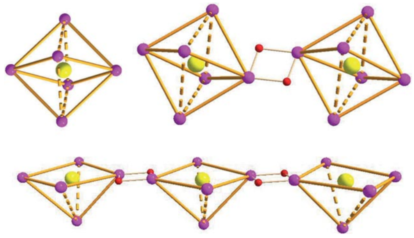
Keywords: Titanium / Zirconium / N ligands / Asymmetric catalysis / Hydroamination



A series of chiral organotitanium and organozirconium amides was prepared. The zirconium amides are active catalysts for the asymmetric hydroamination/cyclization of aminoalkenes, and cyclic amines were obtained in good-to-excellent yields with moderate *ee* values; the titanium amides were not active under the reaction conditions.

Magnetic Cluster Compounds

Three polynuclear copper(II) clusters were obtained by controlling the proportion of Cu^{II} ions to L-alanine. The [NaCu$_6$] cluster in **1** can be described as a Na-centered octahedron and in **2** as an octahedral dimer linked by two carboxylate oxygen atoms. Complex **3** is a chain composed of incomplete octahedron [NaCu$_5$] units linked by two carboxylate oxygen atoms.



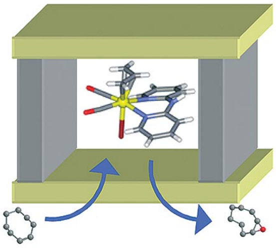
S.-M. Hu, S.-C. Xiang, J.-J. Zhang, T.-L. Sheng, R.-B. Fu, X.-T. Wu* **1141–1146**

Synthesis, Structure, and Magnetic Properties of Three Chiral Sodium-Centered Polynuclear Copper(II) Clusters with L-Alanine

Keywords: Copper / Alanine / Cluster compounds / Octahedral structure / Magnetic properties

Immobilized Mo^{II} Complexes

η^3-Allyldicarbonyl complexes of Mo^{II} were encapsulated in a pillared clay or a porous clay heterostructure and allowed to react with bidentate diimine ligands. A new complex [MoBr(CO)$_2$(η^3-allyl)(2-aminodipyridyl)] was prepared and characterised. The materials are active for the oxidation of *cis*-cyclooctene using TBHP as oxidant.



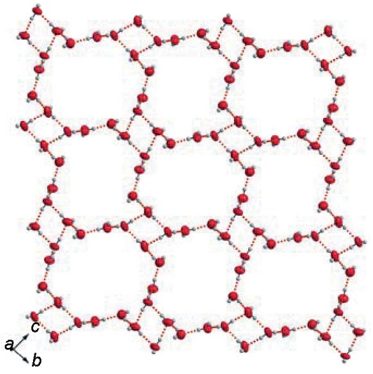
J. C. Alonso, P. Neves, C. Silva, A. A. Valente, P. Brandão, S. Quintal, M. J. Villa de Brito, P. Pinto, V. Félix, M. G. B. Drew, J. Pires, A. P. Carvalho, M. J. Calhorda, P. Ferreira* ... **1147–1156**

Immobilisation of η^3-Allyldicarbonyl Complexes of Mo^{II} with Bidentate Nitrogen Ligands within Aluminium-Pillared Clays

Keywords: Molybdenum complexes / N ligands / Clays / Epoxidation

Topologically Unique Cu Compounds

[Cu$_2$(SIP-O)(bpy)$_2$(H$_2$O)$_2$]·7H$_2$O (**1**) and [Mn(HSIP)(bpy)]$_n$ (**2**) were synthesized. The unprecedented hydroxylation of SIP^{3-} catalyzed by Cu^{2+} produced discrete SIP-O^{4-}-bridged dicopper(II) compound **1**. An unusual 2D-layered water and a discrete water octamer exist in **1**. Compound **2** is a 3D coordination polymer and has two kinds of topologically equivalent 4-connected nodes.



Q.-Y. Liu, Y.-L. Wang, J. Zhao, L. Xu* **1157–1163**

Syntheses, Crystal Structures, and Magnetic Properties of Copper(II) and Manganese(II) Compounds Constructed from 5-Sulfoisophthalic Acid (H$_3$SIP) and 2,2′-Bipyridine (bpy) Ligands

Keywords: Dinuclear copper / Manganese / Hydrothermal synthesis / Crystal structures / Magnetic properties