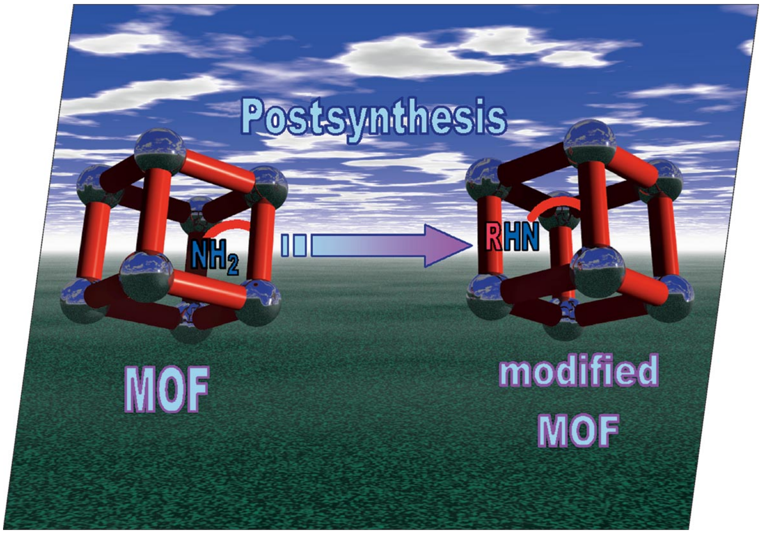
HUNGARY
ITALY
GERMANY
GREECE
BELGIUM
FRANCE
SWEDEN
EUChemSoc
CZECH REPUBLIC
AUSTRIA
PORTUGAL
SPAIN
NETHERLANDS

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 the post-synthetic functional group modification of a Metal–Organic Framework without destroying the original 3D architecture. Details are discussed in the Short Communication by P. Gamez et al. on p. 1551ff. The authors are indebted to the Chemical Research Council of the Netherlands and the Graduate Research School Combination "NRSC Catalysis" for financial support.



CONTENTS

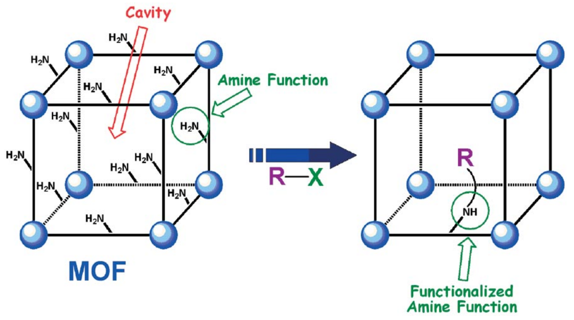
SHORT COMMUNICATIONS

Post-Synthetically Modified MOFs

J. S. Costa, P. Gamez,* C. A. Black, O. Roubeau, S. J. Teat, J. Reedijk **1551–1554**

Chemical Modification of a Bridging-Ligand Inside a Metal–Organic Framework while Maintaining the 3D Structure

Keywords: Metal–organic frameworks / Post-synthetic modifications / Crystal engineering / X-ray structures / Functional cavities



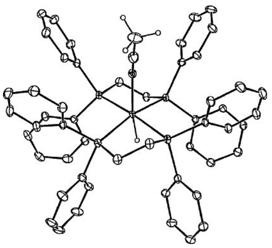
A new metal–organic framework with amino groups oriented inside the pores has been synthesized. The post-synthetic modification of the cavities in this MOF with two different functionalities is for the first time clearly evidenced by X-ray crystallography. The cavities of the MOF can be transformed without modifying the original 3D structure of the MOF.

Phosphaalkyne Complexes

C. Jones,* C. Schulten, A. Stasch **1555–1558**

Synthesis, Characterization and Reactivity of a η^1-Methylphosphaalkyne Complex, $[RuH(dppe)_2(\eta^1\text{-P}\equiv CMe)][CF_3SO_3]$

Keywords: Phosphaalkynes / Main-group elements / Low coordination / Coordination complex



The synthesis and structural characterization of the η^1-methylphosphaalkyne complex, $[RuH(dppe)_2(\eta^1\text{-P}\equiv CMe)][CF_3SO_3]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane], is reported. Its treatment with HBF_4 leads to phosphaalkyne reduction and the formation of a rare PF_2Et complex, $[RuH(dppe)_2(\eta^1\text{-}PF_2Et)][BF_4]$.

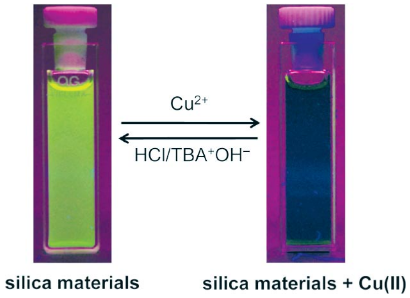
FULL PAPERS

Fluorescent Chemosensors

S. J. Lee, D. R. Bae, W. S. Han, S. S. Lee, J. H. Jung* **1559–1564**

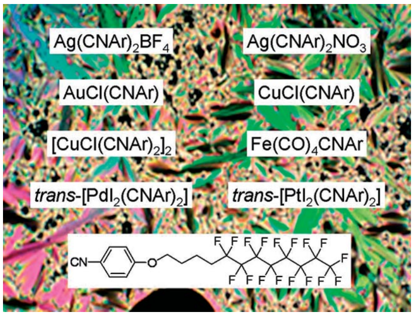
Different Morphological Organic–Inorganic Hybrid Nanomaterials as Fluorescent Chemosensors and Adsorbents for Cu^{II} Ions

Keywords: Adsorbents / Chemosensors / Fluorescence / Nanomaterials / Silica / Nanotubes



FSNT, FMS, and FSNP-15 with an immobilized phenanthroline moiety as a fluorescent receptor were fabricated by a sol–gel reaction, and their binding abilities with metal ions were evaluated by fluorophotometry in water/acetonitrile (8:2, v/v) at pH 7. These silica nanomaterials selectively recognized Cu^{2+} ions among heavy metal ions.

Metallomesogens



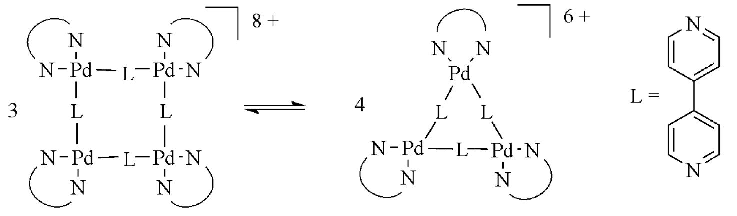
The synthesis of metallomesogens Ag(CNAr)$_2$BF$_4$, Ag(CNAr)$_2$NO$_3$, AuCl(CNAr), CuCl(CNAr), [CuCl(CNAr)$_2$]$_2$, Fe(CO)$_4$CNAr, *trans*-[PdI$_2$(CNAr)$_2$], and *trans*-[PtI$_2$(CNAr)$_2$] containing the fluorous isocyanide ligand CNAr [Ar = C$_6$H$_4$-4-O(CH$_2$)$_4$(CF$_2$)$_8$F] and the examination of their mesomorphic properties is reported.

R. Dembinski,* P. Espinet,* S. Lentijo, M. W. Markowicz, J. M. Martín-Alvarez, A. L. Rheingold, D. J. Schmidt, A. Sniady **1565–1572**

Fluorophobic Effect in Metallomesogens – The Synthesis and Mesomorphism of Ag, Au, Cu, Fe, Pd, and Pt Fluorous Isocyanide Complexes

Keywords: Metallomesogens / Liquid crystals / Fluorinated ligands / Isocyanide ligands / Mesophases

Steric Effects in Pd Complexes



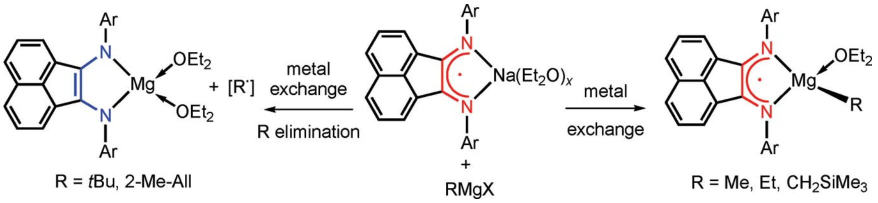
The ratio of the trimeric and tetrameric palladium complexes has shown a strong dependence on the steric properties of the chelating diamines. The trimeric [Pd(en)(4,4′-bpy)]$_3^{6+}$ cation has been observed for the first time.

E. Holló-Sitkei, G. Tárkányi, L. Párkányi, T. Megyes, G. Besenyei* **1573–1583**

Steric Effects in the Self-Assembly of Palladium Complexes with Chelating Diamine Ligands

Keywords: Steric effects / Self-assembly / Supramolecular chemistry / Trimer/tetramer equilibrium / DOSY / X-ray diffraction

New Grignard Reagents



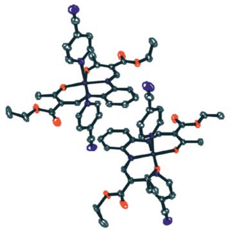
Alkylmagnesium complexes (dpp-bian)MgR (R = Me, **2**; Et, **3**; Me$_3$SiCH$_2$, **4**) are stable both in solution and in the solid state, whereas the equivalent complexes with *tert*-butyl or 2-methylallyl groups are unstable and are prone to undergo reductive elimination of the respective alkyl radicals.

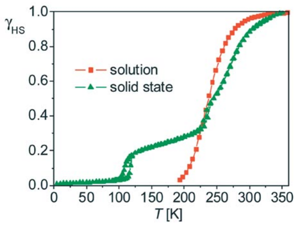
I. L. Fedushkin,* A. G. Morozov, M. Hummert, H. Schumann* ... **1584–1588**

Alkylmagnesium Complexes with the Rigid dpp-bian Ligand {dpp-bian = 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene}

Keywords: Magnesium / N ligands / Alkyl complexes / Structure elucidation

Spin Crossover Complexes





The magnetic and photomagnetic properties of a new iron(II) spin crossover complexes with a N$_4$O$_2$ coordination sphere are presented. The reason for steps during the spin transition is discussed.

B. Weber,* C. Carbonera, C. Desplances, J.-F. Létard **1589–1598**

Stepwise Spin Transition in a Mononuclear Iron(II) Complex with Unusually Wide Plateau

Keywords: Iron / Magnetic properties / Spin crossover / Photomagnetism

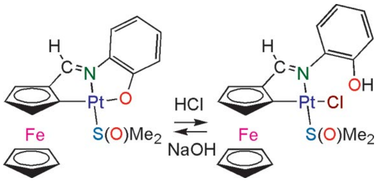
CONTENTS

Platinacycles as Molecular Switches

S. Pérez, C. López,* A. Caubet, X. Solans, M. Font-Bardía 1599–1612

New Heterodimetallic Platinum(II) Complexes Potentially Useful as Molecular Switches

Keywords: Platinum(II) complexes / Ferrocene derivatives / Platinacycles / Molecular switches



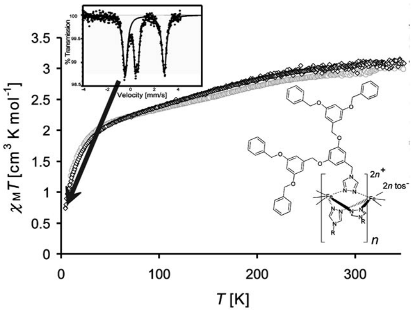
The electrochemical and spectroscopic properties of different families of new platinum(II) complexes containing ferrocenyl units acting as mono-, bi- or terdentate ligands can be switched on and off upon acid/base addition. The ease with which these changes take place depends on several factors such as the mode of binding of the ligand, its conformation, or the nature and arrangement of the monodentate ligand bound to the platinum(II) atom.

Dendron Iron Complexes

P. Sonar, C. M. Grunert, Y. Wei, J. Kusz, P. Gütlich,* A. D. Schlüter* 1613–1622

Iron(II) Spin Transition Complexes with Dendritic Ligands, Part I

Keywords: Fe^{II} spin crossover / Dendron complexes / Mössbauer spectroscopy / Magnetic susceptibility / XRD / DSC measurements



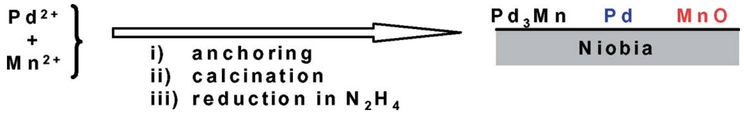
The present study reports on the synthesis and physical characterisation of iron(II) spin crossover complexes with dentritic ligands.

Pd–Mn/Niobia Materials

R. Brayner, F. Villain, L. Gengembre, S. Ammar, F. Bozon-Verduraz* 1623–1631

Niobia-Supported Palladium–Manganese Materials: Synthesis and Structural Investigation

Keywords: Palladium / Manganese / Niobia / XAS / CO adsorption



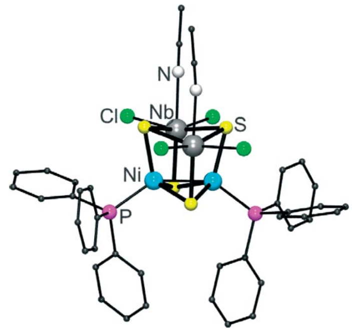
In Pd–Mn/niobia materials prepared by anchoring molecular precursors, calcination, and reduction in hydrazine at low temperature, palladium is distributed between Pd_3Mn nanoparticles and palladium clusters, whereas Mn^{2+} ions are engaged in MnO clusters linked to niobia. Strong Mn–niobia interactions prevent the reduction of Mn^{2+} and induce heterogeneity.

Heterocubane Clusters

B. Bechlars, I. Issac, R. Feuerhake, R. Clérac, O. Fuhr, D. Fenske 1632–1644

Syntheses, Structures and Magnetic Properties of New Chalcogen-Bridged Heterodimetallic Cluster Compounds with Heterocubane Structure

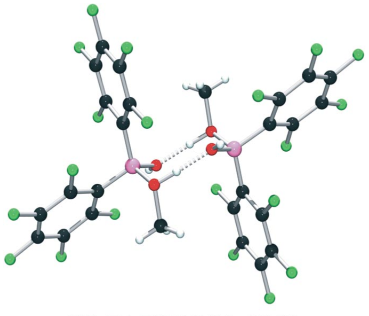
Keywords: Niobium / Tantalum / Transition metals / Clusters / Heterocubanes



Herein we present the syntheses and the molecular structures of several heterodimetallic metal chalcogenide cluster compounds containing a heterocubane core. Magnetic measurements were performed on selected compounds to learn more about the electron distribution within the cluster.

Perfluoroborinic Acid

The complementary Lewis acid–base and hydrogen-bond donor/acceptor properties of $(C_6F_5)_2BOH$ and MeOH give rise to a number of interlaced association equilibria. In particular, hydrogen-bond pairing of the covalent adduct affords a dimer, the key intermediate in the esterification reaction, in fast equilibrium with the acid and ester through intramolecular proton transfer, as revealed by low-temperature NMR spectroscopy.



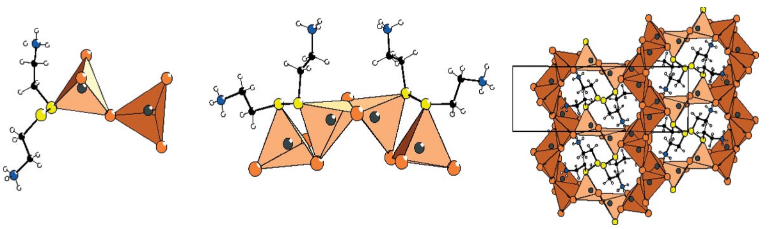
$[(C_6F_5)_2B(OH)(MeOH)]_2$

D. Donghi, D. Maggioni, T. Beringhelli, G. D'Alfonso,* P. Mercandelli,* A. Sironi **1645–1653**

Hydrogen Bonding and Lewis Acid–Base Interactions in the System Bis(pentafluorophenyl)borinic Acid/Methanol

Keywords: Fluoroarylboranes / Lewis acids / Hydrogen bonds / NMR spectroscopy / X-ray diffraction

Cuprous Bromide Salts



Oligomeric and polymeric (1D and 2D) coordination complexes of cuprous bromide with coordinated and noncoordinated cystamine were isolated by a hydrothermal technique. An unusual noncentrosymmetric complex contains both enantiomers. The networks consist of coordination and hydrogen bonds as well as electrostatic attractions between the polar fragments.

N. Louvain, N. Mercier,* M. Kurmoo **1654–1660**

Cu^I–Br Oligomers and Polymers Involving Cu–S(cystamine) Bonds

Keywords: Amines / Disulfides / Copper / Organic–inorganic hybrid composites / Halogens

Medicinal Organometallic Chemistry

Some hydrolysis-resistant organometallic complexes have been prepared and characterised and their cytotoxicity studied in two cancer cell lines. The results indicate that hydrolysis may not be a prerequisite (or the first step) in their mode of action.

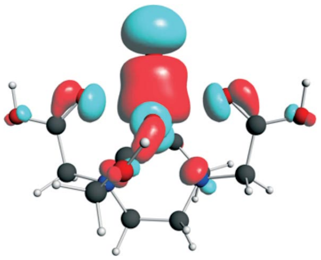
C. A. Vock,* A. K. Renfrew, R. Scopelliti, L. Juillerat-Jeanneret, P. J. Dyson* **1661–1671**

Influence of the Diketonato Ligand on the Cytotoxicities of $[Ru(\eta^6\text{-}p\text{-cymene})(R_2acac)(PTA)]^+$ Complexes (PTA = 1,3,5-triaza-7-phosphaadamantane)

Keywords: Bioorganometallics / Anticancer drugs / Metal-based drugs / Ruthenium / X-ray structure

High-Valent Oxidoiron(IV) Systems

We describe a new class of oxidoiron(IV) compounds in which the ferryl moiety is chelated by an EDTA ligand in its various protonation states. We found all systems to possess a *quintet ground state* and to be catalytically active. In the fully protonated complex, $[FeO{\cdot}EDTAH_4]^{2+}$, H abstraction from methane in the gas phase proceeds with an energy barrier lower than the one computed in the presence of the "Fenton catalyst" $[FeO{\cdot}(H_2O)_5]^{2+}$.



L. Bernasconi,* E. J. Baerends* **1672–1681**

The EDTA Complex of Oxidoiron(IV) as Realisation of an Optimal Ligand Environment for High Activity of FeO^{2+}

Keywords: Alkane hydroxylation / High-valent oxidoiron systems / Fenton reaction / Density functional theory

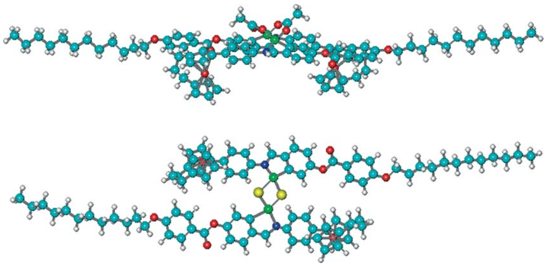
CONTENTS

Liquid Crystals

O. N. Kadkin,* J. An, H. Han,
Yu. G. Galyametdinov 1682–1688

A Novel Series of Heteropolynuclear Metallomesogens: Organopalladium Complexes with Ferrocenophane-Containing Ligands

Keywords: Liquid crystals / Metallomesogens / Palladium / Ferrocene / Heterometallic complexes



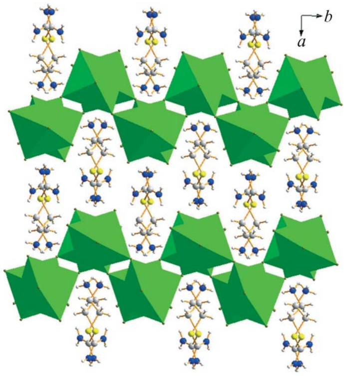
Liquid crystalline heteropolynuclear complexes based on palladium(II) chelates with various ferrocenophane-containing ligands were synthesized.

A <110>-Oriented Perovskite

Y. Li, G. Zheng, J. Lin* 1689–1692

Synthesis, Structure, and Optical Properties of a Contorted <110>-Oriented Layered Hybrid Perovskite: $C_3H_{11}SN_3PbBr_4$

Keywords: Perovskites / <110> orientation / Photoluminescence / Lead / Aminoethylisothiourea



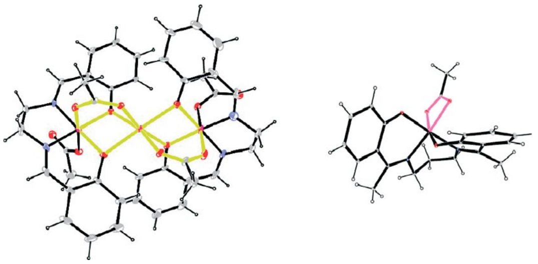
An uncommon contorted <110>-oriented hybrid perovskite ($C_3H_{11}SN_3-PbBr_4$) was obtained. The layered structure is composed of <110>-oriented perovskite-type sheets alternating with dications of the ligand *S*-(2-aminoethyl)isothiourea. The organic ligand plays an important role in constructing the hybrid structure.

Mixed-Valent Cobalt Compounds

S. Chattopadhyay, M. G. B. Drew,
A. Ghosh* 1693–1701

Methylene Spacer-Regulated Structural Variation in Cobalt(II/III) Complexes with Bridging Acetate and Salen- or Salpn-Type Schiff-Base Ligands

Keywords: Cobalt / Mixed valence / Schiff base / N_2O_2 ligands / Crystal structures / DFT calculations



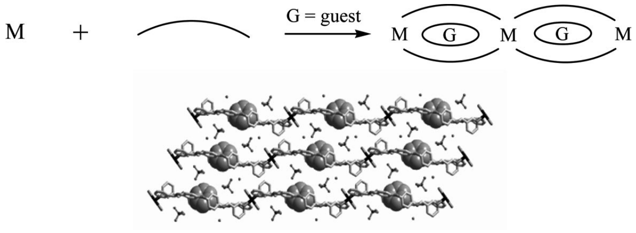
Trinuclear, mixed-valent $Co^{III}-Co^{II}-Co^{III}$ complexes and mononuclear Co^{III} complexes were prepared by regulating the chain length of the diamine fragments of Salen-type Schiff base ligands. In the trinuclear complexes, both acetato and phenoxo groups bridge the low-spin Co^{III} and high-spin Co^{II} centres. The Co^{III} centres in the mononuclear complexes are low-spin and diamagnetic. The formation of trinuclear vs. mononuclear complexes was rationalised by DFT calculations.

Host-Guest Chemistry

Q. Wang, R. Yang, C.-F. Zhuang,
J.-Y. Zhang,* B.-S. Kang,
C.-Y. Su* 1702–1711

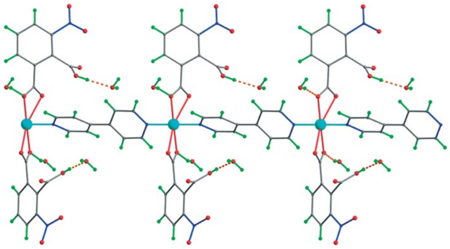
Guest-Inclusion Behavior of Double-Strand 1D Coordination Polymers Based on *N,N′*-Type Schiff Base Ligands

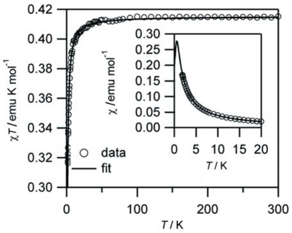
Keywords: Coordination polymers / Schiff base ligands / Double-strand chains / Crystal structures / Guest-inclusion



Four 1D double-strand coordination polymers were obtained from the assembly of three *N,N′*-type Schiff base ligands of distinctive lengths and flexibility with transition-metal ions. These coordination polymers contain the same M_2L_2 basic rings but display different crystal packing fashions, which results in different guest adsorption and desorption properties.

Molecular Magnetism





A Cu^{II} coordination polymer, **1**, exhibits the behaviour of an antiferromagnetically coupled 1D chain, as confirmed by fitting its magnetization at 1.9 K. The comparison of several methods of calculating the susceptibility data indicates that, for the small value of *J* in **1**, all methods are suitable, which validates the use of finite-size calculations for the magnetization.

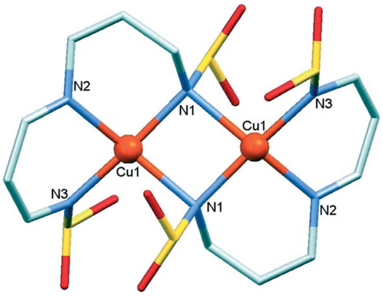
Y.-H. Deng,* J. Liu, B. Wu, C. Ambrus, T. D. Keene, O. Waldmann,* S.-X. Liu,* S. Decurtins, X.-J. Yang 1712–1718

Comparing Models for $S = 1/2$ Heisenberg Antiferromagnetic Chains: The Validity of Different Approaches for Describing a One-Dimensional Coordination Polymer, $[\mathrm{Cu^{II}(HL)_2(4,4'\text{-}bpy)}]_n\cdot 2n\mathrm{H_2O}$ ($\mathrm{H_2L}$ = 3-Nitrophthalic Acid, bpy = Bipyridine)

Keywords: Magnetism / Low-temperature studies / Copper / Bridging ligand / Crystal structure

Sulfonamido Bridges

As other metal complexes with L^{2-}, the crystal structure of $\mathrm{Cu_2(L)_2\cdot 2MeCN}$ {$\mathrm{H_2L}$ = *N*-[2-(tosylamino)benzylidene]-2-[(tosylamino)methyl]aniline} shows a dimeric nature, with a rare double μ_2-N$_{\mathrm{sulfonamido}}$ bridge between the two Cu^{II} ions, which displays seesaw-shaped distorted square-planar geometries and gives rise to an absolutely planar and nearly square-shaped $\mathrm{Cu_2N_2}$ metallacycle that could favour some ferromagnetic coupling.



J. Sanmartín,* F. Novio, A. M. García-Deibe, M. Fondo, N. Ocampo, M. R. Bermejo ... 1719–1726

Dimeric Complexes of a Tridentate Schiff Base Ligand – Crystal Structure of a Cu^{II} Complex with Uncommon μ_2-N$_{\mathrm{sulfonamido}}$ Bridges and Ferromagnetic Behaviour

Keywords: Sulfonamides / Schiff bases / N-donor ligands / Dimeric complexes / Ferromagnetism / Copper