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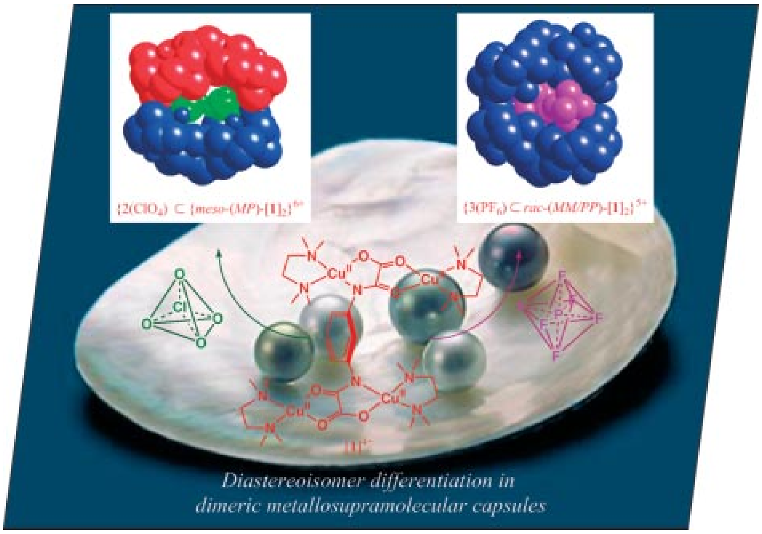
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows unique examples of homo- and heterochiral, dimeric metal capsules resulting from the self-assembly of two helical, bowl-shaped tetranuclear copper(II) complexes that encapsulate different anions in the solid state, like pearls in an oyster (shown as the background). This kind of self-assembled, coordination-bonded motifs are a major topic in metallosupramolecular chemistry because of their binding capabilities and associated host–guest chemistry. However, their magnetic properties are largely unexplored, and here we provide one of the rare magnetic studies on these host–guest systems. For more details on the combined structural and magnetic investigations of this class of synthetic "oyster" molecules, see the article by F. Lloret, Y. Journaux et al. on p. 4569 ff.



CONTENTS

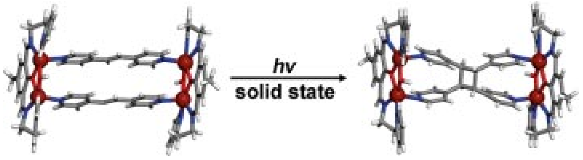
MICROREVIEW

Controlled Solid-State Reactivity

D.-K. Bučar, G. S. Papaefstathiou,
T. D. Hamilton, Q. L. Chu, I. G. Georgiev,
L. R. MacGillivray* .... 4559−4568

Template-Controlled Reactivity in the Organic Solid State by Principles of Coordination-Driven Self-Assembly

Keywords: Self-assembly / Dimerization / Solid-state reactivity / Hydrogen bonds



Principles and applications of solid-state reactivity by coordination-driven self-assembly are described. How the products obtained from templated solid-state reactions are used as organic building units of metal−organic frameworks and coordination capsules is also addressed.

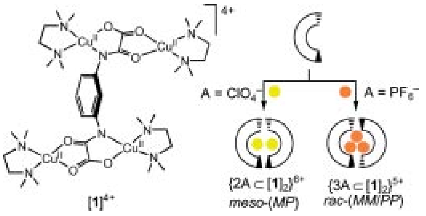
SHORT COMMUNICATIONS

Crystal Engineering

E. Pardo, K. Bernot, F. Lloret,* M. Julve,
R. Ruiz-García, J. Pasán, C. Ruiz-Pérez,
D. Cangussu, V. Costa, R. Lescouëzec,
Y. Journaux* .... 4569−4573

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



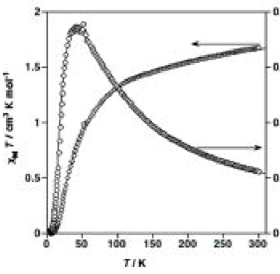
Like pearls within an oyster: a bowl-shaped cationic tetranuclear copper(II) oxamato complex with a helical conformation self-assembles in the solid state to form dimeric molecular capsules, either hetero- (*MP*) or homochiral (*MM*/*PP*), where two perchlorate or three hexafluorophosphate anions are hosted.

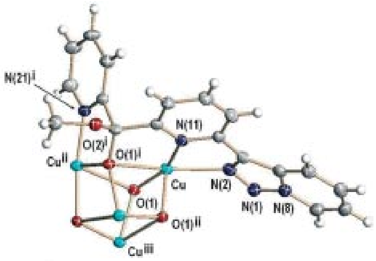
Tetranuclear Copper Cubane

B. Abarca,* R. Ballesteros,
M. Chadlaoui, C. R. de Arellano,
J. A. Real* .... 4574−4578

[(Pyridylcarbonyl)pyridyl]triazolopyridines, Useful Ligands for the Construction of Polynuclear Coordination Compounds − Synthesis, Crystal Structure and Magnetic Properties of a Novel Tetranuclear Copper(II) Cubane

Keywords: Polydentate ligands / Triazolopyridine ligands / Copper(II) complexes / Tetranuclear complexes / Molecular magnetism

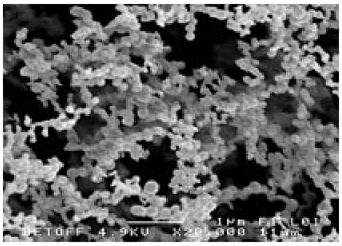




A new tetranuclear cubane Cu_4O_4 complex with S_4 symmetry has been synthesised from assembly of Cu^{II} ions and the polydentate ligand (pyridin-2-yl){6-([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)pyridin-2-yl}methanone. Its crystal structure and magnetic properties have been analysed.

Chromium Mixed Chalcogenide

Chromium oxyselenide was synthesised by chemical vapor synthesis.



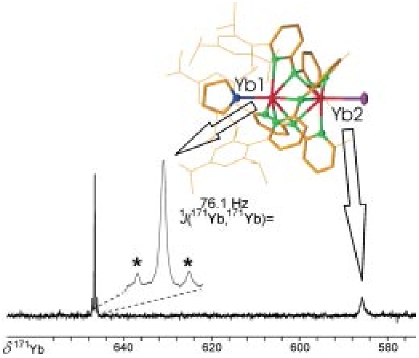
N. D. Boscher, C. J. Carmalt, A. G. Prieto, Q. A. Pankhurst, R. G. Palgrave, I. P. Parkin* **4579–4582**

Synthesis and Charaterisation of Chromium Oxyselenide ($Cr_2Se_{0.7}O_{2.3}$) Formed from Chemical Vapour Synthesis: A New Antiferromagnet

Keywords: Chemical vapour synthesis / Chromium oxyselenide / Antiferromagnet

f-Block Element Spin–Spin Coupling

An f-block-element–f-block-element NMR spin–spin coupling pattern is observed for the first time, and the relevance of such investigations in understanding dimer equilibria and rearrangement chemistry of rather bulky structural ensembles is discussed.



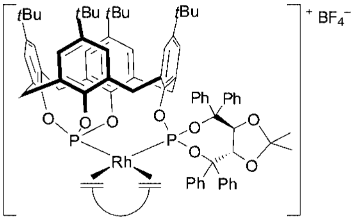
A. M. Dietel, O. Tok, R. Kempe* **4583–4586**

f-Block-Element–f-Block-Element NMR Spin–Spin Coupling

Keywords: Amido ligands / Bimetallic complexes / Dynamic N ligands / NMR spectroscopy / Ytterbium

The Chiral Grail

Chiral calixarene-based diphosphite ligands **3a–d** have been obtained via lower-rim functionalisation of the *p-tert*-butylcalix[4]-arene core. High enantiomeric excesses (up to 94 %) and good activities were obtained in the rhodium-catalyzed asymmetric hydrogenation of prochiral olefins with TADDOL-containing diphosphites **3c**,**d**.



4c

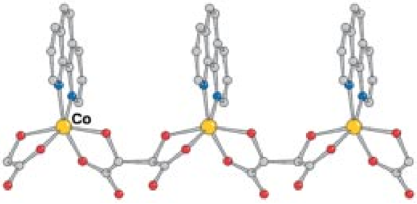
A. Marson, Z. Freixa, P. C. J. Kamer,* P. W. N. M. van Leeuwen* **4587–4591**

Chiral Calix[4]arene-Based Diphosphites as Ligands in the Asymmetric Hydrogenation of Prochiral Olefins

Keywords: Homogeneous catalysis / Stereoselective catalysis / Asymmetric hydrogenation / Calixarenes / Diphosphites

1D Water Cluster

$\{[Co(tart)(phen)]\cdot 6H_2O\}_n$ (**1**) (tart, tartrate dianion; phen, 1,10-phenanthroline) forms a 3D supramolecular network through π-π and H-bonding interactions. A variable-temperature magnetic study **1** has been carried out and the interpretation of the already reported $\{[Co(tart)(bpy)]\cdot 5H_2O\}_n$ (**2**) has been re-visited: both **1** and **2** show weak antiferromagnetic interaction.



S. C. Manna, E. Zangrando, J. Ribas,* N. Ray Chaudhuri* **4592–4595**

Self-Assembled 1D Water Cluster in a Supramolecular Architecture of Co^{II}-(Tartrate)(Phenanthroline/Bipyridine): An Assessment of Magnetic Property

Keywords: Cobalt(II) / Tartrate / Magnetic properties / Water cluster

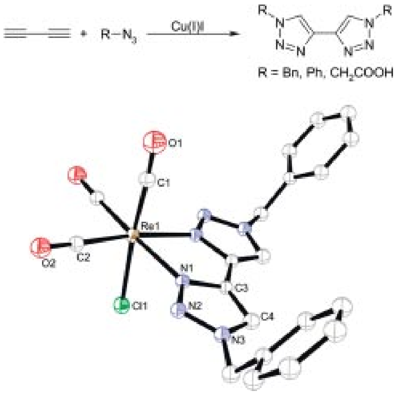
FULL PAPERS

Bi-1,2,3-triazole Ligand Properties

U. Monkowius,* S. Ritter, B. König,*
M. Zabel, H. Yersin 4597–4606

Synthesis, Characterisation and Ligand Properties of Novel Bi-1,2,3-triazole Ligands

Keywords: N ligands / Ligand design / Nitrogen heterocycles / Click reaction / 1,2,3-Triazole



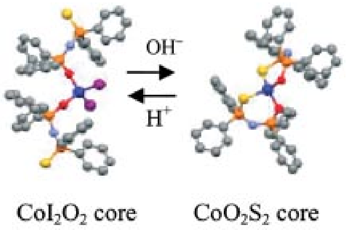
Three bi-1,2,3-triazoles (R-bta; R = Bn, Ph, CH_2COOH) were synthesised by a Cu^I-catalysed "click" reaction to act as potential bidentate, nitrogen-based ligands. The ligand properties were probed by the preparation of Ru^{II}, Cu^I, and Re^I complexes. X-ray crystallographic data are presented for the ligands and complexes as well as the results of electronic absorption spectroscopy.

Tetrahedral Cobalt Complexes

M. C. Aragoni, M. Arca, M. B. Carrea,
A. Garau, F. A. Devillanova,
F. Isaia,* V. Lippolis, G. L. Abbati,
F. Demartin, C. Silvestru, S. Demeshko,
F. Meyer 4607–4614

Tetrahedral Co^{II} Complexes with CoI_2O_2 and CoO_2S_2 Cores – Crystal Structures of $[Co\{HN(OPPh_2)(SPPh_2)\text{-}O\}_2I_2]$ and $[Co\{N(OPPh_2)(SPPh_2)\text{-}O,S\}_2]$

Keywords: Cobalt / O,S ligands / Phosphanes / Sulfides / Density functional calculations / Magnetic properties



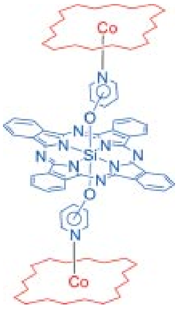
Two Co^{II} complexes were synthesised with the ligand $HN(OPPh_2)(SPPh_2)$, which contains mixed hard (O) and soft (S) donor atoms. The X-ray crystal structures of these compounds show the presence of a CoI_2O_2 and a CoO_2S_2 core. The mutual conversion of the complexes is driven by the protonation/deprotonation of the imido nitrogen atoms.

Phthalocyanine–Porphyrin Arrays

X. Leng, D. K. P. Ng* 4615–4620

Axial Coordination of Porphyrinatocobalt(II) Complexes with Bis(pyridinolato)silicon(IV) Phthalocyanines

Keywords: Phthalocyanines / Porphyrins / Axial coordination / UV/Vis spectroscopy



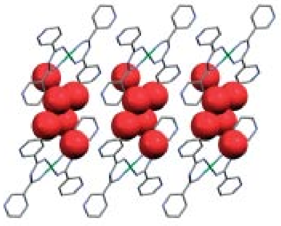
Bis(pyridinolato)silicon(IV) phthalocyanins axially bind to porphyrinatocobalt(II) complexes forming the novel hetero phthalocyanine–porphyrin dyads and triads. The binary complexes are stable and can thus be isolated and spectroscopically characterized.

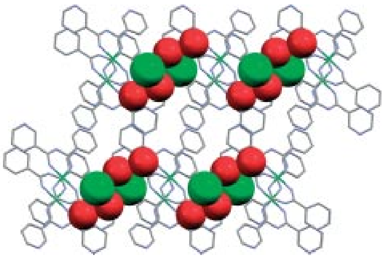
Water–Chloride Clusters

M. N. Kopylovich,* E. A. Tronova,
M. Haukka, A. M. Kirillov,
V. Yu. Kukushkin,* J. J. R. Fraústo da Silva,
A. J. L. Pombeiro* 4621–4627

Identification of Hexameric Water and Hybrid Water–Chloride Clusters Intercalated in the Crystal Hosts of (Imidoylamidine)nickel(II) Complexes

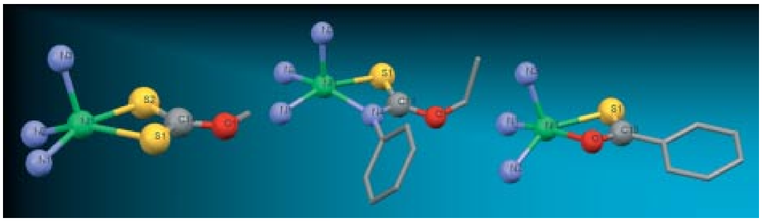
Keywords: Crystal engineering / Hydrogen bonds / Imidoylamidine complexes / Water clusters / X-ray diffraction





Bis(imidoylamidine)nickel(II) compounds reveal the presence, in the solid state, of geometrically similar, but distinct in composition, discrete $(H_2O)_6$ and $[(H_2O)_4(Cl)_2]^{2-}$ clusters. They occupy voids in the crystal cells and display extensive H-bonding interactions with monomeric metal–organic units, thus playing a key role in the formation of 3D H-bonded supramolecular assemblies.

Pentacoordinate Ni^{II} Complexes



The reactivity of hydroxido Ni complexes with CS_2 or PhCNS, in the presence of alcohols, to form *O*-alkyl dithiocarbonate (xanthate) or *O*-alkyl *N*-phenylthiocarbamate pentacoordinate Ni^{II} complexes, respectively, was investigated. The thiocarboxylate complexes were also prepared by the acid–base reaction of these hydroxido complexes with the corresponding thioacid.

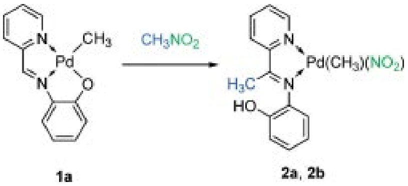
M. D. Santana,* M. Sáez-Ayala, L. García, J. Pérez, G. García 4628–4636

Preparation of Thiocarboxylate, Thiocarbamate and Xanthate Complexes of Pentacoordinate Nickel(II): Insertion of Heterocumulenes Into Nickel(II) Hydroxido Complexes

Keywords: Nickel / Macrocyclic ligands / S ligands / Insertion / NMR spectroscopy / X-ray diffraction

C–N Bond Activation

The reaction of the complex [Pd(κ^3-NN′O)-CH_3] [NN′O = 2-Py-CH=N-(*o*-C_6H_4)O^-] (**1a**) with nitromethane affords a mixture of two compounds in which methylation of the ligand can be observed. The methylation reaction is proposed to occur through nucleophilic attack of the nitronate anion on the iminic carbon atom. DFT calculations are presented in order to support a part of the mechanism of the reaction.



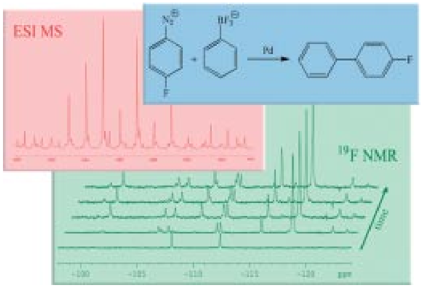
A. M. Arnaiz, A. Carbayo, J. V. Cuevas,* V. Diez, G. García-Herbosa, R. González, A. Martínez, A. Muñoz 4637–4644

Methylation of a Terdentate Schiff Base Ligand *NNO*-Coordinated to Palladium with Nitromethane

Keywords: Palladium / Henry reaction / Nucleophilic attack / Nitroaldol / Schiff bases

Cross-Coupling Mechanisms

This mechanistic study on the palladium-catalysed cross-coupling reaction between aryldiazonium salts and aryltrifluoroborates combines the results obtained from ^{19}F NMR and ESI-MS studies.



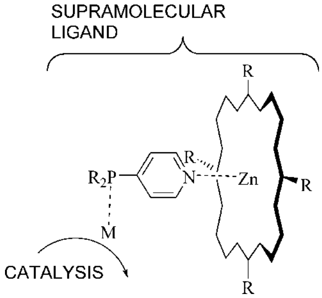
N. Taccardi, R. Paolillo, V. Gallo, P. Mastrorilli,* C. F. Nobile, M. Räisänen, T. Repo 4645–4652

On the Mechanism of Palladium-Catalyzed Cross-Coupling of Diazonium Salts with Aryltrifluoroborates: A Combined ESI-MS/NMR Study

Keywords: Homogeneous catalysis / Metallacycles / Mass spectrometry / Cross-coupling / Diazo compounds

Supramolecular Catalysis

Coordination chemistry has been used to prepare supramolecular ligands. The construction of these ligands is based on selective metal–ligand interactions, leading to well-defined catalyst assemblies. Important catalyst properties such as activity and (enantio)selectivity are fine-tuned by the building blocks used for the assembly formation.



V. F. Slagt, P. Kaiser, A. Berkessel, M. Kuil, A. M. Kluwer, P. W. N. M. van Leeuwen, J. N. H. Reek* 4653–4662

Fine-Tuning Ligands for Catalysis Using Supramolecular Strategies

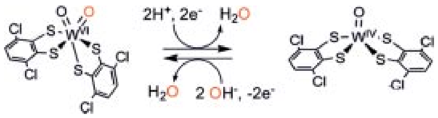
Keywords: Supramolecular catalysts / Self-assembly / Ligand effects / Phosphorus ligands / Porphyrinoids

Coupled Electron−Proton Transfer

H. Sugimoto,* M. Tarumizu, H. Miyake, H. Tsukube .... **4663−4668**

Synthesis and Characterization of Bis(dithiolene) Tungsten(VI), -(V), and -(IV) Complexes and Their Reactivities in Coupled Electron−Proton Transfer: A New Series of Active Site Models of Tungstoenzymes

Keywords: Bioinorganic chemistry / Enzyme models / Molybdenum / S ligands / Tungsten



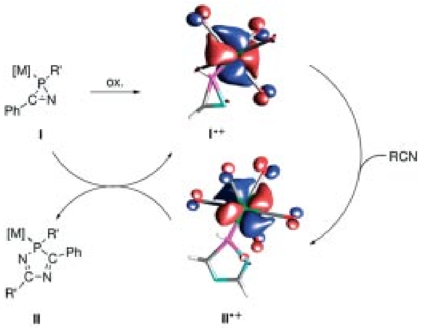
3,6-Dichloro-1,2-benzenedithiolate ($bdtCl_2$), $(Et_4N)_2[W^{VI}O_2(bdtCl_2)_2]$ {$(Et_4N)_2$[**1**]}, $(Et_4N)[W^{V}O(bdtCl_2)_2]$ {(Et_4N)[**2**]}, and $(Et_4N)_2[W^{IV}O(bdtCl_2)_2]$ {$(Et_4N)_2$[**3**]} were synthesized and characterized. The isomerization between the octahedral structures (Δ and Λ forms) of $(Bu_4N)_2$[**1**] was characterized by variable-temperature ^{1}H NMR spectroscopy. $(Et_4N)_2$[**1**] underwent an irreversible reduction at −2.1 V vs. SCEin CH_3CN by coupled electron−proton transfer (CEPT) to yield $(Et_4N)_2$[**3**], while $(Et_4N)_2$[**3**] underwent an irreversible oxidation by the CEPT process at −0.27 V in the presence of 2 equiv. Et_4NOH in CH_3CN to yield $(Et_4N)_2$[**1**]. (Et_4N)[**2**] disproportionated into 0.5 equiv. $(Et_4N)_2$[**1**] and 0.5 equiv. $(Et_4N)_2$[**3**] when treated with 1 equiv. Et_4NOH in CH_3CN.

Ring-Expansion Reactions

H. Helten, C. Neumann, A. Espinosa, P. G. Jones, M. Nieger, R. Streubel* .... **4669−4678**

Evidence for Ligand-Centered Reactivity of a 17e Radical Cationic 2*H*-Azaphosphirene Complex

Keywords: Ligand-centered reactivity / Phosphorus heterocycles / Electron transfer



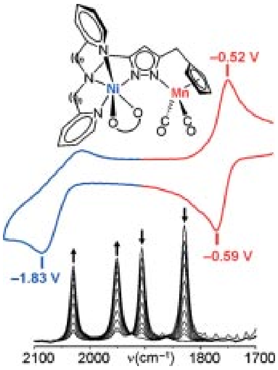
Experimental and theoretical investigations on the selective ring-expansion reactions of 2*H*-azaphosphirene complexes with nitriles are presented. The dependence on the minimum amount of single-electron transfer reagent and the selectivity on the donor abilities of the employed nitriles were also examined. The ligand-centered reactivity of a 17e radical cationic complex was elucidated.

Heterobimetallic Complexes

H. Zhang, S. Dechert, M. Linseis, R. F. Winter, F. Meyer* .... **4679−4686**

Organometallic and Classical Coordination Sites in Highly Preorganized Pyrazolate-Based Hybrid Systems: The Mn/Ni Case

Keywords: Bridging ligands / Cyclopentadienyl ligands / Manganese / Nickel / Heterometallic complexes



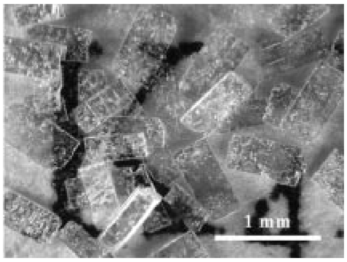
Ligand asymmetry in pyrazolate-bridged heterobimetallic complexes induces strict confinement of redox processes to either the organometallic Mn site or the Werner-type Ni site.

KCl Flux Growth of Metal Oxides

K. Teshima,* Y. Niina, K. Yubuta, T. Suzuki, N. Ishizawa, T. Shishido, S. Oishi .... **4687−4692**

Environmentally Friendly Growth of Layered $K_4Nb_6O_{17}$ Crystals from a KCl Flux

Keywords: Flux growth / Environmental chemistry / Layered compounds / Photocatalyst



Environmentally friendly, high-quality, transparent, and colorless plate-like crystals of $K_4Nb_6O_{17}$ were successfully grown by the evaporation and cooling of a KCl flux.

CORRECTION