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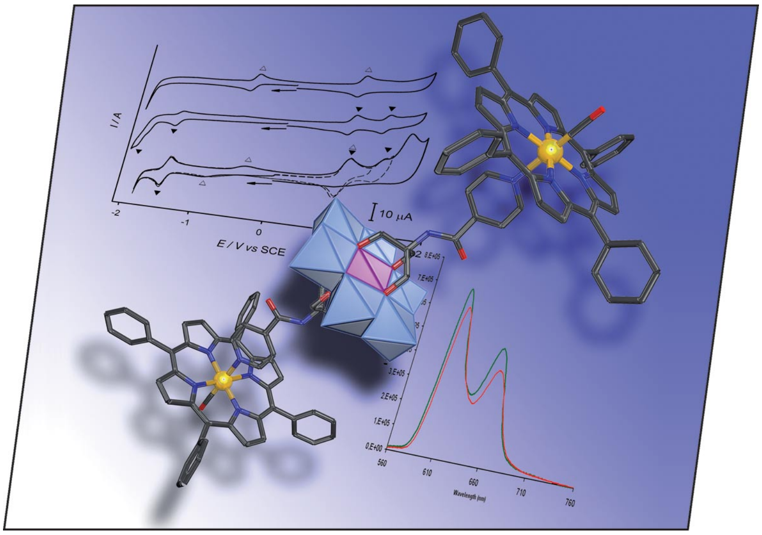
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows the coordination of two porphyrins to a functionalized polyoxometalate and a typical signature from fluorescence spectroscopy and cyclic voltammetry. The combination of porphyrins as photoactive molecules with polyoxometalates as redox-active complexes is a way to elaborate new photocatalysts and photoactive materials. Organic ligands grafted onto the polyoxometalates allow for the control of the architecture of the assembly. Details on this approach are given in the article by L. Ruhlmann, B. Hasenknopf et al. on p. 3433ff.



CONTENTS

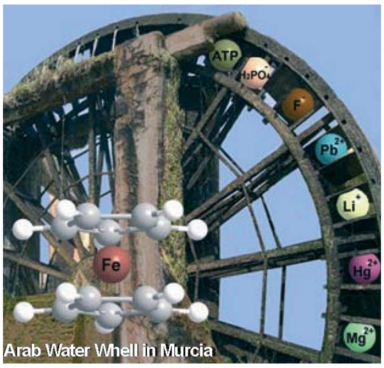
MICROREVIEW

Multi-Faceted Ferrocene Sensors

P. Molina,* A. Tárraga,
A. Caballero **3401–3417**

Ferrocene-Based Small Molecules for Multichannel Molecular Recognition of Cations and Anions

Keywords: Ferrocenes / Electrochemistry / Fluorescence / Chromogenic sensors / Molecular recognition



The sensing properties of new acyclic and cyclic ferrocene-based structural motifs, in which the redox unit is linked by unsaturated aza bridges (azadiene, azine, urea, guanidine, azaheterocycles) to a chromogenic or fluorescent signalling unit, are described.

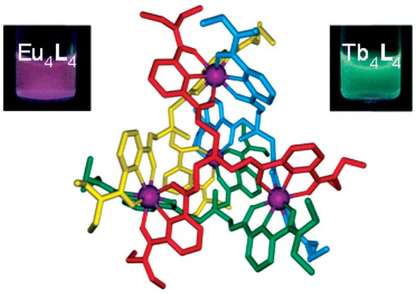
SHORT COMMUNICATIONS

Lanthanide Tetrahedral Assemblies

J. Hamacek,* G. Bernardinelli,*
Y. Filinchuk **3419–3422**

Tetrahedral Assembly with Lanthanides: Toward Discrete Polynuclear Complexes

Keywords: Lanthanides / Tetrahedral / Tetrametallic complexes / Tripodal ligands / Self-assembly



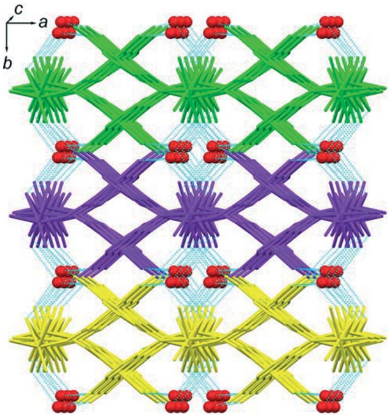
3D arrangement of trivalent lanthanides (Eu–Lu) is controlled through self-assembly with a new tripodal ligand **L**. X-ray crystallography shows that four nine-coordinate cations adopt a regular tetrahedral arrangement in the solid state. These remarkable, highly charged structures are maintained in solution, as demonstrated by NMR spectroscopy, ESI-MS and spectrophotometry.

A Cu/Na Coordination Polymer

M. V. Kirillova, A. M. Kirillov,*
M. F. C. Guedes da Silva,
A. J. L. Pombeiro* **3423–3427**

Self-Assembled Two-Dimensional Water-Soluble Dipicolinate Cu/Na Coordination Polymer: Structural Features and Catalytic Activity for the Mild Peroxidative Oxidation of Cycloalkanes in Acid-Free Medium

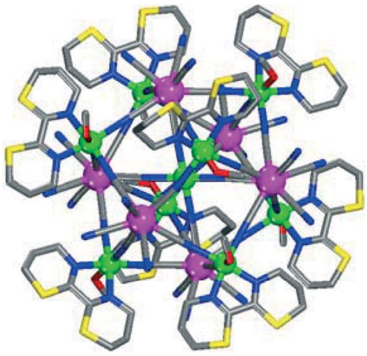
Keywords: Self-assembly / N,O ligands / Supramolecular chemistry / C–H activation / Homogeneous catalysis



The water-soluble Cu/Na coordination polymer $[Cu(\mu\text{-dipic})_2\{Na_2(\mu\text{-}H_2O)_4\}]_n\cdot 2nH_2O$ features a layered 2D metal–organic framework extendable to a 3D supramolecular assembly via multiple hydrogen bonds (blue dotted lines) between adjacent layers (different colours) and involving crystallization water molecules (red). It acts as a catalyst precursor for the mild peroxidative oxidation of cycloalkanes in acid-free medium.

S-Bearing Clusters

A fully capped body-centered cubane cluster Ni_9W_6, whose periphery was modified with sulfur-containing bidentate ligands acting as potential anchoring sites to electrodes and substrates, was prepared. Magnetic studies of this cluster revealed that ferromagnetic couplings are operative through CN bridges, generating an $S = 12$ ground state.



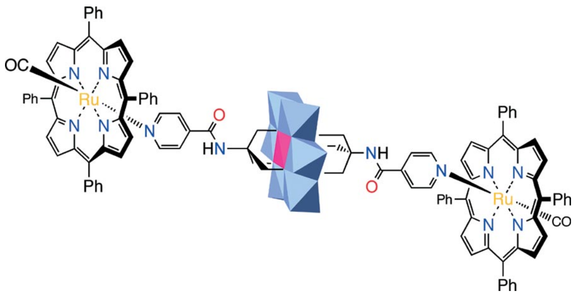
J. H. Lim, H. S. Yoo, J. I. Kim, J. H. Yoon, N. Yang, E. K. Koh, J.-G. Park, C. S. Hong* **3428–3431**

A Facially Capped Body-Centered Ni_9W_6 Cubane Modified with Sulfur-Containing Bidentate Ligands: Structure and Magnetic Properties

Keywords: Nickel / Tungsten / Crystal structures / Magnetic properties / N ligands

FULL PAPERS

Polyoxometalate–Porphyrin Assemblies



Polyoxometalates and metalloporphyrins were assembled by functionalization of Anderson-type molybdates or Lindqvist-type vanadates. Electrochemical and spectroscopical analyses reveal the influence of the organic and inorganic subunits on each other.

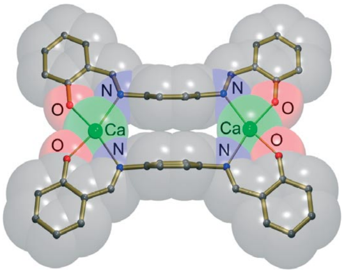
C. Allain, S. Favette, L.-M. Chamoreau, J. Vaissermann, L. Ruhlmann,* B. Hasenknopf* **3433–3441**

Hybrid Organic–Inorganic Porphyrin–Polyoxometalate Complexes

Keywords: Polyoxometalates / Porphyrinoids / N ligands / Electrochemistry / Supramolecular chemistry

Bimetallic Complexes

Bis(salicylaldimine) ligands with rigid bridging units have been converted into bimetallic Mg, Ca and Zn complexes. In some cases homoleptic complexes with two salicylaldimine units have been isolated. For Mg and Ca also bimetallic heteroleptic amide complexes could be isolated. The heteroleptic Mg amide complexes are moderately active in the polymerization of *rac*-lactide giving an atactic polymer.



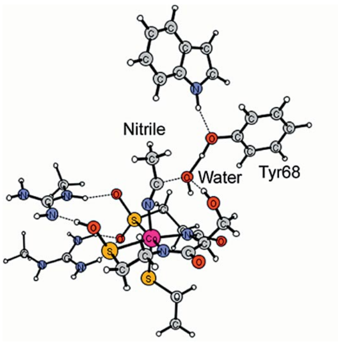
S. Range, D. F.-J. Piesik, S. Harder* **3442–3451**

Binuclear Magnesium, Calcium and Zinc Complexes Based on Bis(salicylaldimine) Ligands with Rigid Bridges

Keywords: Alkaline earth metals / Magnesium / Calcium / Zinc / Polylactide

Nitrile Hydratase Mechanism

Nitrile Hydratase (NHase) catalyzes the conversion of nitriles to amides. Two forms of NHase exist, employing either a low-spin Co^{III} or a Fe^{III} ion in the active site. The precise reaction mechanism of NHase has not been established yet. Here we use density functional theory to investigate a recent proposal that a conserved second-shell tyrosine residue is the catalytic base of NHase.



K. H. Hopmann, F. Himo* **3452–3459**

On the Role of Tyrosine as Catalytic Base in Nitrile Hydratase

Keywords: Nitrile hydratase / Enzyme catalysis / Density functional theory / Reaction mechanism

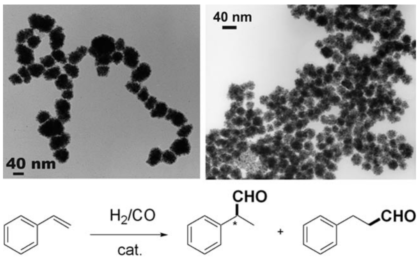
CONTENTS

Rhodium Nanoparticles

M. R. Axet,* S. Castillón, C. Claver,*
K. Philippot,* P. Lecante,
B. Chaudret 3460–3466

Chiral Diphosphite-Modified Rhodium(0) Nanoparticles: Catalyst Reservoir for Styrene Hydroformylation

Keywords: Rhodium / Nanoparticles / Catalysis / Enantioselectivity / Hydroformylation



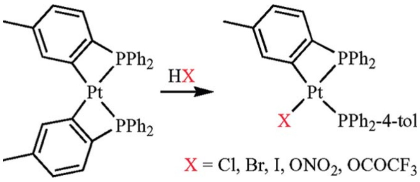
High-pressure NMR spectroscopic studies performed during the course of a reaction shed some light on the behaviour of diphosphite-stabilized rhodium nanoparticles used as catalysts in styrene hydroformylation reaction.

Platinum Complexes

M. A. Bennett, S. K. Bhargava,*
S. H. Privér, A. C. Willis 3467–3481

Selective Cleavage by Acids of One Metal–Carbon σ-Bond of a Bis(*ortho*-platinated) Triarylphosphane: A ^{31}P NMR *trans*-Influence Series Based on the Unit Pt(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)

Keywords: Platinum / *ortho*-Metallated complexes / *trans*-Influence



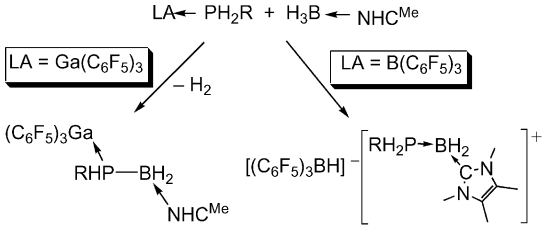
Selective cleavage of one metal–carbon σ-bond in *cis*-[Pt(κ^2-C_6H_3-5-Me-2-PPh_2)$_2$] with strong acids gives complexes of the type *cis*-[PtX(κ^2-C_6H_3-5-Me-2-PPh_2)(PPh_2-4-tol)] (X = Cl, Br, I, ONO_2 and $OCOCF_3$), from which a series of neutral and cationic derivatives can be derived. An extensive *trans*-influence series has been established based mainly on ^{31}P NMR spectroscopic data.

N-Heterocyclic Carbenes

A. Adolf, U. Vogel, M. Zabel,
A. Y. Timoshkin, M. Scheer* ... 3482–3492

N-Heterocyclic Carbenes in Lewis Acid/Base Stabilised Phosphanylboranes

Keywords: Boron / Phosphorus / Gallium / Carbenes / Lewis acids / Lewis bases



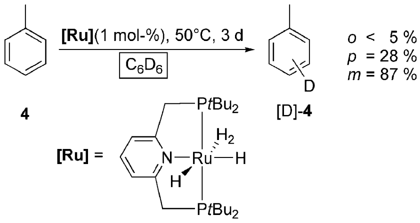
Depending on the Lewis acid, the reaction between $(C_6F_5)_3E{\cdot}PH_2R$ and $BH_3{\cdot}NHC^{Me}$ (E = Ga or B, R = H, Cp*, Ph) leads to different products. The use of $(C_6F_5)_3Ga$ affords phosphanylboranes, whereas the use of $(C_6F_5)_3B$ leads to ionic products. NHC^{Me} was also found to replace NMe_3 in $(C_6F_5)_3B{\cdot}P(Ph)HBH_2{\cdot}NMe_3$ to give the corresponding phosphanylboranes.

Catalytic H/D Exchange

M. H. G. Prechtl, M. Hölscher,
Y. Ben-David, N. Theyssen, D. Milstein,
W. Leitner* 3493–3500

Ruthenium Dihydrogen Complex for C–H Activation: Catalytic H/D Exchange under Mild Conditions

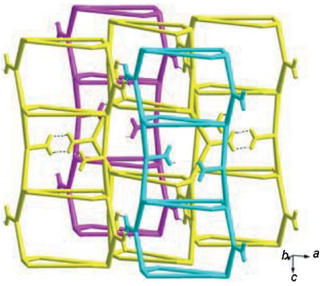
Keywords: Ruthenium dihydrogen complexes / H/D exchange / CH activation / Deuteration / DFT calculations



Catalytic H/D exchange in hydrocarbons by means of a ruthenium dihydrogen complex under mild conditions is investigated by NMR and DFT calculations.

Biphasic Synthesis of MOFs

Low-dimensional Co and Ni trimesate compounds were prepared at the interphase of two immiscible liquids by employing a biphasic route. The structures are stabilized by weak intermolecular forces such as hydrogen bonds, π···π interactions etc., and the studies of the physical properties show interesting magnetic and photoluminescence behaviour.



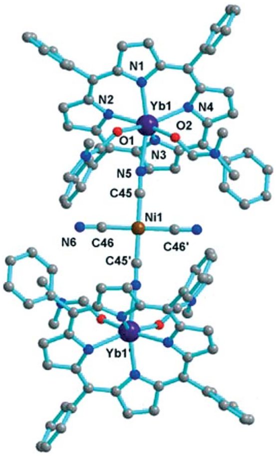
A. Banerjee, P. Mahata,
S. Natarajan* **3501–3514**

The Use of Liquid–Liquid Interface (Biphasic) for the Preparation of Benzenetricarboxylate Complexes of Cobalt and Nickel

Keywords: Metal–organic frameworks / Cobalt / Nickel/ Biphasic synthesis method

Lanthanide Porphyrinates

A series of heterodimetallic, cyanometallate-linked monoporphyrinatolanthanide complexes of ytterbium or erbium and transition metals (Ni, Pt, Fe, Ag) have been synthesized and structurally characterized. Their photophysical studies reveal that these complexes have metalloporphyrin-based and near-infrared lanthanide emissions, the latter bands being quenched by the cyanometallate groups.

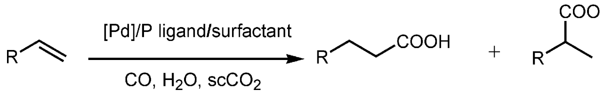


X. Zhu, W.-K. Wong,* J. Guo,
W.-Y. Wong, J.-P. Zhang **3515–3523**

Reactivity of Cationic Lanthanide(III) Monoporphyrinates towards Anionic Cyanometallates – Preparation, Crystal Structure, and Luminescence Properties of Cyanido-Bridged Di- and Trinuclear d–f Complexes

Keywords: Lanthanides / Porphyrins / Cyanometallates / Cyanido-bridged d–f complexes / Near-infrared emission

Carbonylation in $scCO_2$



The catalytic hydrocarboxylation of linear alkenes to carboxylic acids using supercritical carbon dioxide as a solvent was studied. High selectivities in acids have been obtained when adding a perfluorinated surfactant to the reaction mixture. Multinuclear high-pressure NMR spectroscopic studies in [D$_8$]THF and in supercritical CO_2 show the formation of Pd^0 species.

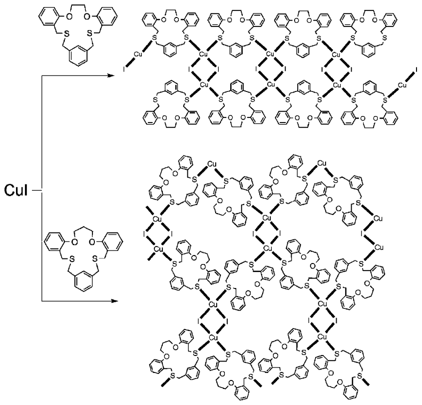
C. Tortosa Estorach, A. Orejón, N. Ruiz,
A. M. Masdeu-Bultó,*
G. Laurenczy* **3524–3531**

Hydrocarboxylation of Terminal Alkenes in Supercritical Carbon Dioxide

Keywords: Hydrocarboxylation / Hydroxycarbonylation / Palladium / Supercritical fluids

Coordination Polymer

Two analogous dithiamacrocycles (17- and 18-membered) are synthesised. Five coordination polymers and one metallo-cyclic dimer were obtained from the reactions of the macrocycles with the silver(I) and copper(I) salts. The versatility of results is discussed in relation to macrocyclic ring flexibility, anions and π-π stacking.



H. J. Kim, M. R. Song, S. Y. Lee,
J. Y. Lee, S. S. Lee* **3532–3539**

Silver(I) and Copper(I) Coordination Polymers Based on Thiaoxa-Macrocycles

Keywords: Macrocycles / Silver / Copper / Coordination polymers

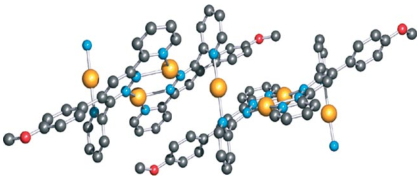
CONTENTS

Silver(I) – as Unpredictable as Ever!

E. C. Constable,* C. E. Housecroft,*
M. Neuburger, S. Reymann,
S. Schaffner 3540–3548

Substituent Effects in the Solid-State Assembly of Silver(I) Complexes of4-Substituted 3,6-Di(2-pyridyl)pyridazines

Keywords: Heterocycle / Pyridazine / Pyridine / Silver / Coordination polymer



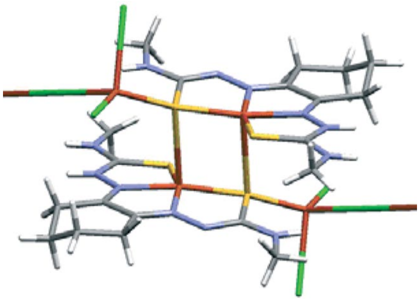
Crystalline products isolated from the 1:1 reactions of $AgBF_4$ and 4-R-3,6-di(2-pyridyl)pyridazine ligands have been structurally characterized, and reveal structure types: $[AgL_2][BF_4]$, $[Ag_2L_2][BF_4]_2$, $\{[Ag_3L_2][BF_4]_3\}_n$ and $\{[Ag_2(NCMe)_2L_2][BF_4]_2\}_n$. Solution ^1H and ^{13}C NMR spectroscopic data are consistent with one ligand environment at room temperature for each complex.

Copper Radiopharmaceuticals

J. P. Holland,* P. J. Barnard, D. Collison,
J. R. Dilworth,* R. Edge, J. C. Green,*
J. M. Heslop, E. J. L. McInnes,
C. G. Salzmann,
A. L. Thompson 3549–3560

💻 Synthesis, X-ray Crystallography, Spectroelectrochemistry and Computational Studies on Potential Copper-Based Radiopharmaceuticals

Keywords: Metal chelates / Radiopharmaceuticals / Density functional calculations / Hypoxia / Spectroelectrochemistry



A new class of metal(II) bis(thiosemicarbazonato) complexes have been characterised as potential hypoxia-selective imaging agents for use in positron emission tomography. Spectroelectrochemical experiments have been used to study the reaction of the copper(I) anion with dioxygen and provide information on the mechanism of hypoxia selectivity.

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* Author to whom correspondence should be addressed.

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