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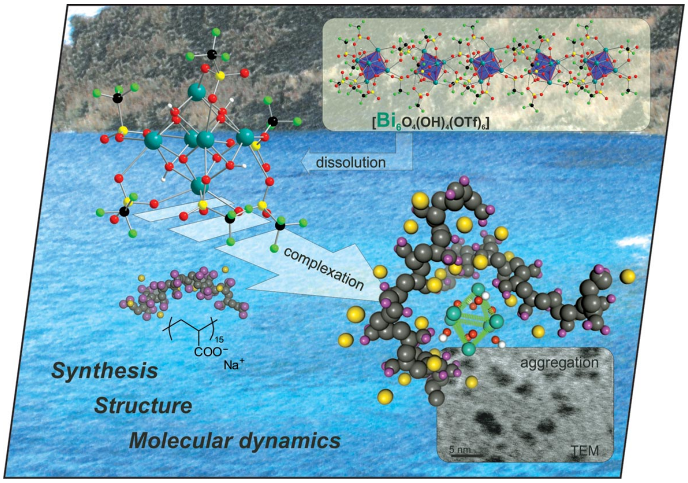
Other ChemPubSoc Europe journals are *Chemistry – A European Journal*, *ChemBioChem*, *ChemPhysChem*, *ChemMedChem*, *ChemSusChem* and *ChemCatChem.*

COVER PICTURE

The cover picture shows a novel hexanuclear bismuth oxido cluster $[Bi_6O_4(OH)_4(OTf)_6]$, which forms a 1D coordination polymer in the solid state but is highly soluble in water and polar organic solvents. The reaction of the bismuth oxido cluster with sodium polyacrylate gave a nano-sized hybrid material still soluble in aqueous solution. A snapshot from a molecular dynamics simulation is shown as an example of the apparent complexation of $[Bi_6O_4(OH)_4]^{6+}$ by polyacrylate in water. The synthesis and structure of $[Bi_6O_4(OH)_4(OTf)_6]$ as well as its complexation with polyacrylate are reported in the article by D. Zahn, M. Mehring et al. on p. 4763ff.



CONTENTS

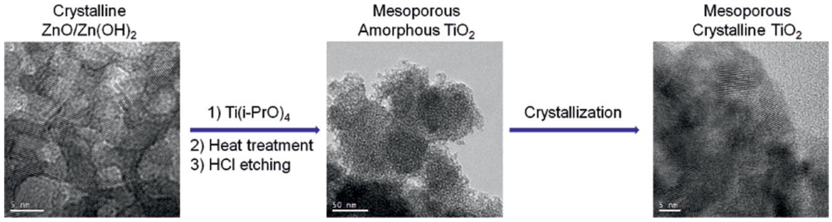
SHORT COMMUNICATIONS

Mesoporous Materials

Y.-K. Hwang, T.-H. Kwon,
S. S. Park, Y.-J. Yoon, Y. S. Won,*
S. Huh* 4747–4751

Preparation of Mesoporous $ZnO/Zn(OH)_2$ Spheres and Their Replication to High Surface TiO_2 Materials

Keywords: Mesoporous materials / Zinc / Titanium / Metal oxides / Photocatalysis



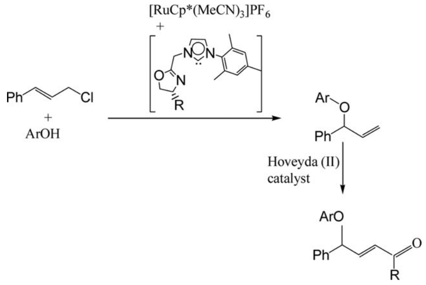
Mesoporous $ZnO/Zn(OH)_2$ composite spheres with high crystallinity were prepared and subsequently used as a hard template for the preparation of crystalline mesoporous TiO_2, which showed a large surface area (202 $m^2 g^{-1}$) and a good photocatalytic activity for the decomposition of methyl orange in an aqueous solution under UV irradiation.

Ru Catalysis

H. B. Ammar, B. B. Hassine,
C. Fischmeister, P. H. Dixneuf,
C. Bruneau* 4752–4756

Imidazolium-Oxazoline Salts in Ruthenium-Catalyzed Allylic Substitution and Cross Metathesis of Formed Branched Isomers

Keywords: Carbene ligands / Allylic substitution / Homogeneous catalysis / Nitrogen heterocycles



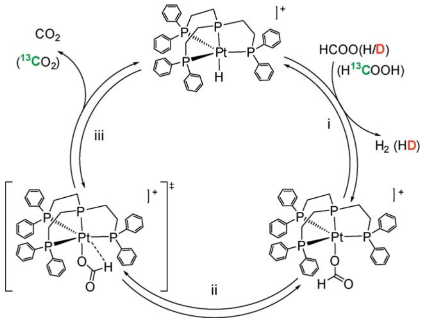
NHC-oxazoline ligands associated to the Cp^*Ru^{II} moiety generate catalysts that orientate the nucleophilic allylic substitution of cinnamyl chloride by phenols towards the regioselective formation of branched products, which, on reaction with Hoveyda(II) catalyst, lead to cross metathesis, and unsaturated functional compounds.

Formic Acid Decomposition Mechanism

T. P. Rieckborn, E. Huber, E. Karakoc,
M. H. Prosenc* 4757–4761

Platinum Complex Catalyzed Decomposition of Formic Acid

Keywords: Platinum / Hydride ligands / Hydrogen storage / C–H activation / Ab initio calculations / Homogeneous catalysis / Formic acid decomposition

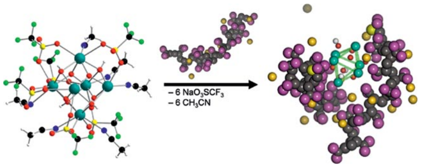


Pt-catalyzed formic acid decomposition in diluted solution yielded dihydrogen at 35 °C. The reaction path was investigated by isotopic labeling studies and DFT calculations revealing a β-H transfer of the intermittent formato ligand to the metal center.

FULL PAPERS

Bismuth Oxido Composites

The novel water-soluble bismuth oxido cluster $[Bi_6O_4(OH)_4(OTf)_6(CH_3CN)_6]\cdot2CH_3CN$ (**1**) was obtained by modification of $[Bi_6O_4(OH)_4](NO_3)_6\cdot H_2O$ with CF_3SO_3H. The synthesis, crystal structure, and complexation behavior of **1** towards polyacrylate were studied by methods including molecular dynamics simulations.



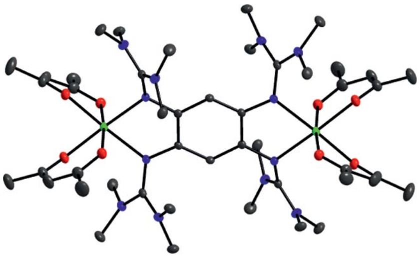
L. Miersch, T. Rüffer, H. Lang, S. Schulze, M. Hietschold, D. Zahn,* M. Mehring* .... **4763−4769**

A Novel Water-Soluble Hexanuclear Bismuth Oxido Cluster − Synthesis, Structure and Complexation with Polyacrylate

Keywords: Bismuth / Cluster compounds / Polymers / Molecular dynamics / Organic−inorganic hybrid materials

Guanidine Ligands

Chelating guanidines with an aromatic backbone have been used as ligands in a number of mono- and dinuclear Ni^{II} and Co^{II} complexes. The structures and properties of the complexes are evaluated.



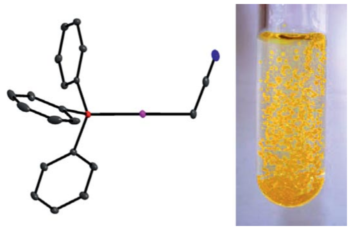
P. Roquette, C. König, O. Hübner, A. Wagner, E. Kaifer, M. Enders, H.-J. Himmel* .... **4770−4782**

Mono- and Dinuclear Ni^{II} and Co^{II} Complexes that Feature Chelating Guanidine Ligands: Structural Characteristics and Molecular Magnetism

Keywords: Guanidines / Nickel / Cobalt / Structure elucidation / Molecular magnetism

C−H Acidity

The first cyanomethyl complex of gold, synthesized by reaction between an Au^I complex and acetonitrile in the presence of a new guanidine N-superbase C−H bond activation of acetonitrile by Au^I in combination with a newly designed nitrogen base leads to the first structurally characterized (cyanomethyl)gold complex.



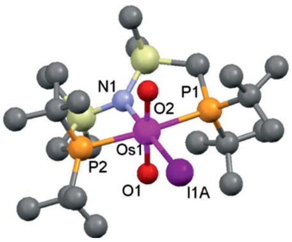
D. Emeljanenko, A. Peters, V. Vitske, E. Kaifer, H.-J. Himmel* ...... **4783−4789**

The First Cyanomethyl Complex of Gold, Synthesized by Reaction of a Au^I Complex with Acetonitrile in the Presence of a New Guanidine N-Superbase

Keywords: Gold / C−H acidity / C−H activation / Guanidine / Superbase

Redox Reactivity of Divalent Osmium

Synthesis of [(PNP)OsI] {PNP = $(tBu_2PCH_2SiMe_2)_2N$} shows this paramagnetic 14-valence electron species to rapidly add H_2 or ethylene, and to split O_2 rapidly at −78 °C to give the hexavalent species illustrated, $[(PNP)Os(O)_2I]$; reaction of [(PNP)OsI] with O-atom transfer reagents gives a product of transposition of amide N with O, [(POP)Os(N)I].



N. Tsvetkov, M. Pink, H. Fan, J.-H. Lee, K. G. Caulton* .... **4790−4800**

Redox and Lewis Acid Reactivity of Unsaturated Os^{II}

Keywords: Osmium / Pincer / Oxygen reduction / Hydrogen / C-H bond cleavage

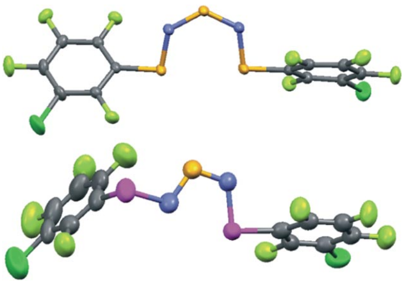
CONTENTS

Inorganic Crystal Engineering

A. G. Makarov, I. Yu. Bagryanskaya, Yu. V. Gatilov, N. V. Kuratieva, A. Yu. Makarov, M. M. Shakirov, A. V. Alexeyev, K. Tersago, C. Van Alsenoy, F. Blockhuys,* A. V. Zibarev* **4801–4810**

The First Observation of the *E,Z* Configuration Of Ar–X–N=S=N–X–Ar (X = S, Se) Chains in the Crystalline State

Keywords: Chalcogens / Crystal engineering / Density functional calculations / Configuration determination / Intermolecular interactions / Supramolecular chemistry



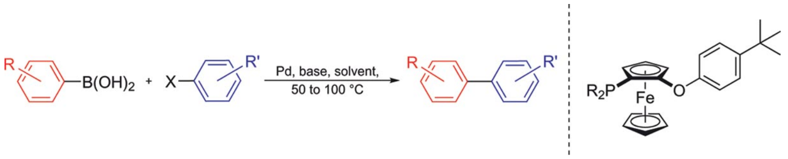
The unique *E,Z* configuration of the title compounds in the crystal is observed for Ar = 3-ClC_6F_4 and X = Se – in the presence of eleven *Z,Z* configurations found by XRD for various Ar and X groups in the hydrocarbon and fluorocarbon series – and explained by specific intermolecular Se···Cl and F···Cl interactions. (Colour code: grey – C, green – Cl, light green – F, blue – N, orange – S, magenta – Se.)

C–C Coupling

D. Schaarschmidt, H. Lang* **4811–4821**

Planar Chiral P,O-Compounds Derived from Ferrocenyl Aryl Ethers

Keywords: Ferrocenes / C–C coupling / Planar chirality / Phosphanes / Metalation



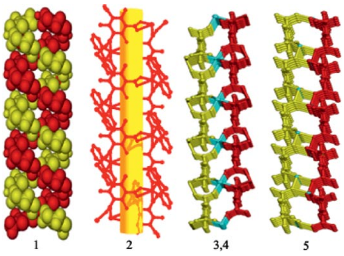
Planar chiral P,O-ferrocenes are excellent ligands in the palladium-mediated C–C coupling of aryl halides and aryl boronic acids. They allow either the conversion of unreactive substrates or reactions to be performed at low catalyst levels. Moreover, multiply *ortho*-substituted biaryls are accessible under mild conditions.

Carboxylate MOFs

H. He, H. Yin,* D. Wang, H. Ma, G. Zhang, D. Sun* **4822–4830**

Preparation, Crystal Structure, and Properties of Five Metal-Organic Complexes Based on a Triangular Nonplanar Carboxylate Ligand

Keywords: Metal-organic frameworks / Hydrothermal synthesis / Ligand effects / Photoluminescence / Crystal growth



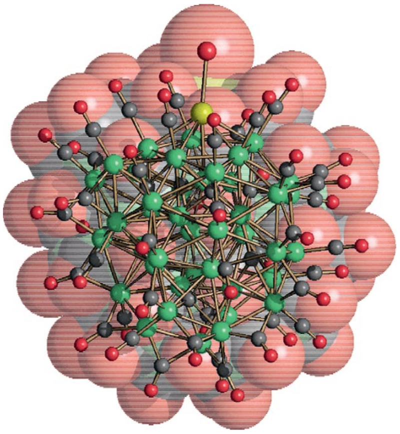
Five metal-organic complexes with four topological structures have been synthesized and characterized based on a nonplanar triangular carboxylate ligand.

Molecular Nanoclusters

A. Bernardi, C. Femoni, M. C. Iapalucci, G. Longoni, S. Zacchini,* S. Fedi, P. Zanello **4831–4842**

Synthesis, Structures and Electrochemistry of New Carbonylnickel Octacarbide Clusters: The Distorting Action of Carbide Atoms in the Growth of Ni Cages and the First Example of the Inclusion of a Carbon Atom within a (Distorted) Ni Octahedral Cage

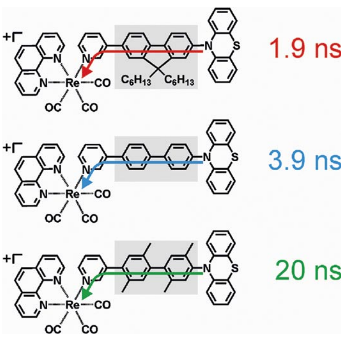
Keywords: Cluster compounds / Carbonyl ligands / Electrochemistry / Nickel / Carbides



High-nuclearity (carbonyl)Ni–Cd octacarbides – displaying highly distorted metal cages, polyhydride nature and marked redox activity – have been obtained. The molecular nature of these compounds at the borderline with colloidal nanoparticles has been assessed by combined structural, spectroscopic and electrochemical studies.

Electron Transfer

The kinetics of a 15 Å electron-transfer step from phenothiazine to a photoexcited rhenium complex depends strongly on the covalent linker between the two redox partners.



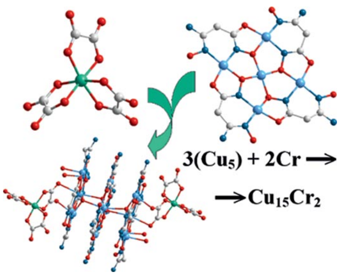
M. E. Walther, J. Grilj, D. Hanss, E. Vauthey, O. S. Wenger* .... 4843−4850

Photoinduced Processes in Fluorene-Bridged Rhenium−Phenothiazine Dyads − Comparison of Electron Transfer Across Fluorene, Phenylene, and Xylene Bridges

Keywords: Electron transfer / Photochemistry / Donor−acceptor systems / Time-resolved spectroscopy / Rhenium

Building Block Approach

The heptadecanuclear complex $\{[Cu_5(ahpha)_4]_3[Cr(C_2O_4)_3]_2 \cdot 14H_2O\}$ was obtained starting from a pentanuclear metallacrown. Magnetic properties of the compound are dominated by exchange interactions within the Cu_5 building block.



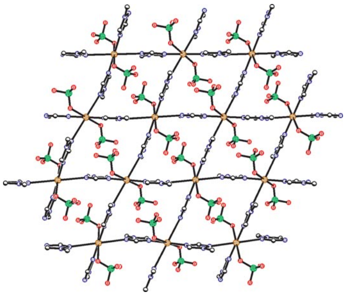
A. V. Pavlishchuk, S. V. Kolotilov,* M. Zeller, L. K. Thompson, I. O. Fritsky, A. W. Addison,* A. D. Hunter .... 4851−4858

A Triple-Decker Heptadecanuclear $(Cu^{II})_{15}(Cr^{III})_2$ Complex Assembled from Pentanuclear Metallacrowns

Keywords: Copper / Chromium / Polynuclear complexes / Magnetic properties / Magnetochemistry / Crown compounds / Metallacrowns / Ethanol sorption

Models for Metal-Mediated Base Pairs

The metal ion coordination behaviour of 1-methyl-1*H*-1,2,4-triazole, serving as a model for the artificial 1,2,4-triazole nucleoside, has been determined. In solution, the 2:1 stoichiometry necessary for the formation of metal-mediated base pairs is adopted. In accordance with stability constants, one- and two-dimensional cationic coordination polymers are observed in the solid state.



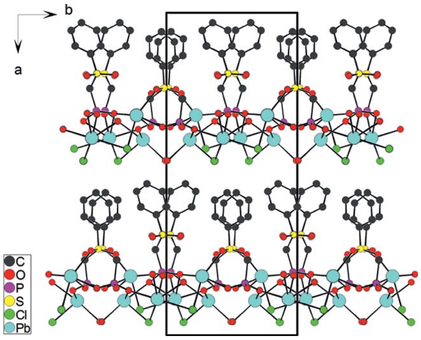
D. A. Megger, J. Kösters, A. Hepp, J. Müller* .... 4859−4864

Silver(I) and Mercury(II) Complexes with 1-Methyl-1,2,4-triazole as Models for Metal-Mediated Base Pairs − Formation of Discrete Complexes in Solution vs. One- and Two-Dimensional Coordination Polymers in the Solid State

Keywords: Silver / Mercury / N ligands / Metal-mediated base pairs / Coordination polymers

Layered Phosphonates

Two lead(II) phosphonates, $[Pb_3(Ph{-}SO_2{-}CH_2{-}PO_3)_2X_2(H_2O)]$ [X = Cl (**1**) and Br (**2**)] were synthesized by hydrothermal reactions. The two isostructural compounds exhibit a lamellar structure with phenylsulfonyl chromophores orienting unilaterally on the inorganic layer of $[Pb_3(PO_3)_2X_2(H_2O)]$. These compounds show second harmonic generation responses comparable to that of KDP (KH_2PO_4).



Z.-Y. Du,* Y.-H. Sun, X. Xu, G.-H. Xu, Y.-R. Xie* .... 4865−4869

Orientation of Second-Harmonic-Generation-Active Phenylsulfonyl Chromophores Attached on Layered Lead(II) Phosphonates

Keywords: Lead / Phosphonates / Crystal growth / Nonlinear optics

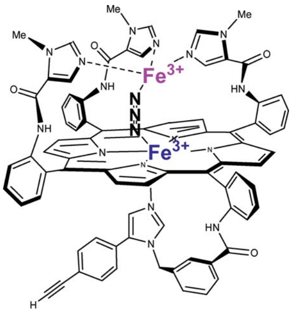
CONTENTS

Azide Binding to a NOR Model

Y. Yang,* A. Dey,
R. A. Decréau **4870–4874**

💻 Spectroscopic Characterization and Competitive Inhibition Studies of Azide Binding to a Functional NOR Model

Keywords: Azides / Azide binding / Nitric oxide reductase model / Competitive inhibition / EPR spectroscopy



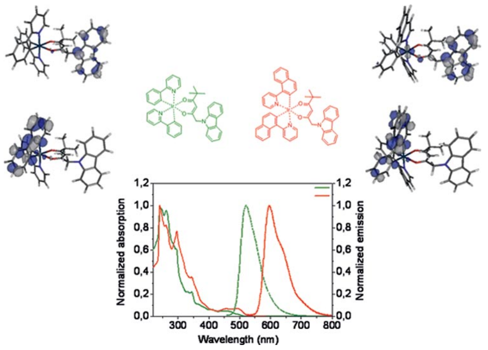
Azide binding to a functional nitric oxide reductase (NOR) model has been investigated in its mixed-valence ($LFe^{III}Fe^{II}$) and fully oxidized ($LFe^{III}Fe^{III}$) forms by FTIR and EPR. The reactivity of nitric oxide with the model compounds in the presence of excess azide supports the proposal that a bis-ferrous instead of a mixed-valence state is the active form of NOR.

Oxygen-Sensitive Ir(III) Emitters

N. Tian, D. Lenkeit, S. Pelz, L. H. Fischer,
D. Escudero,* R. Schiewek, D. Klink,
O. J. Schmitz, L. González,
M. Schäferling,* E. Holder* ... **4875–4885**

💻 Structure–Property Relationship of Red- and Green-Emitting Iridium(III) Complexes with Respect to Their Temperature and Oxygen Sensitivity

Keywords: Iridium / Phosphorescence / Temperature sensitivity / Oxygen sensitivity / Density functional calculations



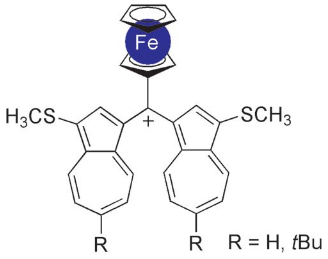
A comparison of the emission intensity of heteroleptic Ir^{III} complexes with unsymmetrical architecture to symmetrical homoleptic Ir^{III} complexes reveals a clear influence by applying changes to temperature and pressure. A general structure–property relationship of oxygen-sensitive Ir^{III} emitters is described by correlating their superior oxygen sensitivity to enhanced phosphorescence lifetimes.

Azulene Chemistry

T. Shoji,* J. Higashi, S. Ito,
N. Morita **4886–4891**

💻 Synthesis, Properties, and Redox Behavior of Ferrocene-Substituted Bis(3-methylthio-1-azulenyl)methylium Ions

Keywords: Azulene / Ferrocene / Carbocations / Cyclic voltammetry / Electrochemistry



Novel ferrocene-substituted bis(3-methylthio-1-azulenyl)methylium ions $\mathbf{5}^+$ and $\mathbf{6}^+$ were synthesized. The redox behavior of $\mathbf{5}^+$ and $\mathbf{6}^+$ was examined by cyclic voltammetry and differential pulse voltammetry, which revealed their amphoteric multistep redox properties. These cations exhibited a significant color change under electrochemical reduction conditions, which was revealed by visible spectroscopy.

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* Author to whom correspondence should be addressed.

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