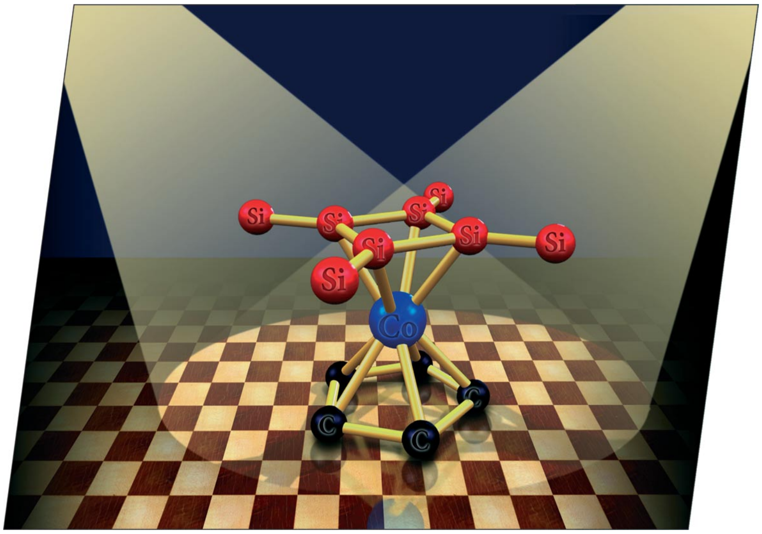
COVER PICTURE

The cover picture shows two spotlights illuminating the structure of the first sandwich complex featuring an all-heavy group 14 element-consisting Si_4-cyclic ligand, namely, a derivative of (η^5-cyclopentadienyl)(η^4-tetrasilacyclobutadiene)cobalt [(η^4-R_4Si_4)-CoCp] (R = SiMe*t*Bu$_2$). The Me and *t*Bu groups on the Si substituents, as well as the H atoms on the Cp ring, are removed for simplicity. The title compound was smoothly prepared by a ligand exchange reaction between the tetrasilacyclobutadiene dianion salt $K^+{}_2\cdot[R_4Si_4]_2$ and [$CpCoI_2$-(PPh_3)]. Systematic comparison of the complex [(η^4-R_4Si_4)CoCp] and its carbon analogue [η^4-($Me_3Si)_4C_4$]CoCp revealed important structural distinctions between the two complexes that result from the different ring sizes of the cyclobutadiene ligands η^4-R_4E_4 (R = SiMe*t*Bu$_2$, E = Si vs. R = $SiMe_3$, E = C). Details of the synthesis of the novel Co complex, as well as of its structural and electronic peculiarities, are discussed in the Short Communication by A. Sekiguchi et al. on p. 5471ff.



CONTENTS

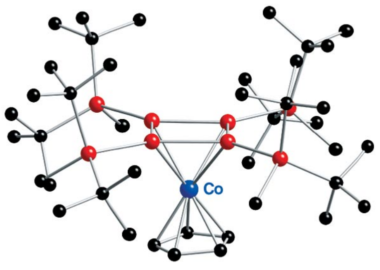
SHORT COMMUNICATION

Sandwich Complex with η^4-Si_4R_4

K. Takanashi, V. Ya. Lee, M. Ichinohe, A. Sekiguchi* 5471–5474

(η^5-Cyclopentteadienyl)(η^4-tetrasila- and η^4-trisilagermacyclobutadiene)cobalt: Sandwich Complexes Featuring Heavy Cyclobutadiene Ligands

Keywords: Cobalt / Cyclobutadiene ligand / Cyclopentadienyl ligand / Germanium / Silicon



(η^5-Cyclopentadienyl)(η^4-tetrasila-cyclobutadiene)cobalt complex **2**

(η^5-Cyclopentadienyl)(η^4-tetrasila- and η^4-trisilagermacyclobutadiene)cobalt sandwich complexes [(η^4-R_4Si_4)CoCp] (**2**) and [(η^4-R_4Si_3Ge)CoCp] (**4**) (R = SiMe*t*Bu$_2$) were synthesized by reaction of the dipotassium salts of tetrasilacyclobutadiene dianion $K^+{}_2\cdot[R_4Si_4]^{2-}$ (**1**) and trisilagermacyclobutadiene dianion $K^+{}_2\cdot[R_4Si_3Ge]^{2-}$ (**3**) with [$CpCoI_2(PPh_3)$]. The structures of the new Co complexes were confirmed by X-ray analysis.

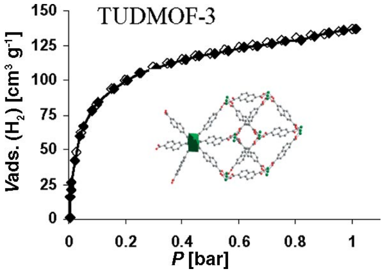
FULL PAPERS

Metal–Organic Frameworks

I. Senkovska, J. Fritsch, S. Kaskel* 5475–5479

New Polymorphs of Magnesium-Based Metal–Organic Frameworks $Mg_3(ndc)_3$ (ndc = 2,6-Naphthalenedicarboxylate)

Keywords: Metal–organic frameworks / Magnesium / 2,6-Naphthalenedicarboxylic acid / Solvent effects / Gas adsorption



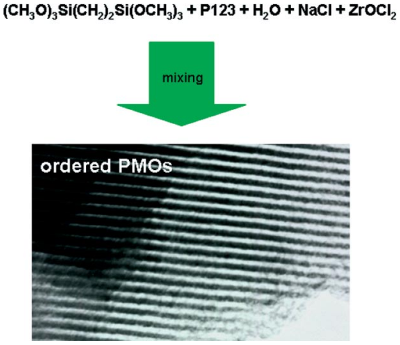
Two new magnesium 2,6-naphthalenedicarboxylate (ndc) metal–organic frameworks, [$Mg_3(ndc)_3(dif)_4$] (**1**) (dif = *N*,*N*-diisopropylformamide) and [$Mg_3(ndc)_3(dmf)_2$-$(CH_3OH)(H_2O)$](dmf) (**2** = TUDMOF-3) (dmf = *N*,*N*-dimethylformamide), have been synthesised. TUDMOF-3 has a permanent porosity with a Langmuir surface area of 632 m^2 g^{-1}, a specific pore volume of 0.21 cm^3 g^{-1} and a hydrogen storage capacity of 1.23 wt.-% (77 K, 1 bar). Compound **1** is not porous.

Hybrid Mesostructures

S.-R. Zhai, S. S. Park, M. Park, M. H. Ullah, C.-S. Ha* 5480–5488

Direct Synthesis of Zr-Containing Hybrid Periodic Mesoporous Organosilicas with Tunable Zirconium Content

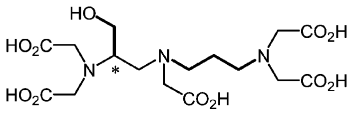
Keywords: Silicates / Template synthesis / Orangic–inorganic hybrid composites / Mesoporous materials



Highly ordered Zr-containing periodic mesoporous organosilicas (ZrPMO) were successfully synthesized, for the first time, by employing a $ZrOCl_2$/NaCl combination as the promoting agent; the addition of extra amounts of acid was not needed throughout the synthetic process.

Contrast Agents

The propylene bridge in the skeleton of the $H_5EPTPACH_2OH$ ligand optimizes the water-exchange rate of the $[Gd(EPTPA\text{-}CH_2OH)(H_2O)]^{2-}$ complex, for efficiency as a MRI contrast agent, as a result of the steric compression imposed around its water binding site, as shown by solution relaxometric characterization. The hydroxymethyl substituent group is useful for conjugation of the reporter group. However, these changes, relative to those incurred by the DTPA chelate, significantly decrease its thermodynamic and kinetic stability.



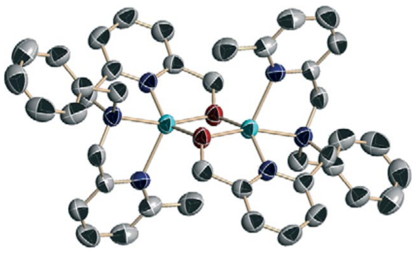
S. Torres, J. A. Martins,*
J. P. André,* G. A. Pereira, R. Kiraly,
E. Brücher, L. Helm, É. Tóth,
C. F. G. C. Geraldes* .... 5489−5499

$H_5EPTPACH_2OH$: Synthesis, Relaxometric Characterization and ^1H NMR Spectroscopic Studies on the Solution Dynamics of Its Ln^{III} Complexes

Keywords: Lanthanides / Contrast agents / MRI / Microscopic protonation scheme / Stability constants

Isomerism of Copper Complexes

The preference for axial or equatorial positioning of the bridging atoms and of the amine or pyridine N centers of tridentate ligands L in $LCu^{II}(\mu\text{-}X)_2Cu^{II}L$ complexes was probed experimentally and by DFT calculations. Their preference for either a *syn* or *anti* configuration in an equatorial/equatorial situation was also evaluated.



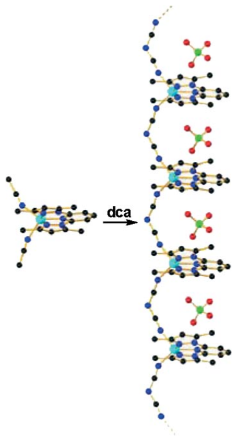
J. Manzur,* A. Vega,* A. M. García,
C. Acuña, M. Sieger, B. Sarkar,
M. Niemeyer, F. Lissner, T. Schleid,
W. Kaim* .... 5500−5510

Coordination Alternatives in Dinuclear Bis(pyridin-2-ylalkyl)benzylaminecopper(II) Complexes with OH^-, RO^-, F^-, or Cl^- Bridges: Experimental Structures and DFT Preferences

Keywords: Copper / EPR spectroscopy / Isomerism / N ligands / Structure

Coordination Oligomers/Polymers

Reactions of three preformed Cu^{II}/bdmpp complexes [bdmpp = 2,6-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridine] with 4,4′-bipy, dicyanamide (dca), azide, and MCl_2 (M = Cu, Co, Ni) lead to a series of homo- and heterometallic coordination oligomers and polymers. Their structures and redox properties were investigated.



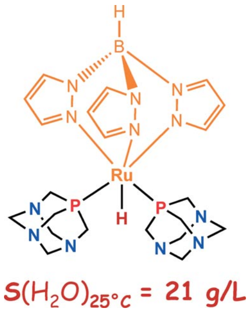
G.-F. Liu, Z.-G. Ren, H.-X. Li,
Y. Chen, Q.-H. Li, Y. Zhang,
J.-P. Lang* .... 5511−5522

Homo- and Heterometallic Coordination Oligomers and Polymers Derived from the Preformed Complexes $[Cu(bdmpp)(MeCN)_2](ClO_4)_2$, $[Cu(bdmpp)(N_3)_2]$, and $[Cu(bdmpp)(N_3)(\mu\text{-}N_3)]_2$ [bdmpp = 2,6-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridine]: Syntheses, Structures, and Redox Properties

Keywords: Copper / Structures / Oligomers / Polymers / Redox properties

Water-Soluble Ruthenium Complexes

A series of [tris(pyrazolyl)borato]ruthenium complexes bearing the water-soluble cage phosphane 1,3,5-triaza-7-phosphaadamantane (PTA) and its boranyl adduct $PTA(BH_3)$, including the water-soluble hydride $[TpRuH(PTA)_2]$, have been synthesised and characterised. Cyclic voltammetric studies in MeCN and dmso generally show reversible $Ru^{II/III}$ oxidation waves and the values of $E_{1/2}{}^{ox}$ reflect the electron-donating character of the ligands, whose Lever electrochemical parameter (E_L) is estimated for the first time.



S. Bolaño, J. Bravo,* J. Castro, M. Mar
Rodríguez-Rocha, M. F. C. Guedes da Silva,
A. J. L. Pombeiro,* L. Gonsalvi,
M. Peruzzini* .... 5523−5532

Synthesis, Reactivity, X-ray Crystal Structures and Electrochemical Behaviour of Water-Soluble [Tris(pyrazolyl)borato]ruthenium(II) Complexes of 1,3,5-Triaza-7-phosphaadamantane (PTA)

Keywords: Electrochemistry / Water-soluble complexes / Pyrazolylborates / Ruthenium / N ligands

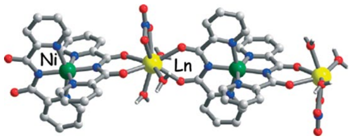
CONTENTS

3d–4f Coordination Polymers

A. M. Madalan, K. Bernot, F. Pointillart, M. Andruh,* A. Caneschi* 5533–5540

First Ni^{II}–Ln^{III} Coordination Polymers Constructed by Using $[Ni(bpca)_2]$ as a Building Block [Hbpca = bis(2-pyridylcarbonyl)amine]: Synthesis, Crystal Structures and Magnetic Properties

Keywords: Nickel / Lanthanides / Heterobimetallic coordination polymers / Magnetic properties



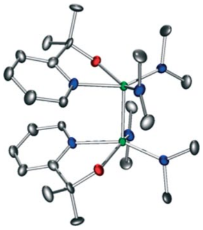
Three new heterobimetallic 1D coordination polymers have been obtained by assembling the $[Ni(bpca)_2]$ complex, as a building block, with lanthanide cations: $[\{Ln(O_2NO)(H_2O)_3\}\{Ni(bpca)_2\}](NO_3)_2\cdot 3H_2O$ (Ln Gd **1**; Tb **2**; Dy **3**). Their static and dynamic magnetic properties were investigated and discussed.

Ditungsten(III) Complexes

O. Coutelier, R. M. Gauvin,*
G. Nowogrocki, J. Trébosc, L. Delevoye,
A. Mortreux* 5541–5547

A New Donor-Stabilized Ditungsten Amido Alkoxido Species: Synthesis, Crystal Structure, Fluxionality, and Grafting onto Silica

Keywords: Tungsten / Metal-metal multiple bonds / Ligand design / Grafting / Silica / Alkyne metathesis



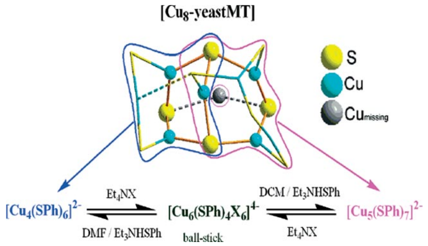
A new dimeric tungsten(III) complex containing amido and chelating pyridine–alkoxido ligands was synthesized through protonolysis of $[W_2(NMe_2)_6]$ by 2-(2-pyridyl)propan-2-ol and fully characterized. Grafting of this compound onto silica has been investigated by elemental analysis, DRIFTS, and solid-state NMR spectroscopy.

Copper–Thiolate Clusters

B. K. Maiti, K. Pal,
S. Sarkar* 5548–5555

Flexible Cu^I–Thiolate Clusters with Relevance to Metallothioneins

Keywords: Metallothioneins / Flexibility / Coordination modes / Copper / Sulfur / Photoluminescence



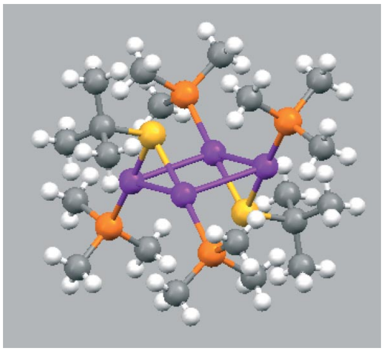
The structural diversity in some Cu–thiol small clusters with relevance to the chemistry of Cu-containing metallothioneins was investigated. Solvent polarity and the copper/thiol ratio may change the local cluster geometry, which causes flexibility of the copper–sulfur bond. These small clusters have superposition motifs in bigger clusters such as Cu_8-yeastMT.

Au–Au Interactions

F. Balzano, A. Cuzzola,
P. Diversi,* F. Ghiotto,
G. Uccello-Barretta 5556–5562

Cationic Gold(I) Phosphanyl Thiolates: Aurophilic Interactions in the Solid State and in Solution

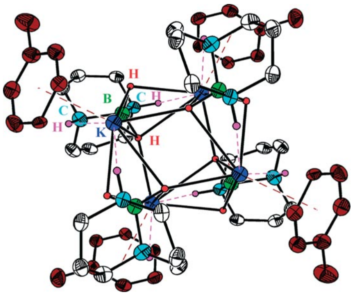
Keywords: Gold / Sulfur / Thiolates / Aurophilicity / Aggregation / ESI MS / NMR spectroscopy



Cationic gold(I) phosphane alkanethiolates of the formula $[Au_2(StBu)(phosphane)_2][BF_4]$ were investigated in solution by MS and NMR spectroscopy. These compounds are dimeric in the solid state and are bound through aurophilic interactions; some of these compounds maintain the integrity of the Au–Au bonds in solution depending on the nature of the phosphane.

Organohydroborate

Based upon single-crystal X-ray diffraction analysis, the potassium salt of the 9-BBN hydroborate anion has a tetrameric structure when associated with toluene, methyl THF, or a mixture of toluene/THF, and THF/diethyl ether. While with the chelating solvent DME, it has a dimeric structure.

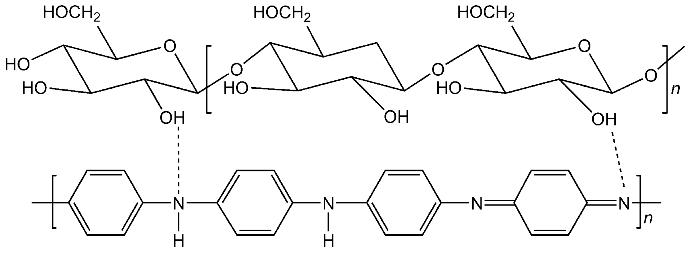


X. Chen, S. Liu, B. Du, E. A. Meyers,
S. G. Shore* 5563–5570

The Structure of Potassium and Tetramethylammonium Salts of the Cyclic Organohydroborate Anion $[H_2BC_8H_{14}]^-$ with Different Solvent Ligands

Keywords: Agostic interactions / X-ray diffraction / Organohydroborate / Potassium salts

Hybrid Materials



Conducting polymer/cellulose fibre composites, using polypyrrole and polyaniline, have been successfully prepared. By utilising the redox active nature of the conducting polymer coatings, silver nanoparticles have been deposited on the surface of the composite fibres. This additionally gives rise to fibres with antimicrobial properties.

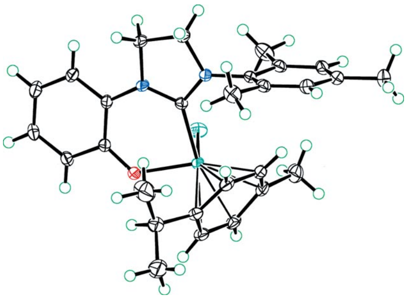
F. M. Kelly,* J. H. Johnston, T. Borrmann,
M. J. Richardson 5571–5577

Functionalised Hybrid Materials of Conducting Polymers with Individual Fibres of Cellulose

Keywords: Polypyrrole / Polyaniline / Cellulose / Fibres / Conductivity / Antimicrobial activity

Olefin Metathesis Catalysts

The use of Ru-based NHC-arene complexes as alternatives to the Grubbs-type catalysts used in olefin metathesis is described.



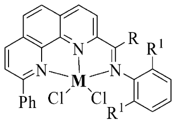
N. Ledoux,* B. Allaert,
F. Verpoort 5578–5583

Ruthenium-Based NHC-Arene Systems as Ring-Opening Metathesis Polymerisation Catalysts

Keywords: Carbene ligands / Homogeneous catalysis / Olefin polymerisation / Ruthenium

Catalytic Ethylene Oligomerization

A series of iron, cobalt and nickel complexes bearing 2-arylimino-9-phenyl-1,10-phenanthrolines has been synthesized, characterized and evaluated for ethylene oligomerization. Most of the complexes show good catalytic activity for ethylene oligomerization, with the cobalt catalysts being more active than their iron analogues.



M = Fe, Co, Ni

S. Jie, S. Zhang,
W.-H. Sun* 5584–5598

2-Arylimino-9-phenyl-1,10-phenanthrolinyl-iron, -cobalt and -nickel Complexes: Synthesis, Characterization and Ethylene Oligomerization Behavior

Keywords: Nitrogen ligands / Late transition metals / Iron / Ethylene / Oligomerization

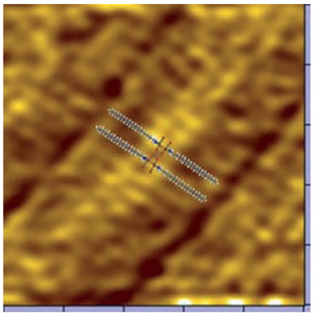
CONTENTS

Octaruthenium Grids on HOPG

D.-L. Shieh, Y.-S. Lin, K.-B. Shiu, J.-L. Lin* 5599–5603

Orientation and Arrangement of Octaruthenium Supramolecules with Alkyl Chains on Graphite

Keywords: Supramolecular chemistry / Scanning tunneling microscopy / Ruthenium



$\{[Ru_2(CO)_4(NH_2C_{16}H_{33})_2](\mu\text{-}O_2CCO_2)\}_4$ / HOPG

The self-assemblies of octaruthenium grid-type supramolecules, $[Ru_2(CO)_4(NH_2C_{16}H_{33})_2](\mu\text{-}O_2CCO_2)_4$, on highly oriented pyrolytic graphite (HOPG) in air and in phenyloctane were studied by scanning tunneling microscopy (STM).

REMOVAL

L.-Y. Li, Q. Yuan, L. Liao,* C.-H. Yan, J. Chen 5605

Removal: “Ultra-Simple Synthesis of Ordered Mesoporous γ-Alumina: High Thermal Stability and Catalytic Activity”