









GERMANY





















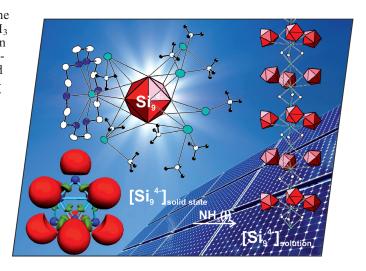


A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

Eur. J. Inorg. Chem. 2009, 4579-4584

The cover picture shows significant parts of the crystal structures of Rb(18-crown-6)Rb₃Si₉·4NH₃ and Rb₄Si₉·4.75NH₃. On the left, the coordination sphere of the nonasilicide anion in the 18-crown-6-containing compound is shown. The second structural part shows the Rb-ammonia-nonasilicide strands found in the crystal structure of Rb₄Si₉·4.75NH₃. The existence of these thermally labile ammoniates demonstrates that it is possible to extract $\mathrm{Si_9}^{4-}$ anions from a ternary solid-state material into a liquid ammonia solution without further oxidation. This opens the door to chemical transformations of bare electron-rich silicon clusters. The ELF picture on the left shows that no evidence for three-center, two-electron bonding can be found, although the Wade-Mingos-Williams rules obviously apply for the prediction of the molecular shape of the anions. Details are discussed in the article by N. Korber et al. on p. 4641ff.



MICROREVIEW

Carbon-Fluorine Bond Activation

R. P. Hughes* 4591-4606

Conversion of Carbon-Fluorine Bonds α to Transition Metal Centers to Carbon-Hydrogen, Carbon-Carbon, and Carbon-Heteroatom Bonds

Keywords: Fluorinated ligands / Iridium / Transition metals / Diastereoselectivity / Reaction mechanisms



The stereoselectivity of activation of the carbon–fluorine bond α to iridium by external protic acids has been studied in pseudo-tetrahedral primary fluoroalkyl complexes of iridium. Migration of internal nucleophiles leads to diastereoselective formation of new carbon–oxygen, carbon–sulfur, carbon–hydrogen, and carbon–carbon bonds.

SHORT COMMUNICATION

Redox-Active Ligands

U. Siemeling,* C. Färber, M. Leibold,

C. Bruhn, P. Mücke, R. F. Winter,

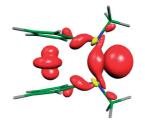
B. Sarkar, M. von Hopffgarten,

G. Frenking 4607-4612



Six-Membered N-Heterocyclic Carbenes with a 1,1'-Ferrocenediyl Backbone: Bulky Ligands with Strong Electron-Donor Capacity and Unusual Non-Innocent Character

Keywords: Carbenes / N-Heterocyclic carbenes / Radicals / Density-functional calculation / Ligand effects / Redox chemistry / Sandwich complexes



A new class of non-innocent ligands: Stable ferrocene-based NHCs are bulky ligands with very strong electron-donor capacity. Their redox activity rests not solely on the ferrocene moiety. They can be oxidised to a radical cation, the spin density of which is located at Fe and the carbene C atom and whose long-lived nature is unprecedented in NHC chemistry.

Molecular Architecture

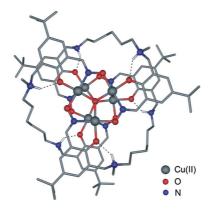
M. Wenzel, R. S. Forgan, A. Faure, K. Mason, P. A. Tasker, S. Piligkos,

E. K. Brechin, P. G. Plieger* 4613-4617



A New Polynuclear Coordination Type for (Salicylaldoxime)copper(II) Complexes: Structure and Magnetic Properties of an (Oxime)Cu₆ Cluster

Keywords: Supramolecular chemistry / Copper / Helical structures / Magnetic properties / Salicylaldoxime

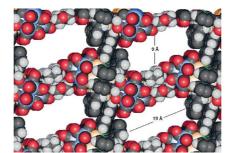


Incorporation of 3-aminomethyl groups on the salicylaldoxime framework aid Cu^{II} to form μ_3 -oxo trinuclear complexes more commonly formed by *trivalent* first transition series metals.



1D Polymers from Clusters

1D chains of formula [{Ag(OC₄H₈)- $\{Rh_6C(CO)_{15}\}Ag(OC_4H_8)\}pyz]_{\infty}$ and [bipy- ${Ag_2Ru_6C(CO)_{16}}(bipy)_2{Ag_2Ru_6C(CO)_{16}}$. 2THF]_∞ were obtained by condensing the carbido cluster anions $[Rh_6C(CO)_{15}]^{2-}$ and [Ru₆C(CO)₁₆]²⁻ with Ag⁺ ions and dinitrogen ligands. In the latter, the metal clusters are connected alternatively by one and two linkers, giving rise to large channels.



R. Della Pergola,* A. Sironi, C. Manassero,

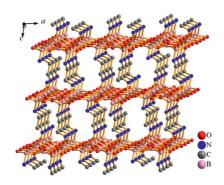
M. Manassero 4618-4621

Chains and Nanochannels Self-Assembled from Carbido Clusters, Silver Ions and Heterocyclic Ligands - Crystal Structures of the 1D Coordination Polymers $[\{AgOC_4H_8\{Rh_6C(CO)_{15}\}AgOC_4H_8\}pyz]_{\infty}$ and $[bipy{Ag_2Ru_6C(CO)_{16}}(bipy)_2{Ag_2}$ $Ru_6C(CO)_{16}$ } • $2C_4H_8O$] $_{\infty}$

Keywords: Cluster compounds / Rhodium / Ruthenium / Silver / Polymerization

Boron Oxide Open Framework

A novel open-framework compound, B₆O₉(en)₂@(H₂en)Cl₂, was synthesized under solvothermal conditions. The framework is built up from neutral [B₆O₉] layers linked by ethylenediamine molecules through coordinative B-N bonds.



M.-C. Liu, P. Zhou, H.-G. Yao, S.-H. Ji, R.-C. Zhang, M. Ji, Y.-L. An* 4622-4624

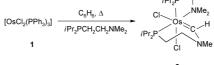
A Novel Boron Oxide Organic Open-Framework Compound: $B_6O_9(en)_2(a)(H_2en)Cl_2$



Keywords: Boron / Template synthesis / Organic-inorganic hybrid composites / Layered compounds / Structure elucidation

The aminocarbene complex cis,cis- $[OsCl_2{\kappa^2(C,P)-CHN(CH_3)CH_2CH_2-}$ $PiPr_2$ { $\kappa^2(P,N)$ - $iPr_2PCH_2CH_2NMe_2$ }] (2), obtained from [OsCl₂(PPh₃)₃] (1) and iPr₂PCH₂CH₂NMe₂ by double C-H activation of one NCH3 group, reacts with PhC≡CH to afford a vinylidene-os-

mium(II) derivative. The reaction of 2 with CO and CNtBu yields ionic compounds by substitution of one chloro ligand.

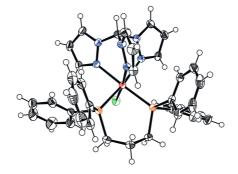


Carbene Osmium Complexes B. Richter, H. Werner* 4625-4628

Synthesis and Reactivity of an Aminocarbene Osmium Complex Formed by Double C-H Activation of a NCH3 Unit

Keywords: Carbene complexes / C-H activation / Osmium / Phosphaneamine / Vinylidene complex

A series of [tris(pyrazolyl)methane]ruthenium complexes supported by phosphane auxiliary ligands were found to display remarkable antiproliferative activity in vitro against the MCF-7 (breast) and HeLa (cervical) cancer cell lines. Color code: green = Cl, blue = N, orange = P, red =



Ruthenium Anticancer Complexes

J. M. Walker, A. McEwan, R. Pycko, M. L. Tassotto, C. Gottardo, J. Th'ng, R. Wang, G. J. Spivak* 4629-4633

[Tris(pyrazolyl)methane]ruthenium Complexes Capable of Inhibiting Cancer Cell Growth



Keywords: Ruthenium / Tris(pyrazolyl)methane / Half-sandwich complexes / Antiproliferative assays / Anticancer agents

Ru.

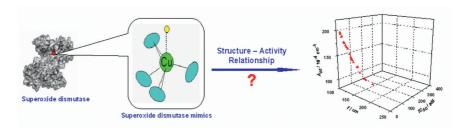
CONTENTS

Cu/Zn Superoxide Dismutase Mimics



Global Structure-Activity Analysis in Drug Development Illustrated for Active Cu/Zn Superoxide Dismutase Mimics

Keywords: Structure—activity analysis / Enzyme mimics / Electron paramagnetic resonance / Copper complexes



The statistical analysis of most of the reported Cu/Zn superoxide dismutase mimics (SODm) indicates that their EPR parameters are directly and linearly related to their activity. Together with the appropriate

redox potentials, this analysis makes it possible to distinguish the specificity of highly active Cu/Zn SODm and serves to streamline further synthetic efforts for drug development.

FULL PAPERS

Si₉⁴⁻ Anions in Solution

S. Joseph, C. Suchentrunk, F. Kraus, N. Korber* 4641–4647

 ${\rm Si_9}^{4-}$ Anions in Solution – Structures of the Solvates ${\rm Rb_4Si_9\cdot 4.75NH_3}$ and ${\rm [Rb(18-crown-6)]Rb_3Si_9\cdot 4NH_3}$, and Chemical Bonding in ${\rm Si_9}^{4-}$

Keywords: Zintl anions / Silicon / Cluster compounds / Ab initio calculations / ELF (Electron Localisation Function)



Whereas the solution chemistry of Ge₉⁴⁻, Sn₉⁴⁻ and Pb₉⁴⁻ is now well established, any evidence that Si₉⁴⁻ might be similarly extracted from solids is still missing.

Supramolecular Chemistry

2,11-Dialkylated 1,12-Diazaperylene Copper(I) Complexes: First Supramolecular Column Assemblies by π - π Stacking between Homoleptic Tetrahedral Metal Complexes, Exhibiting Low-Energy MLCT Transitions

Keywords: Copper / N ligands / Pi interactions / Self-assembly / Immobilization

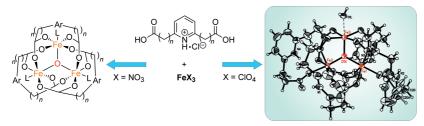


Copper(I) complexes of new "large-surface" ligands have been synthesized and characterized. In the solid state the [Cu-(dipdap)₂]BF₄ (dipdap = 2,11-diisopropyl-

1,12-diazaperylene) complex shows a columnar structure along the crystallographic c axis, held by π - π stacking interactions.



Non-Heme Iron Complexes



2,6-Diacylpyridine ligands with varying tether lengths between the pyridine and the carboxylate groups form Fe complexes. The trinuclear Fe₃(μ_3 -O) core of the complexes was proved by X-ray crystal-struc-

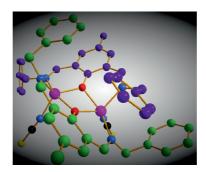
ture analysis and was further supported by spectroscopic and magnetic studies. The Fe complexes were used in comparative Giftype catalytic aerobic oxidations. V. Rabe, W. Frey, A. Baro, S. Laschat,* M. Bauer, H. Bertagnolli, S. Rajagopalan, T. Asthalter, E. Roduner, H. Dilger, T. Glaser, D. Schnieders 4660–4674

Syntheses, Crystal Structures, Spectroscopic Properties, and Catalytic Aerobic Oxidations of Novel Trinuclear Non-Heme Iron Complexes

Keywords: Carboxylate ligands / EPR spectroscopy / EXAFS spectroscopy / Mössbauer spectroscopy / Oxidation

Dicobalt Complexes

The binding of a pseudohalide to a cobalt (II) center drives the self-assembly of two dangling benzyl groups bearing binucleating ligands around the metal and yields a five-coordinate antiferromagnetically coupled [Co₂] complex. The ligands exhibit nonplanar binding modes that are responsible for nonregular coordination architectures often noticed in dicobalt active sites in proteins.

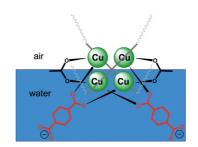


Azido, Cyanato, and Thiocyanato Coordination Induced Distortions in Pentacoordinated $[Co^{II}A(bip)]_2$ (A = NCS $^-$, N $_3$ $^-$, or NCO $^-$) Complexes

Keywords: N,O ligands / Bridging ligands / Cobalt / Structure elucidation / Magnetic properties

Metalloamphiphiles

Metalloamphiphiles capable of accommodating bimetallic and tetrametallic coppercontaining headgroups were synthesized and characterized. These amphiphiles are based on pseudomacrocyclic and openframe ligands and allow for the study of film formation at the air/water interface as a function of core sizes, structural architectures, and subphase changes.



S. S. Hindo, R. Shakya, R. Shanmugam, M. J. Heeg, C. N. Verani* 4686–4694

Metalloamphiphiles with [Cu2] and [Cu4] Headgroups: Syntheses, Structures, Langmuir Films, and Effect of Subphase Changes

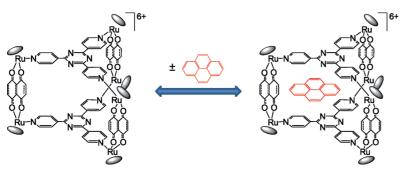
Keywords: Amphiphiles / Copper / Terephthalate / Pseudomacrocyclic / Langmuir films / Brewster angle microscopy / N,O ligands / Interfaces

Host-Guest Chemistry

N. P. E. Barry, B. Therrien* 4695-4700

Host-Guest Chemistry in the Hexanuclear (Arene)ruthenium Metalla-Prismatic Cage [Ru₆(*p*-cymene)₆(tpt)₂(dhnq)₃]⁶⁺

Keywords: Arenes / Host-guest systems / Carceplex / Ruthenium / Supramolecular chemistry



A large cationic triangular metalla-prism, [Ru₆(*p*-cymene)₆(tpt)₂(dhnq)₃]⁶⁺, possessing a portal size smaller than its cavity, has allowed both, permanent and temporary encapsulation of molecules. The host–guest

properties have been studied in solution in the presence of various planar molecules and showed a stability constant of association larger than 4.0×10^4 m⁻¹ for pyrene.

CONTENTS

Aluminium Chemistry

J.-T. Issenhuth, J. Pluvinage, R. Welter,

S. Bellemin-Laponnaz,

S. Dagorne* 4701-4709

Novel Neutral and Cationic Aluminium Alkyl Complexes Supported by Potentially Tridentate O,N,L-Type Aminophenolate Ligands and Their Use in Propylene Oxide Polymerization

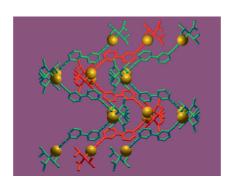
Keywords: Lewis acids / Aluminum / Cations / Polymerization / N,O ligands

Potentially tridentate O,N,L-type aminophenolate chelating ligands were found to be suitable for coordination to aluminium, allowing access to stable neutral and cationic Al alkyl species. Some of these cations were found to be highly active in propylene oxide polymerization under mild conditions to yield atactic poly(propylene oxide) with a moderate polydispersity.

Emissive 2,2'-Bipyridines

Structural and Photophysical Properties of (Phosphane)gold(I)-Decorated 4,4'-Diethynyl-2,2'-bipyridine Ligands

Keywords: Gold / Heterocycles / Alkynes / 2,2'-Bipyridine / Phosphane ligands / Photophysics



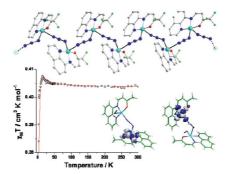
Bis[(phosphane)gold(I)]-decorated 4,4'-diethynyl-2,2'-bipyridine ligands can be prepared from 4,4'-diethynyl-2,2'-bipyridine and R_3 PAuCl (R=Ph, 4-Tol, Et, iPr). The solid-state structures of these derivatives show a dependence upon the presence of aryl- or alkyl-substituted phosphane; the change from ethyl to isopropyl substituents leads to packing differences that result in the propagation of two different polymeric chain motifs, both supported by close Au···Au contacts. In CH_2Cl_2 solution at room temperature, each compound is a dual emitter.

1D Chain Polymers

G. Pilet,* M. Médebielle, J.-B. Tommasino, G. Chastanet,* B. Le Guennic, C. Train 4718–4726

Single End-to-End Azidocopper(II) Chain Based on an Electroactive Ligand: A Structural, Electrochemical, Magnetic and Ab Initio Study

Keywords: Magnetic properties / Chain structures / Azides / Copper



Single end-to-end azide bridges between enaminone-chelated copper(II) ions build one dimensional compounds. In this configuration, the azido bridge mediates a weak ferromagnetic interaction, which is justified by ab initio calculations.

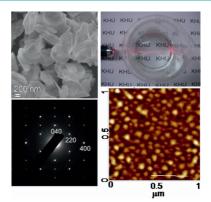
Layered Hydroxy Nitrates

K.-H. Lee, S.-H. Byeon* 4727-4732



Synthesis and Aqueous Colloidal Solutions of $RE_2(OH)_5NO_3\cdot nH_2O$ (RE = Nd and La)

Keywords: Layered compounds / Rare earths / Colloids / Inclusion compounds



A new, simple route was developed to synthesize the complete rare-earth series of the RE₂(OH)₅NO₃·nH₂O family. The hydration of La₂(OH)₅NO₃·nH₂O and Nd₂(OH)₅NO₃·nH₂O synthesized by this nonaqueous solvothermal method yielded transparent aqueous colloidal solutions.

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

If not otherwise indicated in the article, papers in issue 29-30 were published online on October 12, 2009

^{*} Author to whom correspondence should be addressed.