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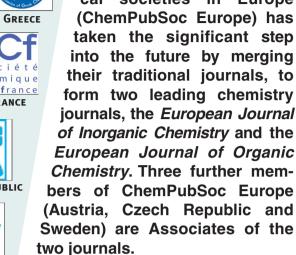












COVER PICTURE

The cover picture shows a harlequin dancing in a room surrounded by transition metals. This character is a theatrical metaphor representing an ambiphilic ligand and its interaction with transition elements, which is the topic of the Microreview. The multiple arms describe the multidentate nature of this family of ligands. One side of his face is sad and represents the Lewis acid (Z) component of the ambiphilic ligand, while the other side is smiling and represents the L moiety, which is the donating component of the ligand. Details are presented by F.-G. Fontaine et al. on p. 5439ff. The artwork was designed by Marie Tremblay.



5431

MICROREVIEW

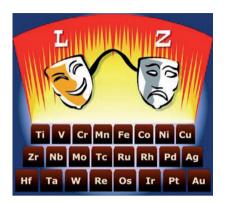
Ambiphilic Ligands

F.-G. Fontaine,* J. Boudreau, M.-H. Thibault 5439-5454



Coordination Chemistry of Neutral (L_n) –ZAmphoteric and Ambiphilic Ligands

Keywords: Ambiphilic ligands / Amphoteric ligands / Bifunctional ligands / Lewis acids



Ambiphilic and amphoteric molecules, which have both a donor and an acceptor group, have great potential in many applications. This microreview will focus on the coordination chemistry of a subclass of these molecules, in which the donor groups can be represented as L_n ligands. The various strategies to overcome aggregation and the reactivity and properties of these complexes will be discussed.

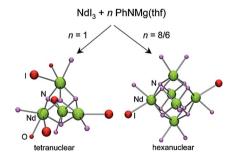
SHORT COMMUNICATIONS

Advances in f-Element Chemistry

J.-C. Berthet,* P. Thuéry, M. Ephritikhine 5455-5459

Polyimido Clusters of Neodymium and Uranium, Including a Cluster with an $M_6(\mu_3\text{-}N)_8$ Core

Keywords: f elements / Neodymium / Uranium / Imido complexes / Cluster compounds / Structure elucidation



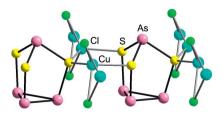
Novel imido clusters of Nd^{3+} involving four or six metal centres and with a cubane or rhombododecahedron core structure were obtained from the reaction of NdI_3 and $\{[PhNMg(thf)]_6\}$ in thf or pyridine. Similar reaction with $UI_3(py)_4$ led to a tetranuclear U^{IV} derivative.

Cage Compounds

P. Schwarz, J. Wachter,* M. Zabel 5460-5463

Novel Coordination Modes for E_4S_3 Cage Molecules (E = P, As) in Unprecedented Quaternary $As_4S_3(CuCl)_n$ (n = 1,2) Solid-State Phases

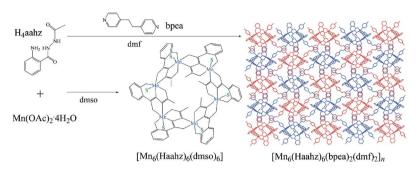
Keywords: Arsenic / Sulfur / Copper / Halides / Coordination modes / Solid-state structures



First examples of the coordination chemistry of the As_4S_3 cage are reported. Compounds $(As_4S_3)(CuCl)_n$, which form in interdiffusion experiments of solutions of As_4S_3 ·M(CO)₅ in CH₂Cl₂ and CuCl_n in CH₃CN (n=1) or CH₃OH (n=2), represent first examples of the novel S-only coordination mode of the intact E_4S_3 cage molecules (E=P,As).



FULL PAPERS



A hexanuclear metallamacrocycle was synthesized by using *N*-acetylaminobenzhydrazide and a manganese ion. The metal—organic framework based on a hexanuclear

metallamacrocycle as a supramolecular building block is quite different from those obtained from similar ligands.

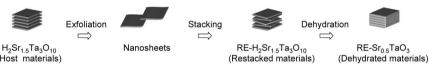
Metal-Organic Frameworks

J. Choi, J. Park, M. Park, D. Moon, M. S. Lah* 5465-5470

A 2D Layered Metal—Organic Framework Constructed by Using a Hexanuclear Manganese Metallamacrocycle as a Supramolecular Building Block

Keywords: Metallacycles / Macrocycles / Supramolecular chemistry / Metal—organic frameworks / Layered compounds

Nanosheet Processing



Metastable $Sr_{0.5}TaO_3$ was prepared by using layer-structured $H_2Sr_{1.5}Ta_3O_{10}$ by direct dehydration and nanosheet processing.

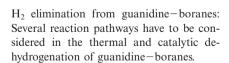
Nanosheet processing can provide a possible route for the synthesis of materials with novel disordered structures.

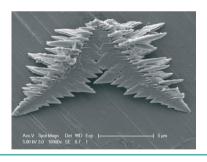
Metastable Sr_{0.5}TaO₃ Perovskite Oxides Prepared by Nanosheet Processing

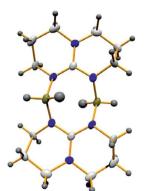
Keywords: Nanotechnology / Nanostructures / Tantalum / UV/Vis spectroscopy / Surface chemistry

Cerium Oxide Dendrites

Highly uniform twofold-shaped CeO_2 dendrites were prepared by using an approach that involves the thermal decomposition of the precursor. Precursors (average size $10 \, \mu m$) were prepared from $Ce(NH_4)_2$ - $(NO_3)_6$ and $CO(NH_2)_2$ in a $H_2O/diethanolamine solution. DEA plays an important role in the formation of the products. The dendritic pattern of the precursor is almost retained in the <math>CeO_2$ product.







D. E. Zhang,* Z. W. Tong,* S. Z. Li, X. B. Zhang, A. L. Ying 5476-5481

A Novel Route Toward Fabrication of Twofold-Shaped CeO₂ Dendrites

Keywords: Nanotechnology / Crystal growth / Absorption / Cyclic voltammetry

Mechanism of Dehydrogenation

O. Ciobanu, F. Allouti, P. Roquette, S. Leingang, M. Enders, H. Wadepohl, H.-J. Himmel* 5482-5493

Thermal and Catalytic Dehydrogenation of the Guanidine–Borane Adducts H_3B -hppH (hppH = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine) and H_3B -N(H)C-(NMe₂)₂: A Combined Experimental and Quantum Chemical Study

Keywords: Dehydrogenation / Homogeneous catalysis / Heterogeneous catalysis / Hydrogen / Boron / Density functional calculations

CONTENTS

Mo Complex Reactivity

Reactions of $(Me_2C)(Me_2S)[(\eta^5-C_5H_3)-Mo(CO)_3]_2$ with Phosphanylalkynes: Rearrangement of Phosphanylalkynes into Phosphido-Substituted Vinylidenyl Ligands by Cleavage of the P-C(alkyne) Bond and Formation of a P-C(alkene) Bond

Keywords: Molybdenum / Phosphorus / Alkynes / Rearrangement / Bridging ligands / X-ray diffraction

Thermal reactions of $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)Mo(CO)_3]_2$ (1) with a series of phosphanylalkynes $Ph_nP(C \equiv CR)_{3-n}$ were reported. P-C(alkyne) bond cleavage and

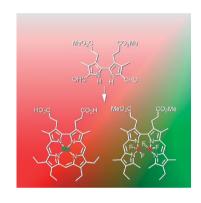
phosphanylalkyne rearrangement products were obtained, in addition to the complexes in which the phosphanylalkynes acted as disubstituted acetylenes.

Biomimetic Porphyrinoids

M. Bröring,* F. Brégier, R. Krüger, C. Kleeberg 5505-5512

Functional Porphyrinoids from a Biomimetically Decorated Bipyrrole

Keywords: Porphyrinoids / Corroles / Heme analogues / Boron / Fluorescence



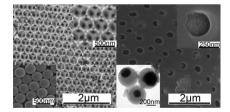
Functional analogues for hemes and phytofluors, a Mn corrole and a bis(bodipy) carrying two adjacent propionate substituents, are available in two steps from a simple bipyrrolic precursor. Hydrolysis of the ester groups to the free acid is successful for the corrole and yields buffer-soluble material, while for the dinuclear bis(bodipy), hydrolysis of B-F bonds is observed.

Hybrid Macroporous Materials

W.-Q. Fan, J. Feng, S.-Y. Song, Y.-Q. Lei, Y. Xing, R.-P. Deng, S. Dang, H.-J. Zhang* 5513-5518

Erbium-Complex-Doped Near-Infrared Luminescent and Magnetic Macroporous Materials

Keywords: Macroporous materials / Near-infrared luminescence / Magnetism

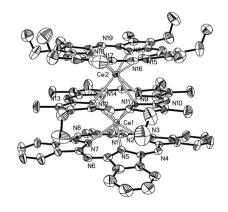


A near-infrared luminescent macroporous material and a near-infrared luminescent/magnetic bifunctional macroporous material, which may offer the opportunity to develop new materials suitable for optical amplifiers, were synthesized by using polystyrene microspheres and Fe₃O₄@polystyrene core—shell nanoparticles, respectively, as templates.

Cerium Sandwich-Type Complexes

Sandwich-Type Heteroleptic *opposite*-(Diazaporphyrinato)cerium Complexes: Synthesis, Spectroscopy, Structure, and Electrochemistry

Keywords: Cyclic voltammetry / Phthalocyanines / Porphyrins / Sandwich complexes



The sandwich-type heteroleptic tetrapyrrole cerium complex $Ce_2(dap)_2(pc)$ was synthesized from $[Ce(acac)_3] \cdot nH_2O$, Li_2pc , and metal-free D_{2h} -type diazaporphyrin. The molecular structure indicated an unexpected asymmetrical disposition of the ligands, with two adjacent dap moieties and one outer pc ring.



One-dimensional chain derivatives of the general formula $[M(acac)_2(\mu\text{-bipyridine})]$ were obtained from (acetylacetonato)-cobalt(II) or (trifluoromethylacetylaceton-

ato)copper(II) derivatives and bipyridine-like bridging ligands. Magnetic susceptibility studies show weak antiferromagnetic interactions along the chain.

Co and Cu 1D Chain Complexes

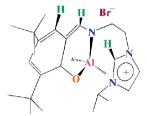
J. Atienza, A. Gutiérrez,*
M. Felisa Perpiñán,
A. E. Sánchez 5524-5531

Cobalt and Copper Coordination Polymers Containing Acetylacetonato-Derived Ligands and Bidentate Pyridine Coligands: Synthesis, Crystal Structures and Magnetic Properties

Keywords: Chain structures / X-ray diffraction / Magnetic properties / N ligands / O ligands

Hydrogen Bonding Interactions

The synthesis, solution properties and reactivity of novel alkylaluminium complexes bearing a modified phenoxyimine ligand containing a pendant imidazolium moiety are reported. Investigation of solution structures by NMR spectroscopy revealed the involvement of the coordinated ligand in hydrogen bonding with halide anions.



Aluminium Complexes of a Phenoxyimine Ligand with a Pendant Imidazolium Moiety: Synthesis, Characterisation and Evidence for Hydrogen Bonding in Solution

Keywords: Aluminium / N,O ligands / Hydrogen bonds

Ligand Transformation

Reactions between $[Ru(PPh_3)_3Cl_2]$ and biacetylmonoxime acetyl-/aroylhydrazones (H_2L) provide ruthenium(III) complexes trans- $[Ru(^tL)(PPh_3)Cl_2]$, where $^tL^-$ represents the N,N,O-donor transformed ligand. In this unique metal-assisted chemical transformation of H_2L , the $-CH_3$ group at the oxime end becomes $=CHPHPh_3$.



R. Raveendran, S. Pal* 5540-5546

 $[Ru(PPh_3)_3Cl_2]-Mediated \quad Transformation \\ of \quad -CH_3 \quad into \quad =CHPHPh_3 \quad in \quad Biacetyl-monoxime \quad Acetyl-/Aroylhydrazones: \quad Ruthenium(III) \quad Complexes \quad with \quad the \quad Transformed \quad Ligands$

Keywords: Ruthenium / Ligand transformation / Redox properties

If not otherwise indicated in the article, papers in issue 34 were published online on November 17, 2008

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