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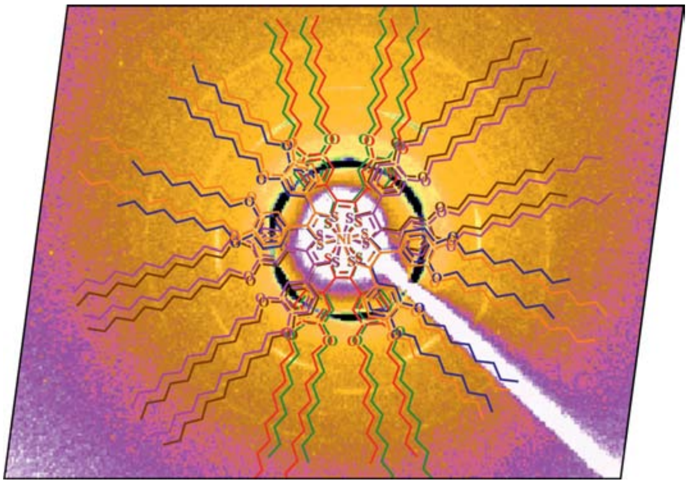
COVER PICTURE

The cover picture shows nickel bis(dithiolene) compounds in which different lengths of alkyl chains are grafted on the periphery of the octasubstituted core molecule. The synthesis affords a mixture, which was analyzed by X-ray diffraction. The obtained X-ray pattern at 70 °C is presented as the background and corresponds to a hexagonal columnar liquid-crystalline phase. Such a pattern is not observed for the corresponding pure isolated compounds. Details are discussed in the article by B. Garreau-de Bonneval, K. I. Moineau-Chane Ching et al. on p. 2663 ff. The authors thank the French National Research Agency (ANR) for supporting this work.



CONTENTS

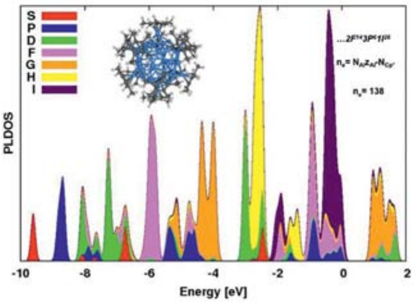
SHORT COMMUNICATIONS

Metalloid Clusters as Superatoms

P. A. Clayborne,* O. Lopez-Acevedo,
R. L. Whetten, H. Grönbeck,
H. Häkkinen* 2649–2652

The $Al_{50}Cp^*_{12}$ Cluster – A 138-Electron Closed Shell (L = 6) Superatom

Keywords: Ab initio calculations / Aluminum / Cluster compounds / Superatoms / Shell models



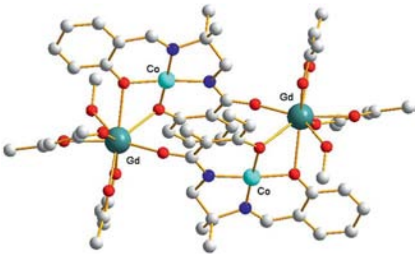
Metal clusters stabilized by a surface ligand shell represent an interesting intermediate state of matter between molecular metal–ligand complexes and bulk metal. We show here that the known cluster $Al_{50}Cp^*_{12}$ can be considered as an analogue to a giant atom (“superatom”) with 138 sp electrons organized in concentric angular momentum shells up to L = 6 symmetry.

Antiferromagnetic Interactions

V. Gómez, L. Vendier, M. Corbella,
J.-P. Costes* 2653–2656

Antiferromagnetic Co–Gd Interactions in a Tetranuclear $[CoGd]_2$ Complex with Low-Spin Square-Planar Co Ions – Role of the Singly Occupied 3d Co Magnetic Orbital

Keywords: Coordination compounds / Cobalt / Gadolinium / Magnetic properties / Lanthanides



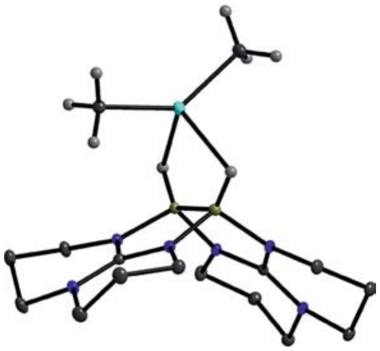
Antiferromagnetic Co–Gd interactions, through a double phenoxo and a single amidato bridge, are active in a tetranuclear $[CoGd]_2$ complex with low-spin Co ions (S = 1/2).

Diborane(4) Ligands

N. Schulenberg, S. Litters, E. Kaifer,
H.-J. Himmel* 2657–2661

Zinc Halide and Alkylzinc Complexes of a Neutral Doubly Base-Stabilized Diborane(4)

Keywords: Boranes / Subvalent compounds / Zinc / Alkyl complexes



The first dialkylzinc complex of a neutral boron hydride ligand was prepared and characterized. The bonding properties in the dialkyl and dihalide complexes were analysed, indicating a complex bonding situation involving all atoms of the ZnH_2B_2 ring.

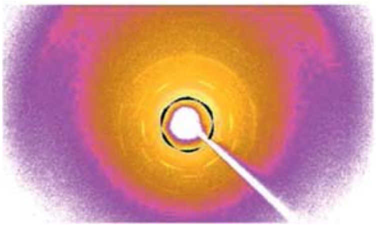
FULL PAPERS

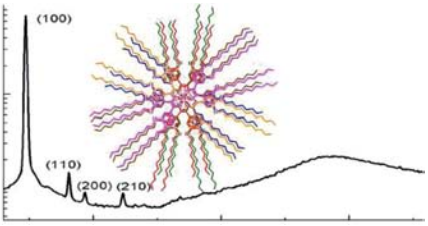
Long Chain Effects on Mesomorphism

T.-T. Bui, O. Thiebaut,
E. Grelet, M.-F. Achard,
B. Garreau-de Bonneval,*
K. I. Moineau-Chane Ching* 2663–2676

Discotic Nickel Bis(dithiolene) Complexes – Synthesis, Optoelectrochemical and Mesomorphic Properties

Keywords: Nickel / S ligands / Liquid crystals / Electrochemistry / Organic electronics

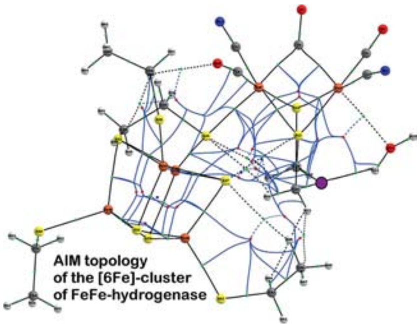




Electrochemical and optical studies as well as multiphase transition behavior are reported for a series of new nickel bis(dithiolene) complexes. The effects of the nature and position of the functional groups attached to the periphery of the complexes are investigated. X-ray diffraction measurements regarding the hexagonal columnar mesophase are reported.

Electron and Spin Density Topology

The electronic structures of the H-cluster and its biomimetic complexes were investigated by density functional theory calculations that use advanced electron and spin density analysis methods, such as Atoms-in-Molecule. We revealed a comprehensive picture of the complex network of intra- and intermolecular interactions that govern the electronic and magnetic properties of the H-cluster.

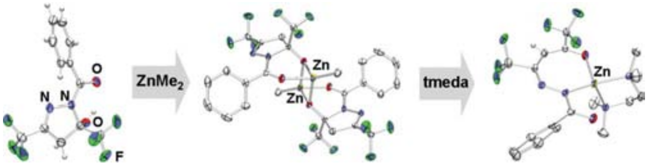


L. J. Giles, A. Grigoropoulos, R. K. Szilagyi* 2677–2690

Electron and Spin Density Topology of the H-Cluster and Its Biomimetic Complexes

Keywords: Cluster compounds / Electronic structure / Spin density / Electron density critical points / Density functional calculations / [FeFe]-hydrogenase

Zinc Complexes



The versatility of 5-hydroxypyrazoline ligands has been demonstrated. Various zinc complexes have been synthesized and characterized resulting in new coordination modes of pyrazoline ligands depending on the reaction conditions; zinc dimers have been observed with a *O*,*O′*-coordination mode, whereas addition of tmeda to the reaction mixture led to the formation of a zinc-containing seven-membered ring system with an *O*,*N*-mode.

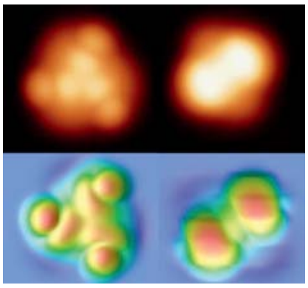
C. I. Someya, S. Inoue, E. Irran, S. Krackl, S. Enthaler* 2691–2697

New Binding Modes of 1-Acetyl- and 1-Benzoyl-5-hydroxypyrazolines – Synthesis and Characterization of *O,O′*-Pyrazoline- and *N,O*-Pyrazoline-Zinc Complexes

Keywords: Zinc / N,O ligands / Coordination modes / Nitrogen heterocycles

UHV-STM on Ruthenium Complexes

Experimental (top) and EHMO-ESQC calculated (bottom) STM image of Ru(dbm)$_3$ adsorbed on a Ag(111) surface at liquid helium temperature.



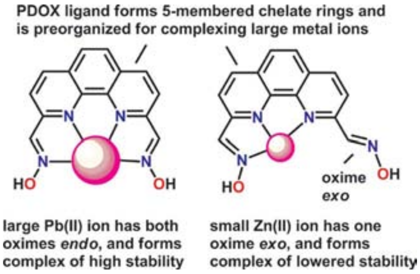
S. Munery, N. Ratel-Ramond, Y. Benjalal, L. Vernisse, O. Guillermet, X. Bouju, R. Coratger, J. Bonvoisin* 2698–2705

Synthesis and Characterization of a Series of Ruthenium Tris(β-diketonato) Complexes by an UHV-STM Investigation and Numerical Calculations

Keywords: Ruthenium / β-Diketonato complexes / Adsorption

Ligand Design

The structure of the Pb^{II} complex of PDOX (1,10-phenanthroline-2,9-dicarboxaldehyde-2,9-dioxime), a ligand that is preorganized for complexing large metal ions by formation of five-membered chelate rings, is reported. The large Pb^{II} ion is coordinated to both oxime nitrogen atoms, unlike PDOX complexes with small metal ions such as Zn^{II} or Cu^{II}. Large metal ions stabilize their PDOX complexes more than their phen (1,10-phenanthroline) complexes.



L. L. Boone, A. E. Mroz, D. G. VanDerveer, R. D. Hancock* 2706–2711

Metal Ion Coordinating Properties of the Highly Preorganized Tetradentate Ligand 1,10-Phenanthroline-2,9-dicarboxaldehyde-2,9-dioxime

Keywords: Ligand design / Structure elucidation / N ligands

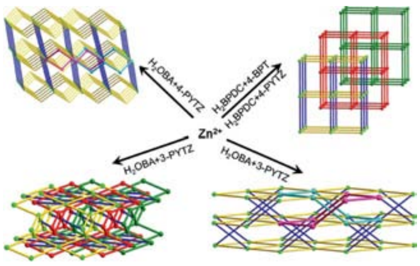
CONTENTS

Metal-Organic Frameworks

J. Li, Y. Peng, H. Liang, Y. Yu, B. Xin, G. Li,* Z. Shi,* S. Feng .... 2712−2719

Solvothermal Synthesis and Structural Characterisation of Metal-Organic Frameworks with Paddle-Wheel Zinc Carboxylate Clusters and Mixed Ligands

Keywords: Metal-organic frameworks / Zinc / Mixed ligands / Interpenetration / Topology / Paddle-wheel cluster



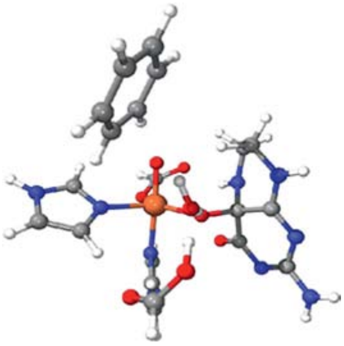
Five 3D interpenetrating metal-organic frameworks have been synthesized, and contain paddle-wheel zinc carboxylate clusters and mixed ligands, which can be regarded as nodes and linkers to generate a variety of topologies. The luminescence properties of the compounds have also been studied.

Iron-Catalyzed Hydroxylation

E. Olsson, A. Martinez, K. Teigen, V. R. Jensen* .... 2720−2732

Substrate Hydroxylation by the Oxido−Iron Intermediate in Aromatic Amino Acid Hydroxylases: A DFT Mechanistic Study

Keywords: Amino acids / Hydroxylation / 5,6,7,8-Tetrahydrobiopterin / Density functional calculations / Iron



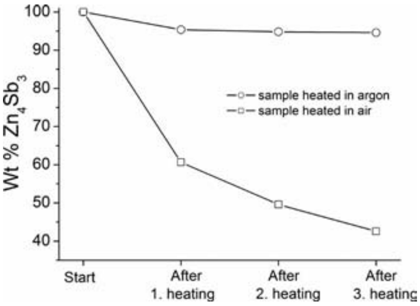
The mechanism of substrate hydroxylation by an $Fe^{IV}=O$ intermediate in the aromatic amino acid hydroxylase (AAH) family of enzymes has been followed by DFT calculations. The mechanism begins with (Fe)-O−C(substrate) bond formation, proceeds through an NIH shift and tautomerization to give the phenol product, and finally regenerates the catalyst by rebinding of ligating water molecules and dissociation of the oxidized cofactor.

Thermoelectric Material

H. Yin, B. L. Pedersen, B. B. Iversen*........................... 2733−2737

Thermal Stability of High Performance Thermoelectric β-Zn_4Sb_3 in Argon

Keywords: Zinc / Antimony / Thermoelectric materials / Thermal stability / Synchrotron diffraction



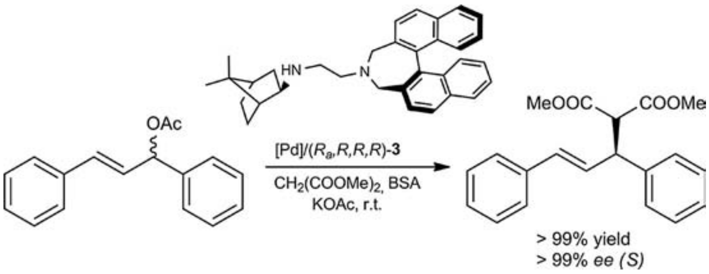
Multi-temperature synchrotron PXRD data were recorded to investigate the thermal stability of thermoelectric Zn_4Sb_3 heated in argon. About 95 wt.-% of original Zn_4Sb_3 is preserved after three heating cycles to 625 K for the sample heated in argon, while only ca. 40 wt.-% remains in the sample heated in air. Comparison of degradation behaviours for different samples suggests a two-process decomposition mechanism of Zn_4Sb_3.

Enantioselective Catalysis

G. Bottari,* A. Meduri, D. Drommi, G. Brancatelli, F. Faraone .... 2738−2745

Synthesis, Coordination Properties and Application of New *N*,*N*-Ligands Based on Bornyl and Binaphthylazepine Chiral Backbones in Palladium-Catalyzed Allylic Substitution Reactions

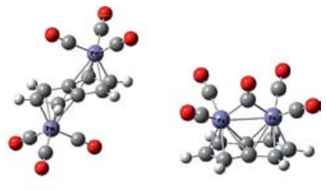
Keywords: Palladium / N ligands / Allylic compounds / Asymmetric catalysis / Enantioselectivity



New dinitrogen chiral ligands were synthesized and investigated in palladium-catalyzed allylic alkylation reactions.

Pentalene Sandwich Complexes

The lowest energy $C_8H_6Fe_2(CO)_6$ structure is *trans*-(η^5,η^5-C_8H_6)$Fe_2(CO)_6$ but a *cis*-(η^5,η^1-C_8H_6)$Fe_2(CO)_6$ structure lies only ca. 3 kcal/mol above this global minimum. The experimentally known *cis*-(η^5,η^5-C_8H_6)$Fe_2(CO)_4$(μ-CO) structure is found to be the lowest energy $C_8H_6Fe_2(CO)_5$ structure by more than 25 kcal/mol (BP86). Two triplet and two singlet *cis*-$C_8H_6Fe_2(CO)_4$ structures lie within 7 kcal/mol of each other (BP86) with the triplet structures having slightly lower energies.



$C_8H_6Fe_2(CO)_6$ $C_8H_6Fe_2(CO)_5$

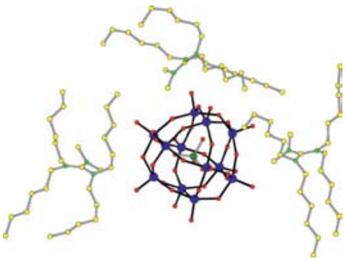
H. Li, H. Feng,* W. Sun, Y. Xie, R. B. King,* **2746–2755**

Binuclear Pentalene Iron Carbonyl Complexes 💻

Keywords: Sandwich complexes / Iron / Hydrocarbons / Pentalene / Density functional calculations

Oxidation Catalysis

Several guanidinium phosphotungstates and guanidinium-based ionic liquids have been synthesized and characterized. Their catalytic performance in epoxidation reactions with hydrogen peroxide was evaluated and compared to similar ammonium and imidazolium compounds. The reaction systems can be recycled and used in at least three consecutive reactions.

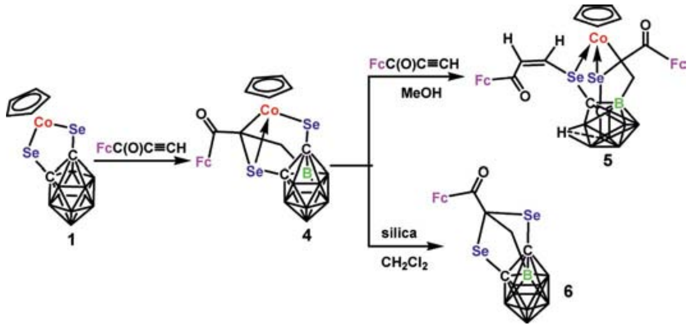


L. Gharnati, O. Walter, U. Arnold, M. Döring* **2756–2762**

Guanidinium-Based Phosphotungstates and Ionic Liquids as Catalysts and Solvents for the Epoxidation of Olefins with Hydrogen Peroxide

Keywords: Oxidation / Epoxidation / Ionic liquids / Polyoxometalates / Guanidinium salts / Hydrogen peroxide

Half-Sandwich Complexes



The reaction of the 16-electron half-sandwich complex $CpCo(Se_2C_2B_{10}H_{10})$ (**1**) with FcC(O)C≡CH leads to **4**, which is able to further react with the alkyne in MeOH to generate **5** containing a *nido*-C_2B_9 cluster. In the presence of silica, **4** can be converted to **6** with loss of the CpCo unit.

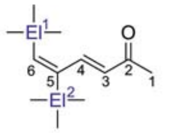
H. Ye, W. Bai, M. Xie, Y. Li, H. Yan* **2763–2768**

Reactivity of a 16-Electron CpCo Half-Sandwich Complex Containing a Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-diselenolate Ligand towards FcC(O)C≡CH

Keywords: Transition metals / Half-sandwich complexes / Cobalt / Chalcogens / Alkynes / Carboranes / B–H activation

Silicon-Containing Odorants

Compounds **1b**–**1d** [(di)sila analogues of the acyclic dienone musk odorant **1a**] were synthesized and characterized for their olfactory properties. C/Si exchange had quite a dramatic effect on the musky-violet odor profile, and on the odor threshold. This indicates that the C-5 substituent is critical for a musky impression, whereas the substituent on C-6 has greater responsibility for floralcy.



1a: El^1 = C, El^2 = C
1b: El^1 = Si, El^2 = C
1c: El^1 = C, El^2 = Si
1d: El^1 = Si, El^2 = Si

M. Geyer, J. Bauer, C. Burschka, P. Kraft, R. Tacke* **2769–2776**

Synthesis and Olfactory Characterization of Novel Silicon-Containing Acyclic Dienone Musk Odorants

Keywords: C/Si exchange / Musks / Odorants / Silanes / Silicon

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* Author to whom correspondence should be addressed.

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