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The EUChemSoc Societies

COVER PICTURE

The cover picture shows the result of the electrochemical oxidation of a square-planar nickel(II) complex. The oxidation state of the metal remains largely unchanged, and the phenoxy ligand is oxidized to the depicted radical cation. Details are discussed in the Short Communication by J. Reedijk et al. on p. 637ff.



SHORT COMMUNICATIONS

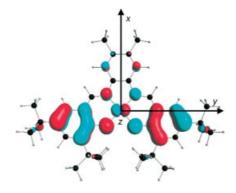
Monoradical Complexes

- L. Benisvy, R. Kannappan,
- Y.-F. Song, S. Milikisyants, M. Huber,
- I. Mutikainen, U. Turpeinen, P. Gamez,
- L. Bernasconi, E. J. Baerends, F. Hartl,
- J. Reedijk* 637-642



A Square-Planar Nickel(II) Monoradical Complex with a Bis(salicylidene)diamine Ligand

Keywords: Phenoxyl radicals / Nickel(II) complexes / Redox chemistry / Spectroelectrochemistry / EPR spectroscopy / Density functional calculations



The square complex $[Ni(^{Me}L)]$ (1^{Me}) $[^{Me}L]$ = the dianionic phenolato form of N,N'-bis(3,5-di-tert-butylsalicylidene)-4,5-dimethyl-1,2-phenylenediamine $(^{Me}LH_2)]$ has been synthesised and characterised. Electrochemical one-electron oxidation of 1^{Me} produces thermally stable $(1^{Me})^+$ [10-295 K]. UV/Vis and EPR spectroscopy, supported by DFT calculations, indicate that $(1^{Me})^+$ is best described as a Ni^{II} monoradical complex and does NOT exist in a Ni^{III} ground state, in contrast to its demethylated counterpart $[Ni(^HL)]^+$ $(1^H)^+$ below 170 K.

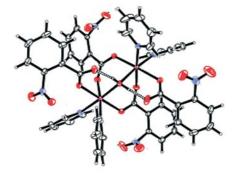
Polymorphism

- A. Karmakar, R. J. Sarma,
- J. B. Baruah* 643-647



Polymorphism in an Aqua-Bridged, Dinuclear 2-Nitrobenzoate Complex of Cobalt(II)

Keywords: Dinuclear cobalt complexes / Aqua-bridged complexes / Polymorphism / Conformers



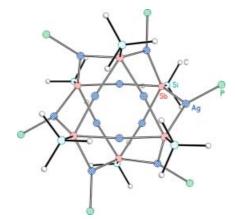
Three polymorphs of a dinuclear, aquabridged cobalt complex $[Co_2(\mu\text{-OH}_2)-(C_5H_5N)_4(\mu\text{-O}_2CC_6H_4\text{-}2\text{-NO}_2)_2(O_2CC_6H_4\text{-}2\text{-NO}_2)_2]$ are structurally characterised. Selective crystallisation of the polymorphs is achieved by controlling the reaction conditions and the crystallisation processes. Reaction of cobalt(II) acetate tetrahydrate with 2-nitrobenzoic acid followed by treatment with excess pyridine leads to the mononuclear complex $[Co(H_2O)_2(C_5H_5N)_2-(O_2CC_6H_4\text{-}2\text{-NO}_2)_2]$.

Antimony Anions

- D. Fenske,* A. Rothenberger,
- S. Wieber 648-651

Synthesis and Characterization of the First Silver Complexes with Antimony Anions

Keywords: Silver / Antimony / Clusters

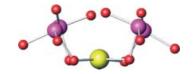


The synthesis and characterization of the silver antimony complexes $[Ag_{12}\{Sb-(SiMe_3)\}_6(PiPr_3)_6]$ (1), $[Ag_4(Sb_4Ph_4)_2-(PiPr_3)_4]$ (2) and $[Ag_4(Sb_6Ph_6)_2(PnBu_3)_4]$ (3) is reported.



Noble Metal Iodates

 K^+ salts of the square-planar noble metal iodate $[M(IO_3)_4]^{n^-}$ ($M=Pd^{II}, Au^{III}; n=2,1$) anions have been prepared under mild hydrothermal conditions, and the structures elucidated to demonstrate that while both are highly polar anions, polar and centrosymmetric extended architectures can form using these building units.



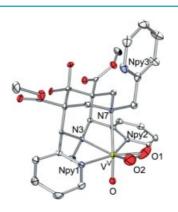
J. Ling,
T. E. Albrecht-Schmitt* 652-655

Square-Planar Noble Metal Iodate $[M(IO_3)_4]^{n-}$ (M = Pd^{II}, Au^{III}; n = 2, 1) Anions and Their Ability to Form Polar and Centrosymmetric Architectures

Keywords: Gold / Palladium / Iodate / Oxo ligands

FULL PAPERS

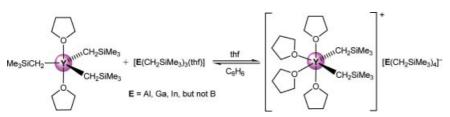
Peroxidovanadium(V) or superoxidovanadium(IV)? Crystallography, spectroscopy and oxidation reactivity are used to answer this question.



Vanadium Bispidine Complexes

Synthesis and Oxidation of Vanadyl Complexes Containing Bispidine Ligands

Keywords: Peroxido complexes / Superoxido complexes / Rigid ligand / Bispidine



The alkyl abstraction reaction of $[YR_3(thf)_2]$ (R = CH₂SiMe₃) with group-13 trialkyl complexes $[(ER_3)_n]$ (E = B, Ga, In: n = 1; E = Al: n = 2) leading to cat-

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ionic yttrium species $[YR_2(thf)_4]^+[ER_4]^-$ (E = Al, Ga, In) shows a strong dependence on the solvent basicity. **Cationic Alkylyttrium**

Alkyl Abstraction from a Trialkylyttrium Complex $[YR_3(thf)_2]$ ($R=CH_2SiMe_3$) Using a Group-13 Element Lewis Acid ER_3 ($E=B,\ Al,\ Ga,\ In)$ — Structural Characterisation of the Ion Pair $[YR_2(thf)_4]^+[GaR_4]^-$ and of ER_3 ($E=B,\ Al,\ Ga$)

Keywords: Yttrium / Lewis acids / Alkyl abstraction / Group-13 elements / Cationic complexes

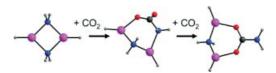
CONTENTS

CO₂ Fixation

H.-J. Himmel* 675-683

CO₂ Fixation by Alkylzinc Amides: A Quantum Chemical Study Motivated by Recent Experimental Results

Keywords: CO₂ fixation / Zinc / Reaction mechanisms / Quantum chemical calculations



The mechanism of CO₂ fixation by monomeric as well as dimeric alkylzinc amides was studied by quantum chemical calculations. The results of this work help us in

the understanding of CO₂ fixation by synthesized alkylzinc amides and also shed light on enzymatic reactivity.

Metal-Organic Polymers

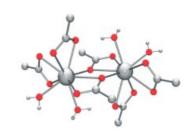
M. C. Bernini, E. V. Brusau, G. E. Narda,* G. E. Echeverria, C. G. Pozzi, G. Punte,

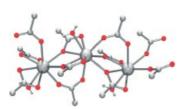
C. W. Lehmann 684-693



The Effect of Hydrothermal and Non-Hydrothermal Synthesis on the Formation of Holmium(III) Succinate Hydrate Frameworks

Keywords: Lanthanides / Hydrothermal synthesis / Hybrid frameworks / Coordination polymers





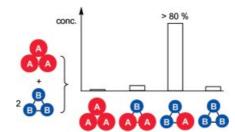
Holmium(III) succinates $[Ho_2(C_4H_4O_4)_3-(H_2O)_4]\cdot 6H_2O$ (1) and $[Ho_2(C_4H_4O_4)_3-(H_2O)_2]\cdot H_2O$ (2) have been synthesized under ambient and hydrothermal conditions, respectively. Single-crystal XRD shows that 1 is a 2D hybrid polymer and 2 presents a 3D architecture showing that hydrothermal conditions favor increasing dimensionality. They were characterized by FTIR and Raman spectroscopy, thermal analysis and magnetic measurements.

Supramolecular Chemistry

Z. Grote, R. Scopelliti, K. Severin* 694-700

Controlled Formation of Mixed-Metal Macrocycles Using Dynamic Exchange Processes and Steric Constraints

Keywords: Dynamic combinatorial chemistry / Metallamacrocycle / Organometallic complex / Rhodium / Ruthenium



Size matters: Steric interactions in combination with dynamic exchange processes can be used to generate mixed-metal macrocycles in high yield. This is demonstrated by the controlled formation of organometallic macrocycles containing different $(\pi\text{-ligand})M$ fragments (M = Rh, Ru).

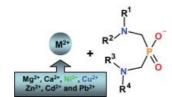
Phosphinic Acid Derivatives

G. Tircsó,* A. Bényei, R. Király, I. Lázár, R. Pál, E. Brücher 701–713



Complexation Properties of the Di-, Tri-, and Tetraacetate Derivatives of Bis(aminomethyl) Acid

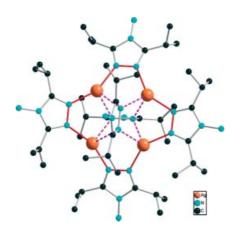
Keywords: Phosphinic acid derivatives / Divalent metal ions / Synthesis / Protonation constants / Stability constants



Acetate derivatives of bis(aminomethyl)-phosphinic acid are synthesized and the stability of the complexes formed with these diamino-di-, -tri-, and -tetracarboxylates involving some endogenous (Mg²⁺, Ca²⁺, Cu²⁺, Zn²⁺) and toxic (Ni²⁺, Pb²⁺, and Cd²⁺) doubly charged metal ions, are reported. The structure of the ligand L³ (tricarboxylate) and the Cu²⁺ complex of L¹ are studied in the solid state.



Reactions of silver(I) salts with 4-amino-3,5-diisopropyl-1,2,4-triazole (L) yield, based on the anion used, dinuclear, triangular or cyclic tetranuclear complexes. Shown here is the tetranuclear cation $[Ag_4L_6]^{4+}$, anions (not shown) are BF₄⁻.

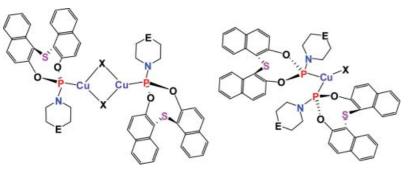


Anion-Dependent Structural Diversity

G. Yang,* Y.-L. Wang, J.-P. Li, Y. Zhu, S.-M. Wang, H.-W. Hou, Y.-T. Fan, S. W. Ng 714-719

Anion-Dependent Structural Diversity in Silver(I) Complexes of 4-Amino-3,5-diisopropyl-1,2,4-triazole

Keywords: Silver / Triazole / Anions



The reactivity of thioether aminophosphonites (L) with group 11 metal derivatives is described. A series of three-coordinate monomeric and dimeric complexes with or without the sulfur coordination are reported. Halogen exchange is observed between [LAuCl] and CuI to form [LAuI] and CuCl.

Thioether Aminophosphonite Complexes

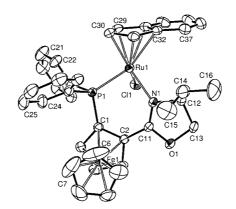
B. Punji, J. T. Mague, M. S. Balakrishna* 720-731

Group 11 Metal Complexes of the Mesocyclic Thioether Aminophosphonites $[-OC_{10}H_6(\mu-S)C_{10}H_6O-]PNC_4H_8E$ (E = O, NMe)

Keywords: Thioether-aminophosphonites / P,S ligands / Copper / Gold

Chiral-at-metal indenyl- and areneruthenium(II) complexes containing the chiral ligand (4S)-2- $[(S_P)$ -2-(diphenylphosphanyl)ferrocenyl]-4-(methylethyl)oxazoline (FcPN) have been synthesised diastereoselectively. The reported complexes include those containing alkynyl, allenylidene, and Fischer-type carbene ligands. The absolute configuration of the ruthenium atoms in representative complexes has been determined by X-ray analyses.

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Half-Sandwich Ruthenium(II) Complexes

A. García-Fernández, J. Gimeno, E. Lastra,* C. A. Madrigal, C. Graiff, A. Tiripicchio 732-741

Half-Sandwich η⁵-Indenyl- and η⁶-Areneruthenium(II) Complexes Bearing the Chiral Ligand (4S)-2- $[(S_n)$ -2-(Diphenylphosphanyl)ferrocenyl]-4-(methylethyl)oxazoline (FcPN)

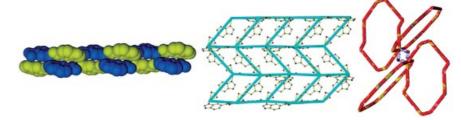
Keywords: N,P ligands / Phosphanes / Indenyl complexes / Arene complexes / Ruthenium

CONTENTS

Cadmium Coordination Polymers

A Series of Cadmium(II) Coordination Polymers Synthesized at different pH Values

Keywords: Cadmium / Polymers / Self-assembly / Photoluminescence



A new family of cadmium(II) coordination polymers has been hydrothermally prepared by the assembly of Cd^{II} with 1H-benzimidazole-5-carboxylic acid. A change

in the pH values resulted in a series of compounds with different compositions and dimensionalities.

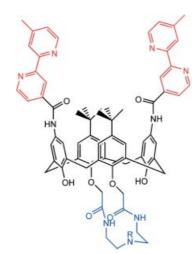
Ruthenium/Manganese Complexes

A. D. Bond, B. S. Creaven, D. F. Donlon, T. L. Gernon, J. McGinley,*

H. Toftlund 749-756

Metal Complexation of Calix[4]azacrown Derivatives – Evidence for Communication Between Upper and Lower Functionalised Rims

Keywords: Calix[4]arene / Macrocyclic ligands / Heterometallic compounds / Copper(II) / Manganese(II) / Ruthenium(II) / EPR spectroscopy



The first example of a binuclear ruthenium(II)/manganese(II) complex, involving the calix[4]arene framework as the bridging ligand (showing two different metal binding centres), is reported.

If not otherwise indicated in the article, papers in issue 4 were published online on January 22, 2007