













SWEDEN



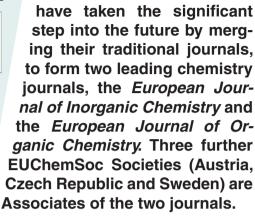


FRANCE









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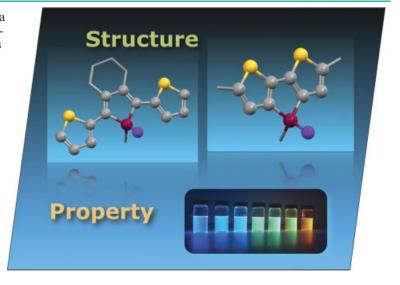






COVER PICTURE

The cover picture shows the schematic structures of a 2,5-dithienylphosphole and a dithieno[3,2-b:2',3'-d]phosphole, as well as the fluorescence properties of materials based on the latter system. These scaffolds are two of the most promising organophosphorus-based building blocks for organic electronics to date. Extensive investigations of their structure-property relationships has laid ground for a variety of applications such as sensing or as an active component in electronic devices. Details on the syntheses, their systematic modifications, as well as the resulting (opto)electronic properties of the materials are presented in the Microreview by M. G. Hobbs and T. Baumgartner on p. 3611ff.



3601

MICROREVIEW

Phosphole Materials

M. G. Hobbs, T. Baumgartner* 3611-3628

Recent Developments in Phosphole-Containing Oligo- and Polythiophene Materials

Keywords: Phosphole / Thiophene / Conjugated materials / Organic electronics / Fluorescence

This Microreview covers the latest developments in phosphole-thiophene hybrid materials for organic electronics and describes how systematic, comprehensive investigations focusing on structure—property relationships can determine the scope and suitability of such materials for optoelectronic applications.

SHORT COMMUNICATION

Air-Stable Pd Catalysts

A. L. Gottumukkala,

H. Doucet* 3629-3632

Activated Aryl Chlorides: Useful Partners for the Coupling with 2-Substituted Thiazoles in the Palladium-Catalysed C-H Activation/Functionalisation Reaction

Keywords: Aryl chlorides / Catalysis / C-H activation / Palladium / Thiazoles

$$R^2$$
 + ArCl $\xrightarrow{PdCl(dppb)(C_3H_5)}$ $\xrightarrow{R^2}$ N $\xrightarrow{R^2$

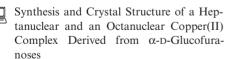
Aryl chlorides are noticeably uncommon partners in coupling reactions with heteroaromatics through C-H activation. We report herein that as little as 1 mol-%

of the air-stable PdCl(dppb)(C₃H₅) complex catalyses the direct coupling of electron-deficient aryl chlorides with 2-substituted thiazole derivatives.

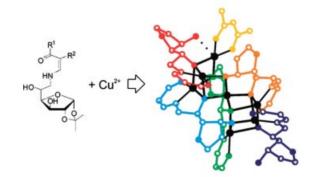
FULL PAPERS

Carbohydrate Copper Complexes

M. Gottschaldt,* R. Wegner, H. Görls, E.-G. Jäger, D. Klemm 3633-3638



Keywords: Carbohydrates / Copper complexes / Cluster compounds



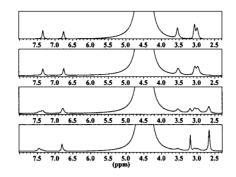
A hepta- and one octanuclear copper(II) complex could be crystallised using 6-(β -keto-enamino)-6-deoxy-1,2-O-isopropylidene- α -D-glucofuranoses as ligands. Due

to the nature of the carbohydrate scaffold they show different and highly asymmetric structures.



Kinetics of Complex Formation

Formation of the complexes $[Ln(DOTAM)]^{3+}$ occurs upon direct encounter between the Ln^{3+} ions and the non-protonated DOTAM ligands in a second-order reaction. Contrary to the formation of $[Ln(DOTA)]^-$ complexes, no intermediates were detected.

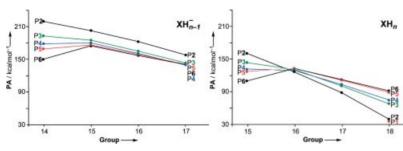


Z. Baranyai, I. Bányai, E. Brücher,*
R. Király, E. Terreno 3639–3645

Kinetics of the Formation of [Ln-(DOTAM)]³⁺ Complexes

Keywords: Macrocyclic ligands / Lanthanides / Kinetics / Reaction mechanisms

Proton Affinities



M. Swart, E. Rösler, F. M. Bickelhaupt* 3646–3654

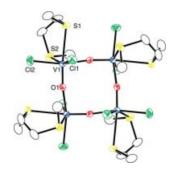
Proton Affinities in Water of Maingroup-Element Hydrides — Effects of Hydration and Methyl Substitution

Keywords: Acidity / Basicity / Density functional calculations / Periodic table / Proton affinities / Thermochemistry / Solvent effects

Proton affinities in water of archetypal anionic (XH_{n-1}^-) and neutral bases (XH_n) across the periodic table (groups

14-18, periods 1-6) are smaller than those in the gas phase but, importantly, they follow similar trends.

The first examples of oxidotrichloridovanadium(V) thioether complexes have been prepared and fully characterised, together with vanadyl(IV) and tetrachloridovanadium(IV) analogues. The structure of a unique tetranuclear oxidovanadium(IV) thioether complex is described.



Vanadium(IV/V) Complexes

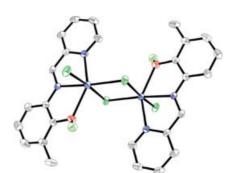
A. L. Hector, W. Levason, A. J. Middleton, G. Reid,* M. Webster 3655-3662

Vanadium(IV) and Oxidovanadium(IV) and -(V) Complexes with Soft Thioether Coordination — Synthesis, Spectroscopic and Structural Studies

Keywords: Vanadium / Thioether / Structural studies

Ferromagnetic Mn Complexes

The chlorido-bridged [Mn(HL)(μ -Cl)Cl]₂ complex with intradimer ferromagnetic coupling through chlorido bridges and weak interdimer antiferromagnetic interaction through hydrogen bonding is reported. A comparison of the magnetic coupling for [Mn(HL)(μ -Cl)Cl]₂ and other structurally similar compounds is discussed.



C.-M. Qi, X.-X. Sun, S. Gao, S.-L. Ma,* D.-Q. Yuan, C.-H. Fan, H.-B. Huang, W.-X. Zhu 3663-3668

Chlorido-Bridged Mn^{II} Schiff-Base Complex with Ferromagnetic Exchange Interactions

Keywords: Manganese / Schiff bases / Magnetic properties

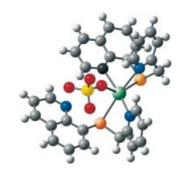
CONTENTS

Terdentate NSN and NNN Ligands

L. Canovese,* F. Visentin, G. Chessa, C. Levi, A. Dolmella 3669-3680

Synthesis, Stability Constant Determination, and Structural Study of Some Complexes of a Zinc Triad Containing Pyridylamine-quinoline and Pyridyl-thio-quinol-

> Keywords: Zinc / Quinoline-based ligands / Fluorescence / Formation constants



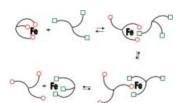
Potentially fluorescent and terdentate ligands bearing nitrogen, sulfur, and a quinoline ring were synthesized and used for the preparation of several complexes of the zinc triad. (Colour code: blue = nitrogen, orange = sulfur, green = mercury, yellow = chlorine, red = oxygen)

Ligand Exchange Reactions

G. Serratrice,* F. Biaso, J.-L. Pierre, S. Blanc, A.-M. Albrecht-Gary 3681-3685

Iron(III) Exchange Process between Hexadentate Tripodal Ligands: Models for the Ternary Complexes

Keywords: Mixed ligands / Iron / Exchange interactions / Siderophores / Tripodal ligands



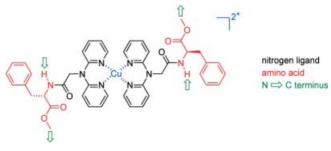
Kinetics of the iron exchange reaction between a tris(catechol) ligand (red circles) and a tris(8-hydroxyquinoline) ligand (green squares) was investigated. The mechanism shows that the reaction occurs step-by-step via ternary complexes having a mixed coordination at the iron center.

Bioinorganic Pair Models

S. I. Kirin, H. P. Yennawar, M. E. Williams* 3686-3694

Synthesis and Characterization of CuII Complexes with Amino Acid Substituted Di(2-pyridyl)amine Ligands

Keywords: Bioconjugates / Bioinorganic chemistry / Copper complexes / Di(2-pyridyl)amine



Cu^{II}L₂ complexes with new amino acidnitrogen ligand derivatives are prepared as potential building blocks in the assembly of inorganic models of double-stranded nucleic acid.

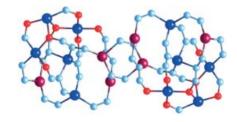
Intervalence Charge Transfer

S. De, S. Chowdhury, J. P. Naskar, M. G. B. Drew, R. Clérac,

D. Datta* 3695-3700

A Hexadecanuclear Copper(I)-Copper(II) Mixed-Valence Compound: Structure, Magnetic Properties, Intervalence Charge Transfer, EPR, and NMR

Keywords: Copper / High-nuclearity complexes / Aggregates / Mixed-valent compounds / Charge transfer / N,O ligands

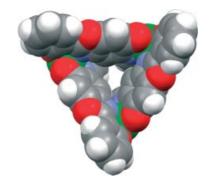


A hexadecanuclear mixed-valence copper complex containing 10 Cu^{II} centers (blue) and 6 CuI centers (purple), isolated with N,O donor ligands gives NMR and shows a broad intervalence charge-transfer band at 1100 nm at room temperature in methanol, and gives an EPR spectrum characteristic of mononuclear CuII at 5 K.



Macrocyclic Complexes

Trinuclear manganese(III) complexes of new unsymmetrical pentadentate Schiff base ligands have been prepared and characterised. The molecular structures are represented as a tripodal pyramid with a small cavity.



M. Muto, N. Hatae, Y. Tamekuni, Y. Yamada, M. Koikawa,*

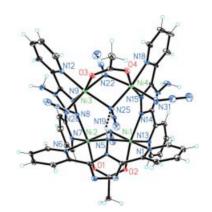
T. Tokii* 3701-3709

Tripodal Trimanganese(III) Complexes of New Unsymmetrical Pentadentate Ligands Derived from 2-(Salicylideneamino)phenol: Syntheses, Crystal Structures and Properties

Keywords: Bridging ligands / Ligand design / Manganese / X-ray structures / Magnetic properties / Redox chemistry

Magnetic Nickel Complexes

Reactions of nickel(II) salts with 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (abpt) generate a tetranuclear nickel(II) rectangle box, neutral dinuclear-, and mononuclear species with two polymorphous phases. The μ : η^1 : η^2 : η^1 coordination mode of the deprotonated [abpt-H] $^-$ ligand is observed in the rectangle box. Temperature-dependent magnetic properties of the dinuclear and tetranuclear complexes were investigated.



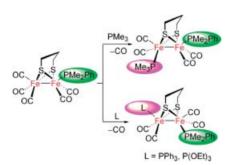
M.-L. Tong,* C.-G. Hong, L.-L. Zheng, M.-X. Peng, A. Gaita-Arińo, J. M. Clemente Juan* 3710-3717

New Reactivity of 4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole: Synthesis and Structure of a Mononuclear Species, a Dinuclear Species, and a Novel Tetranuclear Nickel(II) Rectangle Box, and Magnetic Properties of the Dinuclear and Tetranuclear Complexes

Keywords: Nickel / Polynuclear / Azides / Magnetic properties

Fe-Only Hydrogenase Models

The X-ray analyses show that the PMe₂Ph ligand in the apical position of the starting complex rotates to the basal position of the unsymmetrically disubstituted diiron complexes when PPh₃ and P(OEt)₃ were used as incoming ligands, providing clear evidence for the conformational flexibility of the [Fe(CO)₂L] subunits in the Fe-only hydrogenase model complexes in solution.

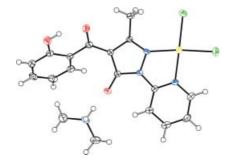


Phosphane and Phosphite Unsymmetrically Disubstituted Diiron Complexes Related to the Fe-Only Hydrogenase Active Site

Keywords: Bioinorganic chemistry / Carbonyl displacement / Diiron complexes / Fe-only hydrogenase / P ligands

Antitumour Agents

Platinum(II) and palladium(II) complexes with 4-(2-hydroxybenzoyl)-2-(pyridin-2-yl)-1*H*-pyrazol-3-ol (HL¹) have been synthesised as potential anticancer compounds. Protonation constants of the ligand and solid-state structures of the complexes are reported. The cytotoxic evaluation revealed that Pt^{II} and Pd^{II} complexes were active in the micromolar concentration range. Color code of ORTEP drawing: blue = N; green = Cl, red = O; yellow = Pt.



Synthesis, Structure, Protolytic Properties, Alkylating and Cytotoxic Activity of Novel Platinum(II) and Palladium(II) Complexes with Pyrazole-Derived Ligands

Keywords: Metal complexes / Platinum / Palladium / Pyrazole ligands / Antitumor agents / Alkylating and cytotoxic activity

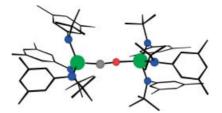
CONTENTS

C-O Activation



Cleavage of CO by Mo[N(R)Ar]₃ Complexes

Keywords: C-O activation / Molybdenum / Three-coordinate complexes / Density functional calculations / Bond cleavage



The reaction of MoL_3 [L = NH_2 and N(tBu)Ar] with CO is explored using DFT in order to rationalise why C-O cleavage is not observed for this system. In contrast, the analogous N_2 reaction results in spontaneous cleavage of N_2 .

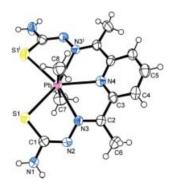
Lead Speciation

J. S. Casas,* E. E. Castellano, J. Ellena, M. S. García-Tasende, F. Namor, A. Sánchez, J. Sordo,

M. J. Vidarte 3742-3750

Methyllead(IV) Derivatives Stabilized by DAPTSC²⁻: Synthesis and Structures of New Diorganolead(IV) Complexes

Keywords: Lead / Diorganolead (IV) complexes / Metallation



Reactions of the pentadentate ligand $H_2DAPTSC$ with $PbMe_2(OAc)_2$ and $PbMePh(OAc)_2$ afforded simultaneously dimethyllead(IV) [or methylphenyllead(IV)] and lead(II) complexes. Their structures in solid state and solution were investigated.

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