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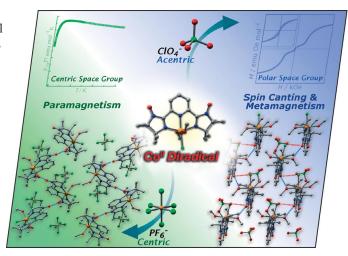
Chem PubSoc

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The cover picture shows that cobalt(II) diradical complexes with centric and acentric counter anions, $[Co\hat{C}l(bisimpy)(MeOH)_2]X$ (X = PF₆ and ClO₄), crystallize in the centrosymmetric and polar space groups of $P2_1/c$ and $Pna2_1$, respectively. The PF_6 salt is paramagnetic down to 1.8 K, whereas the ClO₄ salt shows a weak ferromagnetic longrange order with metamagnetic behavior at 1.8 K. Spin canting can arise from single-ion magnetic anisotropy and/or antisymmetric exchange interaction (Dzyaloshinsky-Moriya interaction). The noncentrosymmetric space group of the latter complex is compatible with both mechanisms. Details are discussed in the Short Communication by H. Oshio et al. on p. 4851ff.



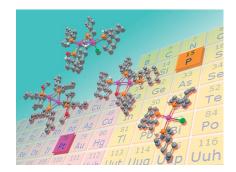
MICROREVIEW

Phosphanido-Bridged Complexes

P. Mastrorilli* 4835-4850

Bridging and Terminal (Phosphanido)platinum Complexes

Keywords: Terminal phosphides / Bridging phosphides / Platinum / Metalloligands / Clusters



The chemistry of both terminal and bridging (phosphanido)platinum complexes has been surveyed. The structural properties, NMR spectroscopic features and reactivity of the various classes of compounds have been highlighted. Phosphanido-bridged dinuclear complexes are subdivided into PtI compounds, hydrido complexes, halido and aryl or alkyl complexes.

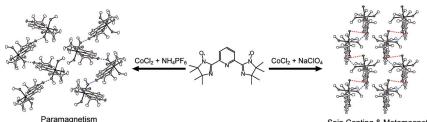
SHORT COMMUNICATIONS

Spin Canting

K. Mitsumoto, T. Shiga, M. Nakano, M. Nihei, H. Nishikawa, H. Oshio* 4851-4855

Spin Canting in a Cobalt(II) Radical Complex with an Acentric Counter Anion

Keywords: Cobalt / Spin canting / Crystal engineering / Organic radicals / Metamagnets



Spin Canting & Metamagnetism

The complex cation [CoCl(bisimpy)-(MeOH)₂]⁺, where bisimpy is an iminonitroxyl diradical with a triplet ground state, crystallizes in the centric $(P2_1/c)$ and the polar (Pna2₁) space groups, respectively, with PF₆⁻ and ClO₄⁻ anions. The PF₆⁻ salt is paramagnetic down to 1.8 K, whereas the ClO₄⁻ salt shows a weak ferromagnetic long-range order with a metamagnetic behavior below 2.7 K.

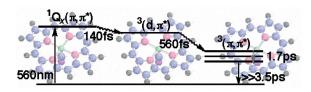
Ultrafast Excited-State Dynamics

I. Iwakura, A. Yabushita, T. Kobayashi* 4856-4860



Ultrafast Vibronic Processes in a Ru-Porphyrin Complex

Keywords: Ruthenium / Photochemistry / Luminescence / Femtochemistry / Laser spectroscopy

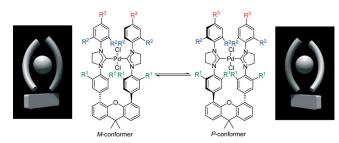


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Analysis of the six-coordinate complexes of Ru^{II}(TPP)(CO)(acetone) (TPP = tetraphenylporphyrin) by using a sub-5-fs pulse revealed that ${}^{1}Q_{x}(\pi,\pi^{*})$ had a lifetime of 140 ± 20 fs and the lifetime of ${}^{3}(d,\pi^{*})$ was 560 ± 150 fs. Stimulated emission due to a spin-forbidden transition from $3(\pi,\pi^*)$ to the ground state was observed for the first time.



Crystal Engineering



We synthesized a series of new bidentate bis(NHC)-Pd complexes with xanthene skeleton. The complexes crystallized in twisted conformations and therefore were chiral at solid state. Homochiral crystals were obtained when cyclic ether was used as the solvent. X-ray analyses indicated that the interaction between the complex and the solvent contributed to formation of the homochiral crystals.

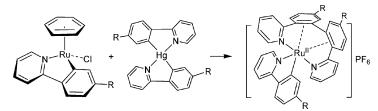
Synthesis, Structure, and Solvent-Induced Spontaneous Homochiral Assembly of Bidentate $\operatorname{Bis}(N,N'$ -diaryl-N-heterocyclic carbene)-Palladium Complexes

Keywords: Carbene ligands / Palladium / Nitrogen heterocycles / Chiral resolution / X-ray diffraction

Intra-C-C Coupling at Ruthenium

Denial of Tris(C,N-cyclometalated) Ruthenacycle: Nine-Membered η^6 -N,N-trans or η^2 -N,N-cis Ru^{II} Chelates of 2,2'-Bis(2-pyridinyl)-1,1'-biphenyl

Keywords: C-C coupling / N ligands / Metallacycles / Ring expansion / Ruthenium / Cyclometalation



The reaction between $[Ru(\eta^6-C_6H_6)(phpy)-Cl]$ and $Hg(phpy)_2$ in methanol, where phpy = 2-(2-pyridinyl)phenyl, leads to the unexpected octahedral $[Ru^{II}(phpy)(pbp)]-PF_6$ complex $\{pbp=2,2'-bis(2-pyridinyl)-preserved and preserved are supplied by the supplied of the preserved are supplied by the supplied by t$

The coordination behaviour of 1.2.4-tri-

1,1'-biphenyl}; pbp forms a nine-membered chelate providing $\eta^6\text{-tetradentate N/}$ $\eta^2\text{-C=C/}\eta^2\text{-C=C/N}$ coordination. The C=C units are weakly bound to the Ru $^{\rm II}$ center and are readily replaced by CO.

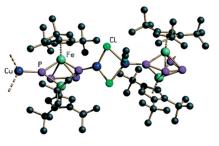
Phosphaferrocene Reactivity

Unexpected Differences in the Coordination Behaviour of 1,2,4-Triphosphaferrocenes towards Cu^I Chloride

Keywords: Supramolecular chemistry / Copper / Fragmentation reactions / Triphosphaferrocenes / Tetraphosphabutadiene ligand

phosphaferrocenes towards Cu^I chloride is decisively influenced by the substitution pattern of the Cp ring attached to iron. For the Cp-substituted derivative a dimeric complex is obtained. In the case of a tri-*t*Bu-substituted Cp''' ligand complex, the triphosphole is fragmented and rearranges into a tetraphosphabutadiene moiety in an iron triple-decker sandwich complex em-

bedded in a CuCl polymer matrix.



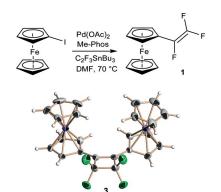
Trifluorovinylferrocene

M. Roemer, D. Lentz* 4875-4878

Synthesis and Reactions of Trifluorovinylferrocene

Keywords: Trifluorovinyl group / Ferrocene / Stille coupling / Hexafluorocyclobutane / Cycloadditions

Excellent reactivity towards nucleophiles, [2+2] cycloaddition, defluoration and CF_2 group transformation: The first metallocene with a trifluorovinyl substituent is an extremely versatile reagent allowing an easy access to dinuclear ferrocenes like 3.



FULL PAPERS

Metal-Metal Bonds

Isomeric Al_2R_4 , Mg_2R_2 Species and Oligomerisation Products: Investigation of Al-Al and Mg-Mg σ Bonding

Keywords: Aluminum / Magnesium / Metal-metal σ bonding / Diradicals / Ab initio calculations / Stability analysis / Low-valent metal compounds



From recent results for compounds that contain metal-metal σ bonds (Mg-Mg, Zn-Zn, Al-Al) and are stable at room temperature, the question arises whether there are diradical intermediates resulting from

'MgR, 'AlR or 'ZnR. Calculations on this subject as well as on oligomeric $(AlR_2)_x$ and $(MgCl)_x$ species show that the synthesis of the metastable solid MgCl, for example, may be possible.

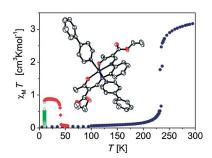
Spin-Crossover Complexes

B. Weber,* E. S. Kaps, C. Desplanches, J.-F. Létard,* K. Achterhold,

F. G. Parak 4891-4898

Synthesis and Characterisation of Two New Iron(II) Spin-Crossover Complexes with N_4O_2 Coordination Spheres — Optimizing Preconditions for Cooperative Interactions

Keywords: Iron / N,O ligands / Magnetism



The magnetic and photomagnetic properties of two new spin-crossover complexes with N_4O_2 coordination are presented. From the data for six spin-crossover complexes, an initial explanation was given with regard to which parameters are responsible for the extent of intermolecular interactions in this type of complex.

(Nitrido)chromium Functionalized POM

V. Lahootun, J. Karcher, C. Courillon,

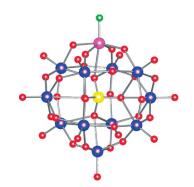
F. Launay, K. Mijares, E. Maatta,*

A. Proust* 4899-4905



A (Nitrido)chromium(V) Function Incorporated in a Keggin-Type Polyoxometalate: $[PW_{11}O_{39}CrN]^{5-}$ – Synthesis, Characterization and Elements of Reactivity

Keywords: Polyoxometalates / Nitrido compounds / Chromium



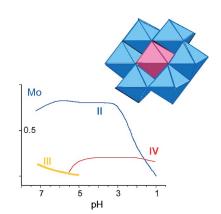
The synthesis of a (nitrido)chromium derivative of a Keggin-type POM is reported. Its characterization is illustrated by various spectroscopic methods and nucleophilic reactivity towards trifluoroacetic anhydride has been established.

Polyoxometalate Complexes

R. I. Maksimovskaya,* V. M. Bondareva, G. I. Aleshina 4906–4914

NMR Spectroscopic Studies of Interactions in Solution during the Synthesis of MoVTeNb Oxide Catalysts

Keywords: Molybdenum / Vanadium / Tellurium / Polyoxometalates / NMR spectroscopy



Three novel polyoxometalate anions, $V_9\text{TeO}_{28}^{5-}$ (I), $V_3\text{Mo}_3\text{O}_{24}^{9-}$ (III), and $V_5\text{Mo}_3\text{TeO}_{27}^{5-}$ (IV), have been observed, in addition to $\text{TeMo}_6\text{O}_{24}^{6-}$ (II), in aqueous $\text{Mo}^{\text{VI}}\text{-VV}\text{-Te}^{\text{VI}}$ solutions in the pH range 8-1, by using ^{51}V , ^{95}Mo , ^{17}O , and ^{125}Te NMR spectroscopy. Upon adding Nb oxalate, the Mo and V oxalates also form.



Zeolite Crystal Growth

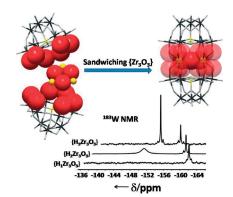
Dodecasil 3C was prepared in the presence of the amino acid DL-histidine as large, single crystals with sizes up to 140 µm.

Controlling the Crystal Growth of Dodecasil 3C by Buffering with DL-Histidine

Keywords: Crystal growth / Zeolites / Solgel / Amino acids

Polyoxometalate Chemistry

Reaction of ZrOCl₂ with A-α-[SiW₉O₃₄]⁹⁻ leads to a "sandwich" complex which consists of a central triangular {Zr₃O₃} core closely embedded between two {SiW₉O₃₄} subunits. Structural characterisation shows that the central {Zr₃O₃} core becomes protonated as a result of a remarkably slow proton transfer within the central triangle.



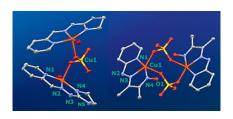
N. Leclerc-Laronze, J. Marrot, M. Haouas, F. Taulelle, E. Cadot* 4920-4926

Slow-Proton Dynamics within a Zirconium-Containing Sandwich-Like Complex Based on the Trivacant Anion a-[SiW₉O₃₄]¹⁰⁻ - Synthesis, Structure and NMR Spectroscopy

Keywords: Polyoxometalate / Zirconium / Tungsten / ¹⁸³W NMR spectroscopy

Cu-Based Frameworks

The synthesis and characterisation (X-ray, FTIR. UV/Vis. emission spectroscopy, electrochemistry) of sulfate-bridged dimeric copper(II) complexes with a 3D network using N-heterocyclic ligands are reported. Electrochemistry shows metal-centred oxidation in both cases. DFT and TDDFT calculations provide useful information on the electronic structures and spectroscopic transitions of the complexes.

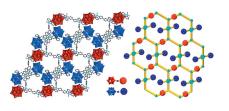


C. Basu, S. Biswas, A. P. Chattopadhyay, H. Stoeckli-Evans. S. Mukheriee* 4927-4935

Sulfate-Bridged Dimeric Copper(II) Complexes with Three-Dimensional Network: Synthesis, Structure and DFT Studies

Keywords: Dimeric copper(II) / Electrochemistry / Density functional calculations

Two unusual polyoxometalate hybrids with copper ions and mixed ligands have been hydrothermally prepared. In one case, dangling polyanion clusters are arranged in a mutual anti orientation about the 2D keleton (see the picture).



Polyoxometalate-Based Hybrids

L. Yuan, C. Qin, X. Wang, E. Wang,* S. Chang 4936-4942

Two Extended Organic-Inorganic Assemblies Based on Polyoxometalates and Copper Coordination Polymers with Mixed 4,4'-Bipyridine and 2,2'-Bipyridine Ligands

Keywords: Polyoxometalates / Hydrothermal synthesis / Organic-inorganic hybrids / Mixed ligands

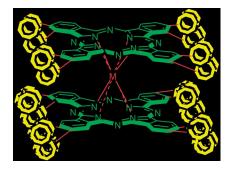
Phthalocyaninatolanthanides

T. Ceyhan, M. A. Özdağ, B. Salih, M. K. Erbil, A. Elmalı, A. R. Özkaya,

Ö. Bekaroğlu* 4943–4950

Synthesis, Characterization, Nonlinear Absorption and Electrochromic Properties of Double-Decker Octakis(mercaptopropylisobutyl-POSS)phthalocyaninatolanthanide(III) Complexes

Keywords: Phthalocyanines / Lanthanides / Nonlinear optics / Optical limiting / Electrochromism



The double-decker phthalocyaninatolanthanide(III) complexes MPc2 (M = Lu, Gd) with eight polyhedral oligomeric silsesquioxanes (POSSs) have been prepared and characterized. Nonlinear absorption and optical limiting properties of 2 and 3 are investigated by means of Z-scan technique.

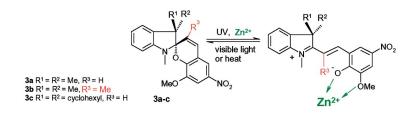
Photoreversible Ion Transportation

C. J. Roxburgh* P. G. Sammes, A. Abdullah 4951-4960



Photoreversible Zn²⁺ Ion Transportation Across an Interface Using Ion-Chelating Substituted Photochromic 3.3'-Indolospirobenzopyrans: Steric and Electronic Controlling Effects

Keywords: Photochromism / Zinc ion transportation / Chelation / Photoreversibility / Spiro compounds



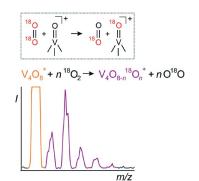
Demonstration of photoreversible zinc ion transportation across an organic/aqueous interface using indolospiropyrans is reported. Biasing of the photodynamic equilibrium, and consequently zinc ion transportation, is further controlled using strategically placed, sterically, and electronically influencing substitutents.

Isotopic Exchange Reactions

S. Feyel, D. Schröder, H. Schwarz* 4961-4967

Gas-Phase Chemistry of Vanadium Oxide Cluster Cations $V_m O_n^+$ (m = 1-4; n =1-10) with Water and Molecular Oxygen

Keywords: Mass spectrometry / Vanadium / Isotopic labeling / Cluster compounds



¹⁶O/¹⁸O exchange reactions of gaseous vanadium oxide cluster cations with oxygenlabeled water and molecular oxygen were probed by mass spectrometry. Degenerate ¹⁶O/¹⁸O exchange with water is primarily obtained for the $V_m O_n^+$ cluster cations with a medium valence state of vanadium, whereas $V_3O_6^+$ and $V_4O_8^+$ are the only cluster cations to activate O_2 .

Bimetallic Palladium Complexes

J. Flapper, P. Wormald, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, C. J. Elsevier, P. C. J. Kamer* 4968-4976

cis, trans - or Both: Steric Bulk Determines Coordination Mode of Dimeric Palladium Complexes with Bridging Pyridine-Phosphane Ligands

Keywords: Bimetallic complexes / Coordination modes / N,P ligands / Palladium / Solid-state NMR



Unique binding mode: A series of bimetallic complexes is synthesized, in which the configuration around the two palladium centers can be cis-cis, trans-trans, or even trans-cis, although both centers are surrounded by the same ligands. The coordination mode can be tuned by variation of the steric bulk of the ligands.



Copper Complexes with Mebdmpza

Two complexes, $[CuCl_2(Mebdmpza)]$ and $[Cu_2(\mu-O_4C_2)Cl_2(Mebdmpza)_2]$, were synthesized by reaction of $CuCl_2$ with the precursor ligand bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) in methanol. The transformation of the ligand Hbdmpza is reversible. $[CuCl_2(Mebdmpza)]$ in water yields $[Cu(bdmpza)_2]\cdot 2H_2O$ and/or waterfree $[Cu(bdmpza)_2]$.

Copper Complexes with the Ligand Methyl Bis(3,5-dimethylpyrazol-1-yl)acetate (Mebdmpza), Generated by In Situ Methanolic Esterification of Bis(3,5-dimethylpyrazol-1-yl)acetic Acid

Keywords: Copper / Pyrazole ligands / Magnetic properties / Ligand design / Antiferromagnetism

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

If not otherwise indicated in the article, papers in issue 30 were published online on October 10, 2008

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