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COVER PICTURE

The cover picture shows a figurative representation of the game of chance involved in attempting to synthesise novel monomeric derivatives of the sterically encumbered polymeric bis(alkyl) complexes $[M(CH_2SiMe_3)_2]_\infty$ (M = Mg, Mn^{II}). A winning hand was achieved by utilising the potent two-electron σ-donor 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), an N-heterocyclic carbene, to yield the first such examples of monomeric three-coordinate $[M(CH_2SiMe_3)_2]\cdot$donor complexes (M = Mg, Mn). Likewise, monomeric three-coordinate species were obtained for the bulkier disilyl-substituted alkyl $[CH(SiMe_3)_2]$ congeners yielding $M[CH(SiMe_3)_2]_2\cdot$IPr (M = Mg, Mn) by displacement of an ether ligand from $M[CH(SiMe_3)_2]_2\cdot$ether by IPr. Determined by X-ray crystallography, the structures of the four new monomers are shown on the faces of the individual playing cards. The diamagnetic magnesium compounds were also characterized in arene solution by ^1H and ^{13}C NMR spectroscopy. Details are discussed in the article by R. E. Mulvey, S. D. Robertson et al. on p. 4675ff. The cover art was composed by one of the authors of the paper, Dr. Jan Klett.

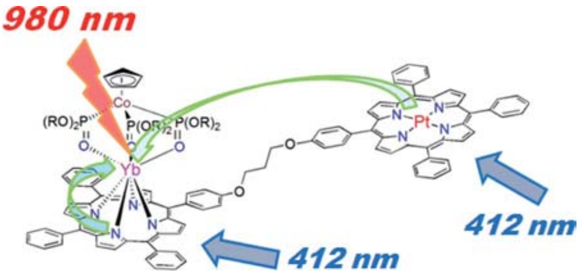
MICROREVIEW

NIR Emissive Ln Complexes

X. Zhu, W.-K. Wong,* W.-Y. Wong,
X. Yang **4651–4674**

Design and Synthesis of Near-Infrared Emissive Lanthanide Complexes Based on Macrocyclic Ligands

Keywords: Lanthanides / Porphyrinoids / Macrocyclic ligands / Luminescence



Various synthetic strategies have been described for encapsulating lanthanide ions into molecular edifices and making use of macrocyclic (viz. porphyrins, phthalocyanines and their derivatives) or acyclic ligands as well as d-transition-metal complexes (i.e. Schiff base and their transition-metal complexes) to sensitize the near-infrared-emitting trivalent lanthanide ions.

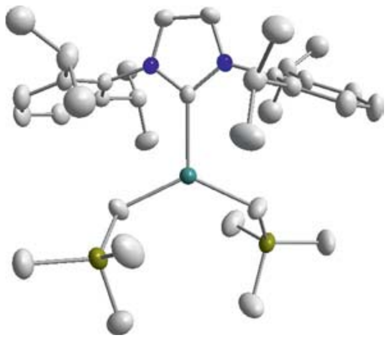
FULL PAPERS

NHC-Induced Monomerization

A. R. Kennedy, J. Klett, R. E. Mulvey,*
S. D. Robertson* **4675–4679**

N-Heterocyclic-Carbene-Induced Monomerization of Sterically Encumbered Dialkylmagnesium and Dialkylmanganese Polymers

Keywords: Alkyl ligands / Magnesium / Manganese / N-heterocyclic carbenes / Structure elucidation



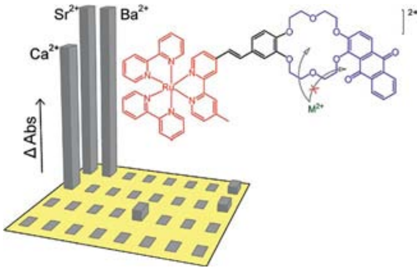
N-heterocyclic-carbene-stabilized adducts of $[(Me_3Si)_{3-}xCH_x]_2M$ ($M = Mg^{II}, Mn^{II}$; $x = 1, 2$) were prepared as monomeric crystalline solids. These products represent rare examples of three-coordinate monomeric dialkyl Mg and Mn complexes, as the parent dialkyl metal species typically prefers either multiple donors or dimerization through anionic bridges to attain a tetrahedral geometry.

Selective Sensing and Preferential Binding

T. Banerjee, M. Suresh, H. N. Ghosh,*
A. Das* **4680–4690**

Competitive binding of $Ba^{2+}$and Sr^{2+} to 18-Crown-6 in a Receptor with a 1-Methoxyanthraquinone Analogue as the Other Binding Site

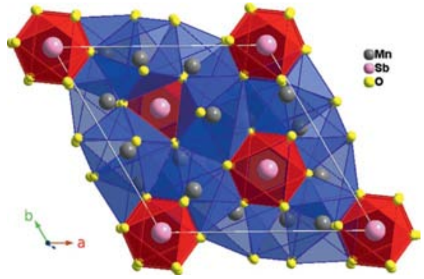
Keywords: Sensors / Receptors / Crown compounds / Alkaline earth metals / Ruthenium



A new Ru^{II}-polypyridyl complex with two probable binding sites for metal ions has been synthesised to which Ca^{2+}, Sr^{2+} and Ba^{2+} were found to bind selectively over all other alkali, alkaline earth, transition and lanthanide metal ions. Studies also confirmed binding of these metal ions solely to the 18-crown-6 and not to the methoxyanthraquinone moiety known to bind alkaline earth metal ions.

Short-Range Spin Order

The crystal structure and magnetic properties of Mn_2InSbO_6 and Mn_2ScSbO_6 were investigated by using a combination of X-ray and neutron powder diffraction, electron microscopy, calorimetric, and magnetic measurements.

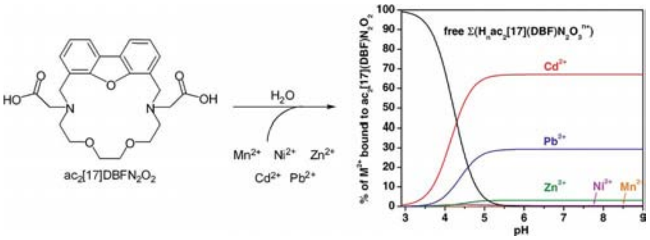


S. Ivanov, P. Nordblad, R. Mathieu, R. Tellgren,* E. Politova, G. André **4691–4699**

Short-Range Spin Order and Frustrated Magnetism in Mn_2InSbO_6 and Mn_2ScSbO_6

Keywords: Complex metal oxides / Magnetic properties / Multiferroics / Neutron diffraction / Structure elucidation

Macrocyclic Ligands



A new diaza crown ether containing a dibenzofuran group and two acetate pendant arms has been prepared. Our results revealed that this compound has a higher affinity for larger metal ions, Cd^{2+} and Pb^{2+}, with a clear preference for cadmium. It was shown that this unusual selectivity pattern is governed by the ring size and rigidity of the macrocycle.

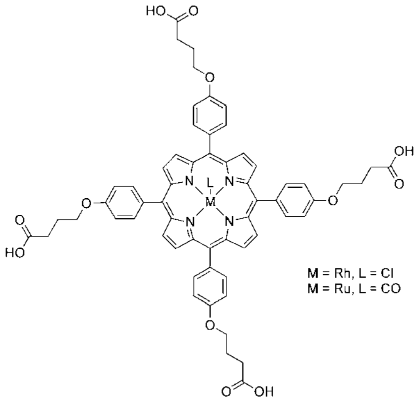
P. Mateus, F. Li, C. V. Esteves, R. Delgado,* P. Brandão, V. Félix **4700–4708**

Properties of Metal Complexes of a New Dioxadiaza Macrocycle Containing a Dibenzofuran Unit and Acetate Pendant Arms

Keywords: Macrocyclic ligands / Crown compounds / Aza crown ethers / Heavy metals / Stability constants / N,O ligands / Environmental chemistry

Aqueous Catalysis

For the first time, porphyrin–metal complexes are used as catalysts for hydrogenation of α,β-unsaturated aldehydes. Two new phosphane-free porphyrin complexes with rhodium and ruthenium were synthesized and used as catalysts for aqueous–organic biphasic hydrogenation of *trans*-cinnamaldehyde. The catalysts can be successfully recycled and reused.

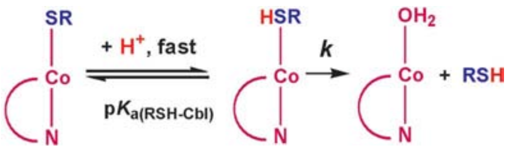


C. Stangel, G. Charalambidis, V. Varda, A. G. Coutsolelos,* I. D. Kostas* **4709–4716**

Aqueous–Organic Biphasic Hydrogenation of *trans*-Cinnamaldehyde Catalyzed by Rhodium and Ruthenium Phosphane-Free Porphyrin Complexes

Keywords: Porphyrinoids / Biphasic catalysis / Hydrogenation / Cinnamaldehyde / Aqueous catalysis

Cobalamin Chemistry



The thiolato derivatives of vitamin B_{12} spontaneously decompose in acidic aqueous solution through a mechanism that involves protonation of the thiolato ligand.

L. A. Schumacher, R. Mukherjee, J. M. Brown, H. Subedi, N. E. Brasch* **4717–4720**

Kinetic Studies on the Decomposition of Thiolatocobalamins in Acidic Solution

Keywords: Bioinorganic chemistry / Kinetics / Reaction mechanisms / Vitamins / Cobalamin

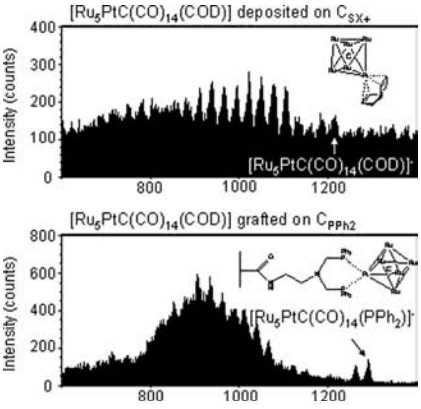
CONTENTS

Cluster Grafting

C. Willocq, D. Vidick, B. Tinant, A. Delcorte, P. Bertrand, M. Devillers, S. Hermans* **4721–4729**

💻 Anchoring of Ru–Pt and Ru–Au Clusters onto a Phosphane-Functionalized Carbon Support

Keywords: Nanoparticles / Cluster compounds / Ruthenium / Carbon support



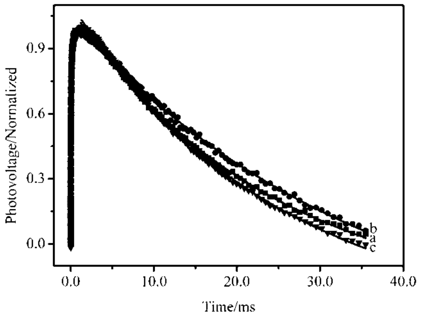
Two clusters, [$Ru_5PtC(CO)_{14}(COD)$] and [$Ru_6Au_2C(CO)_{16}(PPh_3)_2$], were anchored onto a functionalized carbon support (C_{PPh_2}). In combination with other techniques, secondary ion mass spectrometry (SIMS) proved the covalent binding of the intact Ru_5Pt cluster but showed a loss of Au atoms from the Ru_6Au_2 species. Model reactions in solution confirmed the anchoring mechanism by ligand exchange.

Dye-Sensitised Solar Cells

K. Pan, W. Zhou, G. Tian, Q. Pan, C. Tian, T. Xie, Y. Dong, D. Wang, H. Fu* **4730–4737**

💻 Dye-Sensitised Solar Cells Based on Large-Pore Mesoporous TiO_2 with Controllable Pore Diameters

Keywords: Solar cells / Mesoporous materials / Nanoparticles / Photovoltage transient / Interfacial electron transfer / Electrolyte percolation / Adsorption



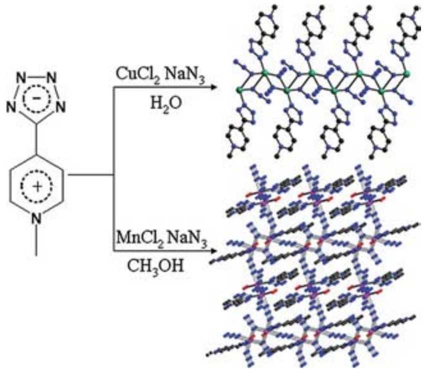
A series of dye-sensitised solar cells (DSSCs) has been fabricated on the basis of meso-TiO_2 with large controllable pore sizes (6.5, 8.2 and 11.0 nm). The DSSC with the 8.2 nm meso-TiO_2 photoelectrode has the highest photoelectrical conversion efficiency as evidenced by the photovoltage transient.

Molecular Magnets

X.-B. Li, Y. Ma, X.-M. Zhang, J.-Y. Zhang, E.-Q. Gao* **4738–4744**

💻 Azide-Bridged Copper(II) and Manganese(II) Compounds with a Zwitterionic Tetrazolate Ligand: Structures and Magnetic Properties

Keywords: Coordination polymers / Copper / Magnetic properties / Manganese / Azides



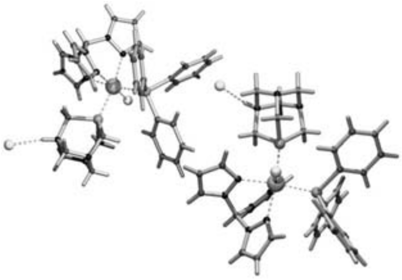
A pyridinium tetrazolate zwitterion as an auxiliary ligand led to two coordination compounds that have different azide-bridging networks. The 1D Cu^{II} compound magnetically behaves as a ferromagnetic quasi-dimer, while the Mn^{II} compound behaves as a 3D antiferromagnet.

Scorpionate Complexes

S. Miguel, J. Diez, M. P. Gamasa, M. E. Lastra* **4745–4755**

Synthesis and Structural Features of New Ruthenium(II) Complexes Containing the Scorpionate Ligands Tris(pyrazol-1-yl)methanesulfonate (Tpms) and Tris(pyrazol-1-yl)methane (Tpm)

Keywords: Ruthenium / Scorpionate ligands / Phosphane ligands / N,O ligands



New ruthenium(II) complexes containing the scorpionate ligands tris(pyrazol-1-yl)methanesulfonate (Tpms) and tris(pyrazol-1-yl)methane (Tpm) and water soluble 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane (PTA) and 1-R-PTA ligands have been synthesized. For the Tpms ligand two coordination modes, N,N,N and N,N,O, have been structurally characterized.

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* Author to whom correspondence should be addressed.

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

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