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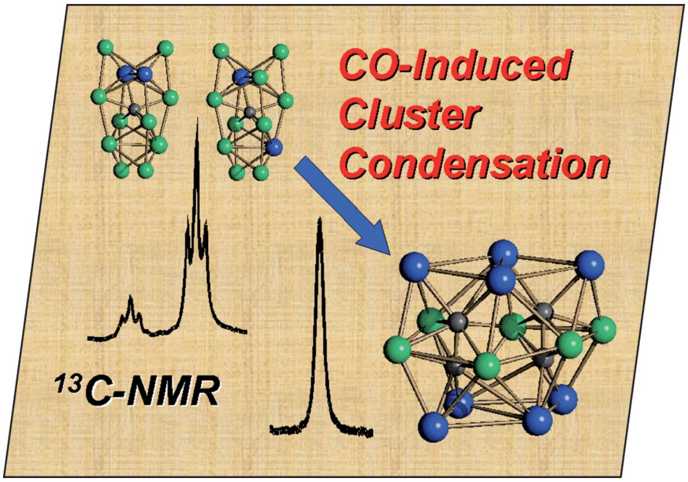
A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows a rare example of CO-induced cluster condensation rather than degradation to lower nuclearity species. Thus, the heterobimetallic mono-carbide $[Ni_{10}Rh_2C(CO)_{20}]^{2-}$ is transformed into the bis-acetylide $[Ni_6Rh_8(C_2)_2(CO)_{24}]^{4-}$ after exposure to a CO atmosphere. The compounds have been characterised by X-ray diffraction and ^{13}C NMR spectroscopy. NMR spectroscopic studies point out that the mono-carbide exists as two isomers, and coordination of Rh atoms to the interstitial carbide atom is very effective in shortening its longitudinal relaxation time (T_1) by approximately two orders of magnitude relative to homometallic Ni carbido clusters. Details are discussed in the article by S. Zacchini et al. on p. 2487ff.



CONTENTS

MICROREVIEW

Ruthenium Cages

B. Therrien* **2445–2453**

Arene Ruthenium Cages: Boxes Full of Surprises

Keywords: Arene ligands / Bioinorganic chemistry / Ruthenium / Self-assembly / Supramolecular chemistry

Self-assembly of arene ruthenium building blocks has allowed the construction of cationic metalla complexes of different architectures and functionalities. They show host–guest properties, perform photochemical [2+2] cycloadditions, encapsulate molecules and possess biological activities. This microreview covers synthetic and structural aspects of these metalla-cages as well as their most promising applications.

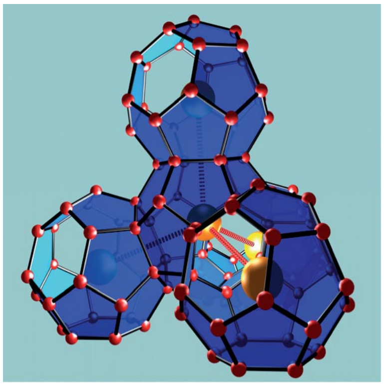
SHORT COMMUNICATIONS

Ge Clathrates

A. M. Guloy,* Z. Tang, R. Ramlau,
B. Böhme, M. Baitinger,
Yu. Grin* **2455–2458**

Synthesis of the Clathrate-II $K_{8.6(4)}Ge_{136}$ by Oxidation of K_4Ge_9 in an Ionic Liquid

Keywords: Clathrates / Cage compounds / Zintl anions / Oxidation / Ionic liquids



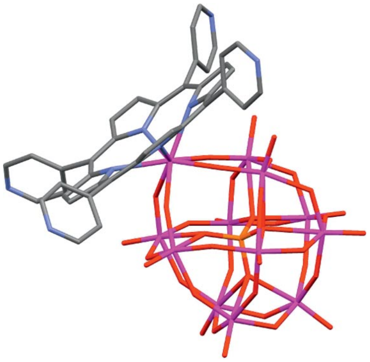
A new metastable binary compound, $K_{8.6(4)}Ge_{136}$, crystallizing in the clathrate-II structure, was synthesized by the oxidation of K_4Ge_9 by an ionic liquid.

Porphyrin–Polyoxometalate Complexes

A. Falber, B. P. Burton-Pye, I. Radivojevic,
L. Todaro, R. Saleh, L. C. Francesconi,
C. M. Drain* **2459–2466**

Ternary Porphyrinato Hf^{IV} and Zr^{IV} Polyoxometalate Complexes

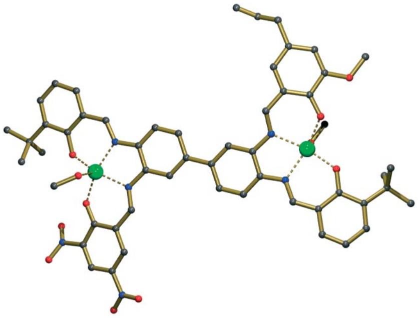
Keywords: Porphyrinoids / Polyoxometalates / Photochemistry / Nanostructures



Porphyrins and polyoxometalates are widely studied molecules because of their tunable physical and chemical properties. A ternary complex is formed when Hf^{IV} or Zr^{IV} metal ions coordinate *both* a porphyrin and a lacunary defect in a polyoxometalate. A crystal structure of a Hf^{IV} complex and spectroscopic data suggest that Hf^{IV} or Zr^{IV} porphyrins can bind to oxide surfaces by the protruding metal ion.

Templated Synthesis

A templated approach toward fully nonsymmetrical bis-metallo(salphen) complexes is described. The dinuclear species can be selectively and stepwise built from useful monometallic triimine precursors. In one case, the presence of different peripheral substituents in both metallosalen units allowed for different reactivity behaviour and site-selective conversion.



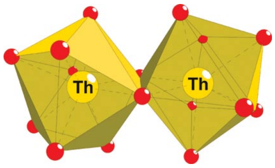
A. M. Castilla, S. Curreli,
N. M. Carretero, E. C. Escudero-Adán,
J. Benet-Buchholz,
A. W. Kleij* 2467–2471

Templated Synthesis and Site-Selective Conversion of Completely Nonsymmetrical Bis-Metallosalphen Complexes

Keywords: Nonsymmetrical complexes / N,O ligands / Diastereoselectivity / Templated synthesis / Zinc

Actinide Coordination Chemistry

The novel thorium(IV)(BT)$_2$ hydrate (BT^{2-} = 5,5′-Bitetrazolate) exhibits a salt-like structure (XRD). Density functional (DFT) calculations on gas-phase molecular clusters, employing a relativistic *large-core* pseudopotential and a large *valence-only* (7s7p5d2f1g)/[6s5p4d2f1g] basis set for Th^{IV}, confirm the identification of [(μ-OH)$_2$-Th$_2$(H$_2$O)$_{14}$]$^{6+}$ as the cation in thorium(IV)-(BT)$_2$ hydrate.



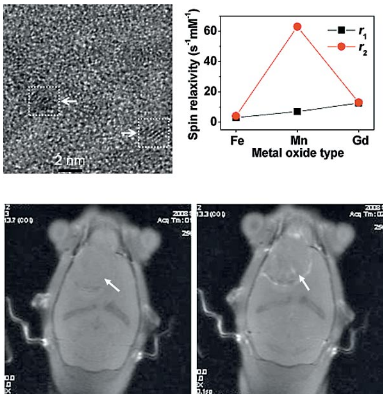
R. W. H. Pohl, J. Wiebke, A. Klein,*
M. Dolg, N. Maggiarosa 2472–2476

A New 5,5′-Bitetrazole Thorium(IV) Compound: Synthesis, Crystal Structure and Quantum Chemical Investigation

Keywords: Actinides / Bitetrazole / Hydrates / Thorium / X-ray diffraction / Density functional calculations

Nanoparticles for MR Imaging

A one-pot synthesis for water-soluble ligand-coated *ultra small* paramagnetic or superparamagnetic metal oxide nanoparticles is developed and used in molecular MRI. The iron oxide, manganese oxide, and gadolinium oxide nanoparticles are coated with hydrophilic and biocompatible ligands. The ligand-coated *ultra small* gadolinium oxide nanoparticles are superior candidates as T_1 MRI contrast agents.

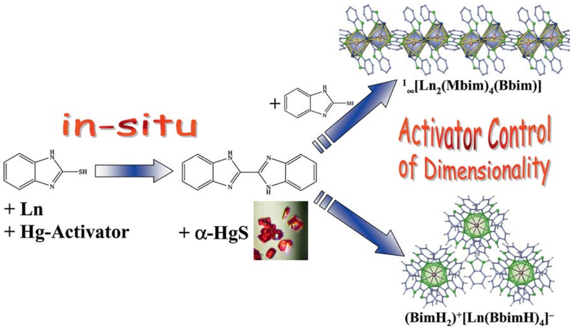


J. Y. Park, E. S. Choi, M. J. Baek,
G. H. Lee,* S. Woo,
Y. Chang* 2477–2481

Water-Soluble *Ultra Small* Paramagnetic or Superparamagnetic Metal Oxide Nanoparticles for Molecular MR Imaging

Keywords: Colloids / Imaging agents / Nanostructures / Nanotechnology

Coordination Polymers



Activator-controlled in situ ligand syntheses by C–S bond cleavage are used for the formation of thiolate amide coordination polymers. Hg functions both as activator for lanthanide metals in the reaction with 2-mercaptobenzimidazole and promotes the C–S bond cleavage with formation of 2,2′-bibenzimidazole. The reaction path leading to different products can be controlled by the amount of mercury.

A. Zurawski, E. Wirnhier,
K. Müller-Buschbaum* 2482–2486

Activator-Controlled High Temperature In-Situ Ligand Synthesis for the Formation of Rare Earth Thiolate Amide Coordination Polymers

Keywords: In situ synthesis / Coordination polymers / Lanthanides / Thiolates / C–S bond cleavage

CONTENTS

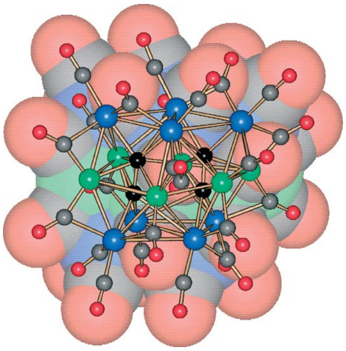
FULL PAPERS

Metal Carbonyl Clusters

C. Femoni, M. C. Iapalucci, G. Longoni, S. Zacchini* 2487–2495

Hetero-Bimetallic Ni-Rh Carbido Carbonyl Clusters: Synthesis, Structure and ^{13}C NMR of $[Ni_{10}Rh_2C(CO)_{20}]^{2-}$, $[Ni_9Rh_3C(CO)_{20}]^{3-}$ and $[Ni_6Rh_8(C_2)_2(CO)_{24}]^{4-}$

Keywords: Nickel / Rhodium / Cluster compounds / Carbonyl ligands / Carbides



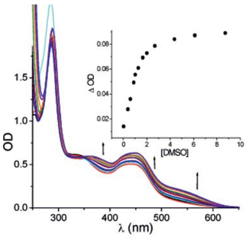
The new hetero-bimetallic $[Ni_{10}Rh_2C(CO)_{20}]^{2-}$ and $[Ni_9Rh_3C(CO)_{20}]^{3-}$ clusters were prepared by reacting $[Ni_9C(CO)_{17}]^{2-}$ with $[Rh(cod)Cl]_2$. Degradation leads to the bis-acetylide $[Ni_6Rh_8(C_2)_2(CO)_{24}]^{4-}$. ^{13}C NMR studies indicate that coordination of Rh atoms to the interstitial carbide is very effective in shortening its longitudinal relaxation time compared to homometallic Ni carbido clusters.

Chromogenic Sensor

A. Ghosh, S. Verma, B. Ganguly,* H. N. Ghosh,* A. Das* 2496–2507

Influence of Urea N–H Acidity on Receptor–Anionic and Neutral Analyte Binding in a Ruthenium(II)–Polypyridyl-Based Colorimetric Sensor

Keywords: Ruthenium(II) complexes / Sensors / Urea / Ab initio calculations



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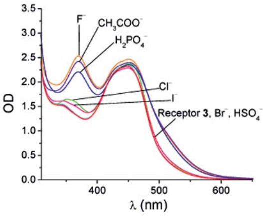
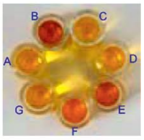




3

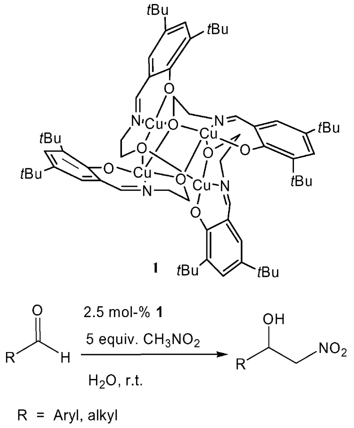
The influence of the relative acidity of pendant H_{urea} atoms on binding affinities towards neutral and anionic analytes is described. Receptor **2** (A) + X; X = DMSO (B), DMF (C); Receptor **3** (A) + A^-; A^- = F^- (B), Cl^-/Br^- (C/D), CH_3COO^- (E), $H_2PO_4^-$ (F), HSO_4^- (G).

Henry Reaction

S. Jammi, T. Punniyamurthy* ... 2508–2511

Synthesis, Structure and Catalysis of Tetranuclear Copper(II) Open Cubane for Henry Reaction on Water

Keywords: C–C bond formation / Copper / Henry reaction / Heterogeneous catalysis / Water



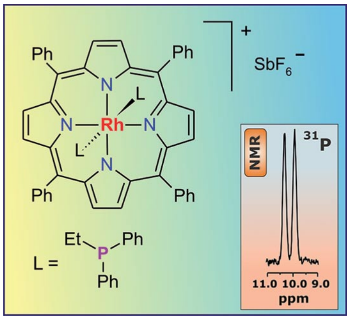
The synthesis and application of the new copper(II) open cubane cluster **1** are described for the addition of nitroalkanes to carbonyl compounds on water. The cluster **1** is free from additives and can be recycled without loss of activity.

Rhodium–Porphyrins

O. Q. Munro,* G. L. Camp, L. Carlton 2512–2523

Structural, ^{103}Rh NMR and DFT Studies of a Bis(phosphane)Rh^{III}–Porphyrin Derivative

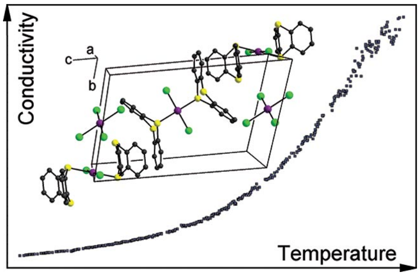
Keywords: ^{103}Rh NMR spectroscopy / Porphyrin / Density functional calculations / GIAO / Phosphanes



Indirect detection of the ^{103}Rh NMR spectra of a bis(phosphane)Rh^{III}–porphyrin derivative, $[Rh(TPP)(PEtPh_2)_2]SbF_6$, by polarisation transfer from ^{31}P afforded ^{103}Rh chemical shifts in the range δ = 2480–2590 ppm from 213 to 333 K. DFT simulations at the PBE1PBE/3-21G** level of theory were used to determine stable in vacuo structures and shielding tensors (GAIO method) for the complex.

Semiconductive Complexes

The new (thianthrene)gold(III) complex salt $[AuCl_2(TA)_2][AuCl_4]$, synthesized in liquid SO_2, has a black appearance, an ionic structure and is a semiconductor with low activation energy. If dissolved in chloroform, the ions are converted to an isomeric form built of discrete complexes of $[AuCl_3(TA)]$ indicating a solvent-dependent equilibrium.



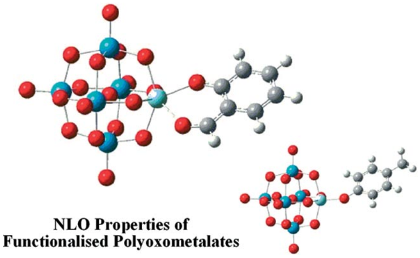
R. T. Tjahjanto, J. Beck* 2524–2528

Synthesis and Characterization of Semiconductive Dichloridobis(thianthrene)-gold(1+) Tetrachloridoaurate(1−)

Keywords: Sulfur heterocycles / Gold / Sulfur dioxide / Semiconductors

Polyoxometalates

We report a theoretical study, based on DFT and TD-DFT calculations, of the bonding nature, first hyperpolarizabilities, electronic transitions, and charge transfer involved in the nonlinear optical response of aryloxide and salicylaldehyde derivatives of $[XW_5O_{18}]^{3-}$ (X = Zr or Ti).



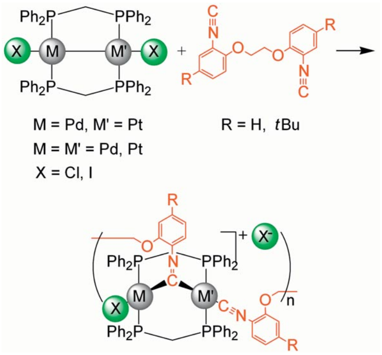
J. Zhuang, L. Yan, C. Liu, Z. Su* 2529–2535

A Quantum Chemical Study of the Structure, Bonding Characteristics and Nonlinear Optical Properties of Aryloxido and Salicylaldehydo Derivatives of $[XW_5O_{18}]^{3-}$ (X = Zr or Ti)

Keywords: Polyoxometalates / Organic-inorganic hybrid composites / Natural bond analysis / Nonlinear optics / Density functional calculations

Organometallic Polymers

The complexes XM(μ-dppm)$_2$M′X react with 1,2-bis(2-isocyanophenoxy)ethanes (diNC) in a 1:1 molar ratio to give the corresponding polymers $\{[\{M(\mu\text{-dppm})_2\text{-}M'X\}(diNC)]X\}_n$. These polymers are luminescent in solution at 77 K, showing strong luminescence bands in the range 500–800 nm with lifetimes of between 0.2 and 5.6 μs.



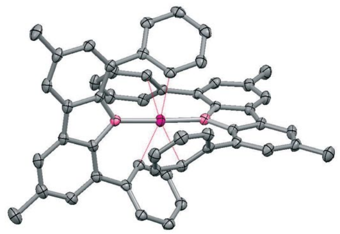
S. Clément, S. M. Aly, J. Husson, D. Fortin, C. Strohmann, M. Knorr,* L. Guyard, A. S. Abd-El-Aziz, P. D. Harvey* 2536–2546

A-Frame-Containing Organometallic Oligomers Constructed From Homo- and Heterobimetallic M(μ-dppm)$_2$M′ (M/M′ = Pd, Pt) Building Blocks

Keywords: Platinum / Palladium / Polymers / Isocyanide ligands / Luminescence

Amido Complexes

The coordinatively and electronically unsaturated transition-metal complexes $(1,8\text{-}Ph_2\text{-}3,6\text{-}Me_2C_{12}H_4N)_2M$ (M = Cr–Co) have been synthesised and the solid-state structures of the manganese and iron systems determined. Solid-state magnetic measurements reveal high spin metal centres which are confirmed by computational calculations for the model complexes $M(1,8\text{-}Ph_2C_{12}H_6N)_2$ (M = Cr–Co).



A. E. Ashley, A. R. Cowley, J. C. Green, D. R. Johnston, D. J. Watkin, D. L. Kays* 2547–2552

Synthesis and Characterisation of Low-Coordinate Transition-Metal Complexes Stabilised by Sterically Demanding Carbazolido Ligands

Keywords: N ligands / Amido complexes / Transition metals / Open-shell complexes / Low-coordinate complexes

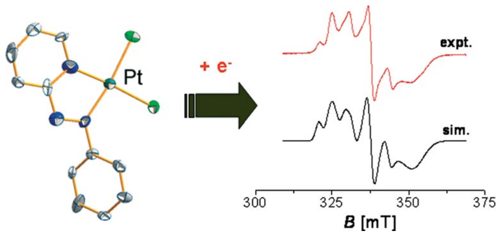
CONTENTS

Azo Complexes

S. Roy, I. Hartenbach,
B. Sarkar* .... 2553−2558

Structures, Redox and Spectroscopic Properties of Pd^{II} and Pt^{II} Complexes Containing an Azo Functionality

Keywords: Platinum / Palladium / Azo compounds / EPR spectroscopy / Cyclic voltammetry



Reduction of the structurally characterized complexes [PdCl$_2$(pap)], [PtCl$_2$(pap)], and [(az)Pd(μ-Cl)$_2$Pd(az)] leads to radical intermediates where the spin is predominantly located on the azo part of the complexes. The radical anion [PtCl$_2$(pap)]$^{\bullet-}$ shows unusually large ^{195}Pt hyperfine coupling and *g* anisotropy for this type of complex.

CORRECTIONS

S. Roy, I. Hartenbach, B. Sarkar* ... 2559

Structures, Redox and Spectroscopic Properties of Pd^{II} and Pt^{II} Complexes Containing an Azo Functionality

Keywords: Platinum / Palladium / Azo compounds / EPR spectroscopy / Cyclic voltammetry

I. A. Kotzé, W. J. Gerber, J. M. Mckenzie,
K. R. Koch* 2560

Self-Association of [Pt^{II}(1,10-Phenanthroline)(*N*-pyrrolidyl-*N*-(2,2-dimethylpropanoyl)thiourea)]$^+$ and Non-Covalent Outer-Sphere Complex Formation with Fluoranthene through π−Cation Interactions: A High-Resolution ^{1}H and DOSY NMR Study

Keywords: Noncovalent interactions / Pi interactions / NMR spectroscopy / Diffusion coefficients / Association constants

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* Author to whom correspondence should be addressed.

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