

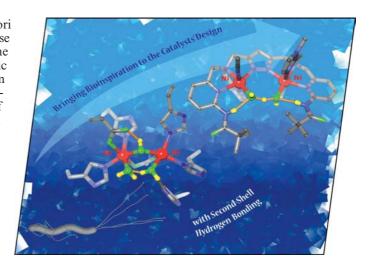


**EurJIC** is а iournal ChemPubSoc Europe, a union of 16 European chemical societies formed for the purpose of publishing high-quality science. All owners merged their national journals to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry.

Other ChemPubSoc Europe journals are Chemistry – A European Journal, ChemBioChem, ChemPhysChem, ChemMedChem, ChemSusChem and ChemCatChem.

# COVER PICTURE

The cover picture shows (i) a Helicobacter pylori that produces large amounts of the enzyme urease to survive in the acidic human stomach, (ii) the urease active site, and (iii) a bioinspired bimetallic complex that features second-shell hydrogen bonding akin to the situation in the metalloenzyme. The article by F. Meyer et al. on p. 4161ff reports the synthesis of an elaborate new ligand scaffold that is decorated with peripheral groups for H-bonding interactions and its speciation with nickel(II) in solution. The crystallographic structure of a dinickel(II) complex reveals a bridging HO···H···OH unit in the bimetallic cavity, which is involved in an extensive network of hydrogen bonds. Such systems might become useful for studying effects of the secondary coordination sphere in biomimetic substrate transformations.



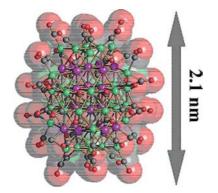
# **MICROREVIEW**

## **Molecular Nanoparticles**

S. Zacchini\* ...... 4125-4145

Using Metal Carbonyl Clusters To Develop a Molecular Approach towards Metal Nanoparticles

Keywords: Cluster compounds / Carbonyl ligands / Transition metals / Nanochemistry / Structure elucidation



High-nuclearity molecular metal carbonyl clusters (MCCs) are perfectly (atomically) monodisperse, ligand-stabilised metal nanoparticles with nanometric dimensions and perfectly defined structures and physical properties. Moreover, they may be used as building blocks to assemble functionalised molecular nanomaterials or as precursors of metal nanostructures.

# SHORT COMMUNICATIONS

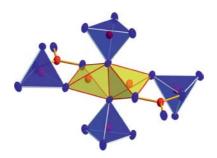
#### **High-Pressure Borates**

S. C. Neumair, S. Vanicek, R. Kaindl, D. M. Többens, C. Martineau, F. Taulelle, J. Senker, H. Huppertz\* ...... 4147-4152



HP-KB<sub>3</sub>O<sub>5</sub> Highlights the Structural Diversity of Borates: Corner-Sharing BO<sub>3</sub>/ BO<sub>4</sub> Groups in Combination with Edge-Sharing BO<sub>4</sub> Tetrahedra

Keywords: Borates / High-pressure chemistry / X-ray diffraction



The new potassium borate HP-KB<sub>3</sub>O<sub>5</sub> impressively illustrates the structural diversity in borates. HP-KB<sub>3</sub>O<sub>5</sub> is the first borate exhibiting all three possible conjunctions: corner-sharing BO3 groups, corner-sharing BO<sub>4</sub> units, as well as edge-sharing BO<sub>4</sub> tetrahedra.

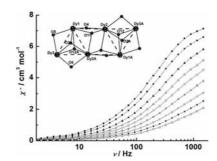
#### **Towards SMMs**

H. Ke, L. Zhao, Y. Guo, J. Tang\* ...... 4153-4156



A Dy<sub>6</sub> Cluster Displays Slow Magnetic Relaxation with an Edge-to-Edge Arrangement of Two Dy<sub>3</sub> Triangles

Keywords: Dysprosium / Cluster compounds / Magnetic properties / Slow magnetic relaxation



A novel Dy<sub>6</sub> cluster with two edge-to-edge Dy<sub>3</sub> triangles exhibits slow magnetization relaxation, thus enriching the structure correlation to magnetic properties of the Dy<sub>3</sub> triangle family.

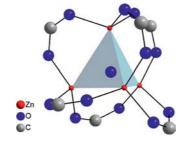
## **Carbon Dioxide Activation**

S. Schulz,\* S. Schmidt, D. Bläser, C. Wölper ...... 4157-4160

Direct Carboxylation of Zincocene Cp\*2Zn

Keywords: Zinc / CO2 activation / X-ray diffraction

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Zincocene activates CO2 with the formation of  $[Zn_4(\mu_4-O)(O_2CCp^*)_6]$  (1), whose structure is comparable to that of basic zinc acetate.



# **FULL PAPERS**

New pyrazolate-derived compartmental ligands have been developed that feature peripheral amido groups as potential H-

bonding sites. In a dinickel(II) complex these second sphere amido groups support an intramolecular HO···H-OH bridge within the bimetallic cavity through a network of hydrogen bonds.



## **Biomimetic Complexes**

T. Graef, J. Galezowska, S. Dechert, F. Mever\* ...... 4161-4167

Decorating the Second Coordination Sphere in Pyrazolate-Based Dinickel(II) Complexes with H-Bond Donors

Keywords: Bioinorganic chemistry / Dinuclear complexes / Nickel / N ligands / Hydrogen bonding / Potentiometric titration

# **Cu-Crosslinked Artificial Tripeptides**

J. A. Gallagher, L. A. Levine, M. E. Williams\* ...... 4168-4174

Anion Effects in Cu-Crosslinked Palindromic Artificial Tripeptides with Pendant Bpy Ligands

Keywords: Self-assembly / Molecular recognition / Copper / Anion effects

Metal-coordination-based self-assembly of artificial peptide duplexes is used to make multimetallic assemblies from a bipyridinesubstituted tripeptide by simultaneous addition of ligand-substituted aminoethylglycine monomers to both ends of a bpysubstituted diamine. The UV/Vis absorbance and EPR spectra reveal that the trimetallic CuII structures have aniondependent geometries and interactions between metal ions.

## **Water-Soluble Catalysts**

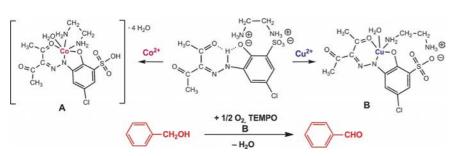
M. N. Kopylovich, K. T. Mahmudov, M. Haukka, P. J. Figiel, A. Mizar, J. A. L. da Silva,

A. J. L. Pombeiro\* ...... 4175-4181

Water-Soluble Cobalt(II) and Copper(II) Complexes of 3-(5-Chloro-2-hydroxy-3sulfophenylhydrazo)pentane-2,4-dione as Building Blocks for 3D Supramolecular Networks and Catalysts for TEMPO-Mediated Aerobic Oxidation of Benzylic Alcohols

Keywords: Cobalt / Copper / Supramolecular Network / Homogeneous catalysis / Water-soluble catalyst / Oxidation / Hydrogen bonds

**Doping of Carbon Nanotubes** 



Water-soluble cobalt(II) and zwitterionic copper(II) complexes have been synthesized, and the latter is catalytically active in

the TEMPO-mediated aerobic oxidation of benzylic alcohols in aqueous media.

H. Tantang,\* J. Xiao, J. Wei, M. B. E. Chan-Park, L.-J. Li,\* Q. Zhang\* ...... 4182-4186

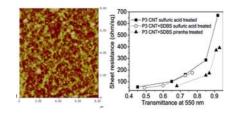
Low-Cost and Ultra-Strong p-Type Doping of Carbon Nanotube Films by a

Piranha Mixture

dopants. There are many dopants available; however, most of them are either not strong enough or involve high-cost chemicals. Herein we introduce low-cost and ultrastrong dopants for carbon nanotube conductive films.

One way to improve the conductivity of

carbon nanotube films is by introducing

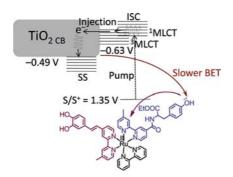


# **CONTENTS**

## **Charge Separation**

Interfacial Electron Transfer Dynamics of Two Newly Synthesized Catecholate Bound Ru<sup>II</sup> Polypyridyl-Based Sensitizers on TiO<sub>2</sub> Nanoparticle Surface — A Femtosecond Pump Probe Spectroscopic Study

**Keywords:** Ruthenium / Nanoparticles / Electron transfer / Electron-donating group / Time-resolved spectroscopy



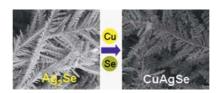
Sensitization of nanocrystalline TiO<sub>2</sub> with Ru<sup>II</sup>—polypyridyl complexes with secondary electron-donating groups (tyrosine and phenol) has been performed. After electron injection, the secondary electron-donating groups transfer the electron to oxidized Ru<sup>III</sup>, and the BET reaction slows down due to poor overlap between the injected electron and the hole localized in the electron-donating group.

#### **Metal Dendrites**

Y. Gao,\* Z. Zheng, Y. Tian, Y. Zhang, Y. Zhang .......4198-4203

Growth and Transformation Mechanism of Ternary CuAgSe Dendrites from Binary Ag<sub>2</sub>Se Dendrites

**Keywords:** Dendrimers / Nanoparticles / Copper / Silver / Selenium / Synthetic methods / Template synthesis



The new nano approach for the synthesis of CuAgSe dendrites at room temperature can be regarded as a successful chemical alternative to the recently developed electrochemical atomic layer epitaxy deposition technique for chalcogenides.

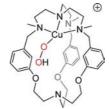
# **Biomimetic Complexes**

L. Chaloner, M. S. Askari, A. Kutteh, S. Schindler,

X. Ottenwaelder\* ...... 4204–4211

Formation and Reactivity of a Biomimetic Hydroperoxocopper(II) Cryptate

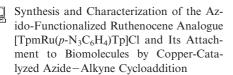
**Keywords:** Biomimetic complexes / Copper / Oxidation / Peroxides / Oxygen-atom transfer



The oxidation of a Cu<sup>II</sup> complex with a tren-based tetradentate coordinating cryptand is investigated. Reaction of the complex with basic hydrogen peroxide results in a net oxygen atom transfer to the ligand. Variable-temperature stopped-flow kinetic studies and mass spectrometry indicate the presence of an intermediate in the oxygenation process, which is identified as a Cu<sup>II</sup>-hydroperoxo species.

#### **Biocompatible Sandwich Complexes**

J. Zagermann, K. Klein, K. Merz, M. Molon, N. Metzler-Nolte\* ... 4212–4219



**Keywords:** Bioconjugates / Cycloaddition / Azides / Microwave synthesis / Peptides / Ruthenium / Scorpionates / Sandwich complexes



R = (CH<sub>2</sub>)<sub>2</sub>-CO-Val-OtBu, (CH<sub>2</sub>)<sub>2</sub>-CO-Tyr-Gly-Gly-Phe-Leu-OH

The scorpionate ligand  $p\text{-BrC}_6H_4\text{Tp}$  (Tp') is a precursor for the azido-functionalized mixed Tp sandwich compound [TpmRu(p-N<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Tp)] utilizing copper-catalyzed azidonation [Tpm: tris(pyrazolyl)methane;

Tp: tris(pyrazolyl)borate]. Further, the suitability of [TpmRu(p-N<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Tp)] in Cu-catalyzed azide—alkyne cycloaddition (Cu-AAC) is outlined by coupling to alkynyl-functionalized biomolecules.



#### **Guanidine Ligands**

The reaction between activated bicyclic tetramethylbisurea and 1,2-diaminobenzene or 1,2,4,5-tetraaminobenzene affords new aromatic compounds functionalized with bicyclic guanidino groups, which are used as chelating ligands in mononuclear and dinuclear Ni, Pd, and Pt complexes. Experiments with a Ni complex showed a moderate activity in olefin oligomerization yielding mostly  $C_6$  hydrocarbons.



U. Wild, E. Kaifer, H.-J. Himmel\* ...... 4220–4233

Redox Chemistry and Group 10 Metal Complexes of Aromatic Compounds with Bulky Bicyclic Guanidino Groups



**Keywords:** Redox chemistry / Nickel / Palladium / Platinum / Guanidine / Coordination compounds

## Zeolitic/Mesoporous Materials

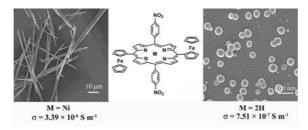
A trade-off needs to be made between pronounced zeolitic character and high mesoporosity due to the competition between zeolite and mesopore formation in a one-pot templating strategy.



New Insights in the Formation of Combined Zeolitic/Mesoporous Materials by using a One-Pot Templating Synthesis

**Keywords:** Zeolites / Mesoporous materials / Hydrothermal synthesis / Composites / One-pot templating synthesis

#### Nanostructures



A ferrocene-porphyrin deravitive and its nickel congener have been designed and synthesized, and their self-assembly properties have been investigated. The results of a comparative investigation reveal

the effect of the Ni-O metal-ligand coordination bond on molecular packing conformations, morphologies, and semiconductor properties of the self-assembled nanostructures.

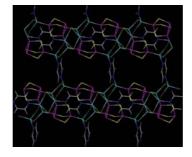
P. Zhu,\* P. Ma, Y. Wang, Q. Wang, X. Zhao,\* X. Zhang\* ........... 4241–4247

Organic Nanostructures with Controllable Morphology Fabricated from Ferrocene— Porphyrin Derivatives: Effect of Metal— Ligand Coordination on the Morphology, Dimensions, and Semiconductor Properties of Self-Assembled Nanostructures

**Keywords:** Porphyrinoids / Sandwich complexes / Nanostructures / Self-assembly / Semiconductors

# **Coordination Polymers**

The synthesis of hybrid polymers combining organic P,P' (dppe) or N,N' (pyz) ligands,  $P_4S_3$  and copper(I) halides (X=Cl,Br,I) is described. The dimensionality of the products is determined by the size and steric requirements of the organic ligands. These range from mononuclear [CuX-(PEt\_3)\_2(P\_4S\_3)] to 3D frameworks such as 3D-[(CuBr)\_3(P\_4S\_3)(pyz)].



 $P_4S_3$  and  $P_1P'$  or  $N_1N'$  Donors as Competitive Building Blocks in Copper(I) Coordination Polymers

**Keywords:** Coordination polymers / Copper / Phosphorus / Sulfur / N ligands

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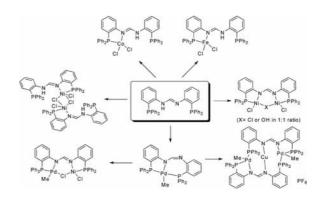
#### **Coordination Chemistry**

K.-s. Son, D. M. Pearson, S.-J. Jeon, R. M. Waymouth\* ...... 4256–4261



Synthesis and Structural Diversity of Mono-, Di- and Trinuclear Complexes with N,N'-Bis[(2-diphenylphosphanyl)phenyl]-formamidine

**Keywords:** Heterometallic complexes / Coordination chemistry / N,P ligands / Metal-metal interactions



A series of homo-/heterometallic mono-/multinuclear complexes of *N,N'*-bis[2-(diphenylphosphanyl)phenyl]formamidine was prepared and characterized. The effect of metal radii on the resulting complex

geometry was investigated, comparing homo- versus heterometallic dinuclea complexes. A butterfly structure around the central metal core was found in the mixed-metal trinuclear PdCuPd complex.

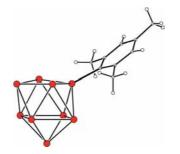
#### **Functionalized Zintl Ions**

C. B. Benda, J.-Q. Wang, B. Wahl, T. F. Fässler\* ...... 4262–4269



Syntheses and  $^{1}H$  NMR Spectra of Substituted Zintl Ions  $[Ge_{9}R_{n}]^{(4-n)-}$ : Crystal Structures of  $[Ge_{9}R]^{3-}$  (R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, CHCH<sub>2</sub>) and Indication of Tris-Vinylated Clusters

**Keywords:** Zintl anions / Cluster compounds / Germanium



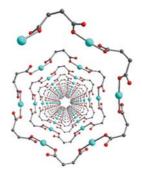
The mono-substituted  $[Ge_9R]^{3-}$  polyanions  $(R = Mes \text{ and } CHCH_2)$  were synthesized from  $[Ge_9]^{4-}$  solutions with  $Ag_4Mes_4$  and  $Me_3SiC\equiv CSiMe_3$ , respectively. <sup>1</sup>H NMR experiments confirm the crystal structures of both of the isolated crystals of the salts  $[K([2.2.2]\text{crypt})]_3[Ge_9Mes]$  and  $[K([18]\text{crown-6})]_2\{(\eta^5-C_5H_5)[K([18]\text{crown-6})]_2\}-[Ge_9(CHCH_2)]$  and hint for the tris-vinylated cluster  $[Ge_9(CHCH_2)_3]^-$ .

#### Coordination Networks of Nickel(II)

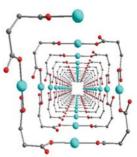
S. Das, S. Maloth, S. Pal\* ..... 4270-4276

Nickel(II) Coordination Polymers – 4,4′-Bipyridine-Connected Six- and Four-Fold Metal-Succinate Helices and Their Corresponding Chiral and Achiral Networks

**Keywords:** Coordination polymers / Nickel / Helical structures / Chirality / Solvothermal synthesis



The nickel(II) coordination polymers [Ni-(suc)(bipy)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>·2*n*H<sub>2</sub>O (1) and [Ni-(suc)(bipy)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>·*n*H<sub>2</sub>O (2) are reported. The nickel–succinate helices are right-handed sixfold in 1 and both right- and left-handed fourfold in 2. The guest water molecules are in intra- and interhelical chan-

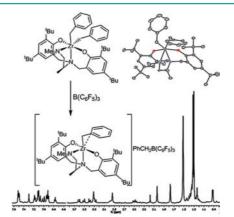


nels in 1 and 2, respectively. Hexagonally packed 4,4'-bipyridine-bridged homochiral sixfold helices produce a chiral 7<sup>5</sup>.9 network in 1, whereas 4,4'-bipyridine-bridged racemic fourfold helices generate an achiral 6<sup>5</sup>.8 network in 2.



# **Olefin Polymerization Catalysts**

Neutral and cationic titanium and zirconium complexes supported by chiral tripodal diamine bis(phenolate) ligands are described. Monocationic species with noncoordinated anions and  $\eta^2$ -benzyl binding were obtained upon  $B(C_6F_5)_3$  treatment of the dibenzyl complexes. The catalytic properties of the compounds as olefin polymerization catalysts were assessed.



Chiral Diamine Bis(phenolate)  $Ti^{IV}$  and  $Zr^{IV}$  Complexes – Synthesis, Structures and Reactivity



**Keywords:** Titanium / Zirconium / Chiral ligands / Polymerization

If not otherwise indicated in the article, papers in issue 26 were published online on September 6, 2011

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

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