



























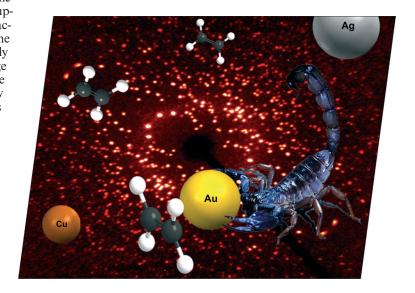




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic and Sweden) are Associates of the two journals.

## **COVER PICTURE**

The cover picture shows the formation of coinage metal (copper, silver, gold) complexes of ethylene supported by scorpionate ligands on an X-ray diffraction background (because the article focuses on the structurally characterized molecules). Thermally stable molecules containing bonds between coinage metal atoms and ethylene are still rare but have grown in number significantly over the last few years. Tris(pyrazolyl)borate (commonly known as scorpionate) ligands have played a major role in this chemistry. Indeed, they have served as the supporting ligands in the isolation of the first ethylene adduct of all three coinage metal ions. Most of the resulting complexes feature  $\kappa^3$ bonded scorpionate ligands, while a few others show rare  $\kappa^2$ -coordination (as depicted here, a gold atom held by a scorpion with the scorpion's tail up). Details are presented in the Microreview by H. V. R. Dias and J. Wu on p. 509ff. H. V. R. D. gratefully acknowledges the Robert A. Welch Foundation (grant Y-1289) for providing financial support for his research.



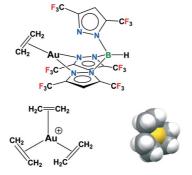
## **MICROREVIEW**

### Metal-Ethylene Complexes

H. V. R. Dias,\* J. Wu ...... 509-522

Structurally Characterized Coinage-Metal— Ethylene Complexes

**Keywords:** Ethylene / Crystallography / Gold / Silver / Copper



Thermally stable Cu<sup>I</sup>, Ag<sup>I</sup>, and Au<sup>I</sup> complexes of ethylene are limited and get increasingly sparse as one descends the group 11 triad towards gold. Recently, there have been some notable developments in this field, including the isolation of coinagemetal adducts with more than one ethylene molecule on a metal center. This article focuses on such adducts that have been synthesized and characterized by X-ray crystallography.

# **FULL PAPERS**

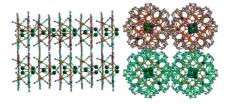
#### **Platinum-Salen Complexes**

X. Lü, W.-Y. Wong, W.-K. Wong\* ...... 523–528



Self-Assembly of Luminescent Platinum-Salen Schiff-Base Complexes

**Keywords:** Platinum / Schiff bases / Photoluminescence / Self assembly



The hydrogen-bonding interactions from two different solvate forms of the platinum(II) MeO-salen Schiff-base complex together with various coordination bonds were shown to induce the self-assembly of such transition-metal Schiff base systems and the formation of 3-D heterometallic structures

#### **Antitumour Platinum Complexes**

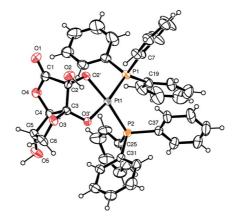
P. Bergamini,\* E. Marchesi, V. Bertolasi, M. Fogagnolo, L. Scarpantonio,

S. Manfredini, S. Vertuani,

A. Canella ...... 529-537

New Coordination Modes of L-Ascorbic Acid and Dehydro-L-ascorbic Acid as Dianionic Chelating Ligand for Platinum

**Keywords:** Ascorbic acid / Dehydroascorbic acid / Platinum / Antitumour agents / Drug delivery / Drug design

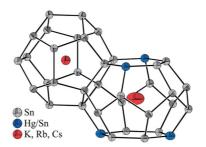


A variety of coordination modes of L-ascorbic acid as an anionic bidentate ligand to Pt<sup>II</sup> are described, including the new mode as a O5,O6-diolate chelating ligand. The first platinum complex containing dehydro-L-ascorbic acid and its X-ray crystal structure are reported. Its antiproliferative activity in vitro was found to be superior to cisplatin on both a cisplatin-sensitive and a cisplatin-resistant cell line.



#### **Hg-Substituted Clathrates**

The Hg-substituted type-I clathrates  $A_8Hg_4Sn_{42}$  (A=K,Rb or Cs) crystallize in the cubic space group  $Pm\bar{3}n$  and constitute diamagnetic, charge-balanced Zintl phases without homogeneity range. Differential thermal analyses show that the stability of the title compounds increases significantly with increasing size of the encaged alkalimetal atoms.



Α.	Kaltzoglou,	S. Ponou,	
T.	F. Fässler*	•••••	538 - 542

Synthesis and Crystal Structure of Mercury-Substituted Type-I Clathrates  $A_8Hg_4Sn_4~(A=K,\,Rb,\,Cs)$ 

**Keywords:** Clathrate / Differential thermal analysis / Mercury / Stannides / Crystal structure / Zintl phases

## **Group 13 Hydrazides**

Three different structural motifs were obtained by the reactions of methylhydrazine with the trimethyl compounds of aluminum, gallium, and indium: a simple adduct  $Me_3Ga \leftarrow N(H)(Me) - NH_2$ , a sesqui compound  $(Me_2Al)_3[\mu-NH-N(H)Me]_6Al$  together with its dissociated dinuclear form, and bicyclic compounds of the general composition  $(EMe_2)_4(HN-NMe)[N(H)-N(H)-Me)]_2$  (E=Ga,In).



W. Uhl,\* T. Abel, A. Hepp, S. Grimme, M. Steinmetz ...... 543-551

Different Reactivity Patterns in the Reactions of the Homologous Trimethylelement Compounds  $EMe_3$  (E = Al, Ga, In) with Methylhydrazine

**Keywords:** Aluminum / Gallium / Indium / Hydrazides / Heterocycles

### **Allenic Ligands**

$$R^1$$
,  $R^2$   $ML_n$   $R^2$   $ML_n$   $R^2$   $R^2$ 

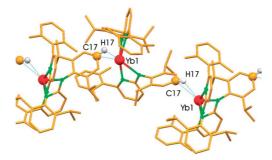
Allenic bipyridines are novel, axially chiral ligands for transition metal catalysis. They form 1:1- or 2:2 complexes with  $\mathrm{Cu}^+$  and

Ag<sup>+</sup> ions that were characterized in solution and in the solid state.

Synthesis and Complexation Properties of Allenic Bipyridines, a New Class of Axially Chiral Ligands for Transition Metal Catalysis

**Keywords:** Allenes / Axial chirality / Bipyridines / Catalysis / Transition metal complexes

#### **Agostic Interaction**



Strong intermolecular C<sub>Aryl</sub>-H agostic interactions have been observed for a sterically engineered Yb<sup>II</sup> amidopyridine complex. The compound could only be stabilized in a small steric and synthetic "win-

dow" because small variations of the ligand's bulkiness and the synthetic procedure result in a drastically different chemistry.

Small Steric Variations in Ligands with Large Synthetic and Structural Consequences

**Keywords:** Agostic interactions / Amidopyridine ligands / Aminopyridinato ligands / N ligands / Ytterbium

## **CONTENTS**

#### **Cu-Mediated Radical Additions**

W. T. Eckenhoff, S. T. Garrity, T. Pintauer\* ...... 563-571

Highly Efficient Copper-Mediated Atom-Transfer Radical Addition (ATRA) in the Presence of Reducing Agent

**Keywords:** Catalysis / Copper / ATRA / Reducing agent



The synthesis, characterization and exceptional activity of  $Cu^I(TPMA)Br$  and  $[Cu^{II}(TPMA)Br][Br]$  complexes in ATRA reactions of polybrominated compounds to alkenes in the presence of reducing agent (AIBN) was reported.

#### **Pd Pincer Catalysts**

A. M. Sheloumov,\* P. Tundo, F. M. Dolgushin, A. A. Koridze\* ...... 572-576

Suzuki Aryl Coupling Catalysed by Palladi-um Bis(phosphane) Pincer Complexes Based on Ferrocene; X-ray Structure Determination of  $\{PdCl[\{2,5-(tBuPCH)C_5H\}Fe(C_5H_5)]\}OTf$ 

**Keywords:** Metallocenes / Homogeneous catalysis / Phase-transfer catalysis / Cross-coupling reactions / X-ray diffraction

$$R' = R \cdot PR_{2}$$

$$Pd - Cl$$

$$Pd -$$

Palladium P,C,P pincer complexes 1-3 catalyse Suzuki aryl coupling under homogeneous conditions as well as in multiphase systems (triphase system: organic/Aliquat

336/aqueous solvent); the X-ray structure of complex 3, in which the iron atom is oxidised, has been determined and compared with that of its neutral precursor 2.

## Polymer-Anchored VIVO Complexes

M. R. Maurya,\* U. Kumar, I. Correia, P. Adão, J. Costa Pessoa ........... 577-587

A Polymer-Bound Oxidovanadium(IV) Complex Prepared from an L-Cysteine-Derived Ligand for the Oxidative Amination of Styrene

**Keywords:** Polymer-anchored vanadium complex / Heterogeneous catalysis / Oxidative amination of styrene / EPR spectroscopy

The oxidovanadium(IV) complex, PS-[VO-(sal-cys)·DMF], has been prepared from polystyrene-bound ligand PS-H<sub>2</sub>sal-cys, characterized, and used for the oxidative

amination of styrene, in mild basic conditions, with secondary amines (diethylamine, imidazole, and benzimidazole).

#### **Rhenium Perovskites**

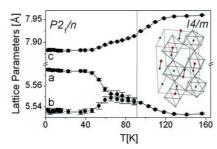
M. Retuerto,\* M. J. Martínez-Lope, M. García-Hernández,

M. T. Fernández-Díaz,

J. A. Alonso ...... 588-595

Crystal and Magnetic Structure of  $Sr_2MReO_6$  (M = Ni, Co, Zn) Double Perovskites: A Neutron Diffraction Study

**Keywords:** Perovskite phases / Rhenium / Neutron diffraction / Crystal structure / Magnetic structure / Antiferromagnetism

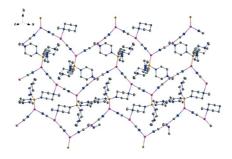


Sr<sub>2</sub>MReO<sub>6</sub> (M = Ni, Co, Zn) double perovskites were studied by neutron powder diffraction (NPD) analysis. The crystal structure at room temperature is tetragonal, but at low temperatures, Co and Zn oxides undergo structural transition to monoclinic symmetry. The magnetic structures of Sr<sub>2</sub>NiReO<sub>6</sub> and Sr<sub>2</sub>CoReO<sub>6</sub> display different arrangements of the Ni<sup>2+</sup> and Co<sup>2+</sup> spins.



## Carbon Coupling

The reactions of tris(4-methylpiperazin-1-yl)phosphane,  $P(NC_4H_8NMe)_3$  (1) with Group 10 and 11 metal derivatives are described. The formation and crystal structures of tetranuclear  $Cu_4X_4$  cubane-type complexes and a two-dimensional  $Ag^ICN$  polymeric sheet are reported. The catalytic utility of 1 in Suzuki cross coupling reactions of aryl bromides with phenylboronic acid is also described.

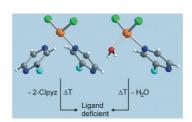


C. Ganesamoorthy, J. T. Mague, M. S. Balakrishna\* ...... 596-604

Tris(4-methylpiperazin-1-yl)phosphane, P- $(NC_4H_8NMe)_3$ : Synthesis, Structural Studies, Group 10 and 11 Metal Complexes and Catalytic Investigations

**Keywords:** Phosphanes / Group 10 and 11 metal complexes / Cubane-like structure / Homogeneous catalysis / C-C coupling

Five new zinc(II) halide coordination compounds with 2-chloroprazine as ligand were prepared and were structurally characterized and investigated for their thermal reactivity. It is shown that the same ligand-deficient intermediates are independently prepared if the pure 2-chloropyrazine complexes or the mixed 2-chloropyrazine/water complexes are decomposed.



### Thermal Behavior of Zn Complexes

G. Bhosekar, I. Jeß, N. Lehnert, C. Näther\* ...... 605-611

Synthesis, Crystal Structure and Thermal Reactivity of [ZnX(2-chloropyrazine)] (X = Cl, Br, I) Coordination Compounds

**Keywords:** Coordination compounds / Synthesis / Crystal structure / Thermal reactivity / Zinc / Halides

DFT calculations have been carried out to investigate the in vacuo structures of six different Cu(3-Clip-Phen) complexes. It has been found that the length of the bridge connecting the two phenanthroline ligands is crucial for the consequent copper geometry. In addition, the cleavage ability of these complexes is associated with their coordination environment.

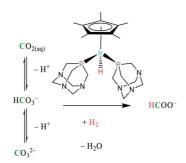


## **Computational Study of Nucleases**

Influence of the Copper Coordination Geometry on the DNA Cleavage Activity of Clip-Phen Complexes Studied by DFT

**Keywords:** 3-Clip-Phen / DNA cleavage / Design / DFT / Reorganization energy

The new compounds, [Cp\*Ir(PTA)Cl<sub>2</sub>] (1) and [Cp\*Ir(PTA)<sub>2</sub>Cl]Cl (2), have been synthesised and characterised in solution and the solid state. Complex 2 operates as a pre-catalyst in the hydrogenation of hydrogen carbonate in aqueous solution, the catalytically active [Cp\*Ir(PTA)<sub>2</sub>H]<sup>+</sup> has been identified.



#### **Iridium-Catalysed CO<sub>2</sub> Reduction**

M. Erlandsson, V. R. Landaeta, L. Gonsalvi,\* M. Peruzzini, A. D. Phillips, P. J. Dyson, G. Laurenczy\* ....... 620-627

(Pentamethylcyclopentadienyl)iridium-PTA (PTA = 1,3,5-Triaza-7-phosphaadamantane) Complexes and Their Application in Catalytic Water Phase Carbon Dioxide Hydrogenation

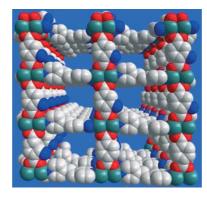
**Keywords:** Reduction / Iridium(III) complexes / Water-soluble ligands / Hydrogenation / Catalysis

# **CONTENTS**

### **Crystal Engineering**

From Interwoven to Noninterpenetration: Crystal Structural Motifs of Two New Manganese-Organic Frameworks Mediated by the Substituted Group of the Bridging Ligand

**Keywords:** Supramolecular frameworks / Crystal engineering / Manganese / Bimetallic units



The syntheses and structures of two novel manganese—organic compounds, [Mn(2-atp)(bipy-eta)<sub>0.5</sub>]<sub>n</sub> and {[Mn(tp)(bipy-eta)<sub>1.5</sub>]·  $2H_2O$ }<sub>n</sub>, are described. The experimental results indicate that variations in the molecular self-assembly are influenced by the substituted group in the bridging ligands.

# **CORRECTION**

M. Jakonen, P. Hirva, T. Nivajärvi, M. Kallinen, M. Haukka\* ...... 635 Surface-Assisted Synthesis and Behavior of Dimetallic Mixed-Metal Complexes  $[M_2Cl_2(\mu\text{-}Cl)_4(CO)_6M'(L)_2]$  (M = Ru, Os; M' = Fe, Co; L =  $CH_3CH_2OH$ ,  $H_2O$ )

**Keywords:** Ruthenium / Osmium / Cobalt / Iron / Synthesis design

If not otherwise indicated in the article, papers in issue 3 were published online on January 15, 2008