



























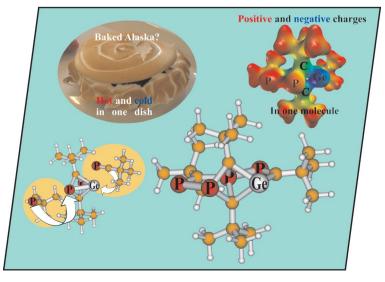




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

# **COVER PICTURE**

The cover picture shows the zwitterionic cage  $GeP_4C_4(tBu)_4$  (bottom right) with separated positive (red) and negative (blue) charges (see the electrostatic potential map, top right). The compound forms in a smooth reaction from the neutral  $\eta^4$ -Ge complex and two *t*BuCP phosphaalkynes (bottom left). Details are discussed in the article by M. D. Francis et al. on p. 1761ff.



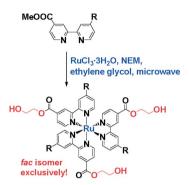
## SHORT COMMUNICATIONS

#### **Stereocontrol in Coordination**

A. Grabulosa, M. Beley, P. C. Gros\* ...... 1747–1751

Remarkable Effect of 4-Substituted 2,2'-Bipyridine Ligands on the Stereochemistry of Ruthenium(II) Complexes

**Keywords:** Unsymmetrical bipyridines / Ruthenium / Stereocontrol / *trans* influence / Solvent effects

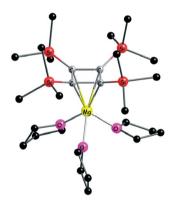


[RuL<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> complexes containing 4-alk-oxycarbonyl-substituted unsymmetrical bipyridine ligands (L) have been obtained exclusively as the *fac* isomers by simple reaction of L with ruthenium(III) chloride in ethylene glycol under microwave irradiation.

#### **6π-Electron Aromatics**

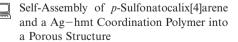
Tetrakis(trimethylsilyl)cyclobutadiene Dianion Alkaline Earth Metal Salts: New Members of the  $6\pi$ -Electron Aromatics Family

**Keywords:** Calcium / Cyclobutadiene dianion / Magnesium / Silicon / Solid-state structures

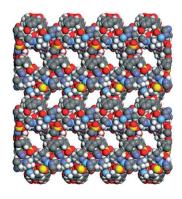


The magnesium and calcium salts of the tetrakis(trimethylsilyl)cyclobutadiene dianion,  $[Mg(thf)_3]^{2+}[(Me_3Si)_4C_4]^{2-}$  and  $[Ca(thf)_n]^{2+}[(Me_3Si)_4C_4]^{2-}$ , were synthesized by the reduction of tetrakis(trimethylsilyl)cyclobutadiene with metallic magnesium or calcium, respectively. X-ray analysis of the magnesium salt shows a planar four-membered ring, featuring a diagnostic  $\eta^4$ -coordination to the magnesium atom.

## p-Sulfonatocalix[4]arene



**Keywords:** Supramolecular chemistry / *p*-Sulfonatocalix[4]arene / Silver / Coordination polymers / Porous structures



A novel porous material constructed from *p*-sulfonatocalix[4]arene molecules and a Ag<sup>I</sup> coordination polymer has been structurally characterized. It is sustained by metal—ligand bonding, hydrogen bonding and host—guest interactions.



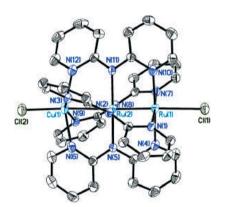
## **FULL PAPERS**

$$tBu \qquad P \equiv C - tBu \qquad tB$$

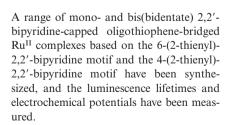
The zwitterionic cage compounds 7 and 8 have been synthesized from group-14 1,3-

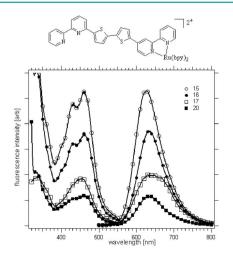
diphosphacyclobutadienyl complexes and tBuCP.

The nonplanar dipyridylamide ligand is widely used to stabilize homonuclear strings made of three  $M^{\rm II}$  atoms in  $M_3({\rm dpa})_4L_2$  complexes. Heterometallic frameworks such as  ${\rm Co^{II}Pd^{II}Co^{II}(dpa)_4Cl_2}$  can also be obtained. The metal strings presented here are heterometallic, nonsymmetric and mixed-valent, and a  $[Ru_2]^{5+}$  moiety was coupled with a  $Cu^+$  or  $Ni^+$  atom.



We report the synthesis, structural characterisation and magnetic studies of hexanuclear heterometallic M<sub>2</sub>Cr<sub>4</sub>, in which the coordination hole is selective for Sr and Pb ions, and trinuclear CaCr<sub>2</sub> clusters constructed from identical dinuclear chromium(III) complexes creating a "tetradentate compartmental ligand".





## **Organophosphorus Cage Compounds**

M. D. Francis,\* P. B. Hitchcock, J. F. Nixon, L. Nyulászi ....... 1761–1766

Reactivity of  $[M(\eta^4-P_2C_2tBu_2)]$  (M = Ge, Sn) with *tert*-Butylphosphaethyne, P=CtBu: Synthesis, Structural Characterisation and Computational Studies of the Novel Zwitterionic Organophosphorus Cage Compounds  $[MP_4C_4tBu_4]$  (M = Ge, Sn)

**Keywords:** Cage compounds / Phosphorus / Tin / Germanium / NMR spectroscopy / DFT calculations / Zwitterion

## **Heterometal String Complexes**

G.-C. Huang, M. Bénard,\* M.-M. Rohmer, L.-A. Li, M.-J. Chiu, C.-Y. Yeh, G.-H. Lee, S.-M. Peng\* ....... 1767–1777

Ru<sub>2</sub>M(dpa)<sub>4</sub>Cl<sub>2</sub> (M = Cu, Ni): Synthesis, Characterization, and Theoretical Analysis of Asymmetric Heterometal String Complexes of the Dipyridylamide Family

**Keywords:** Molecular wires / Mixed-metal complexes / Metal-metal interactions / Magnetic properties / Electrochemistry / Density functional calculations

#### **Heterometallic Cluster Chemistry**

Gh. Novitchi,\* V. Ciornea, S. Shova, A. Gulea, J.-P. Costes,

A. K. Powell\* ...... 1778–1783

Heterometallic  $M_2Cr_4$  ( $M^{II} = Sr$ , Pb) Clusters Assembled by  $Tris(\mu$ -aqua) Bridges

**Keywords:** Chromium / N,O Ligands / Heterometallic compounds / Magnetic properties

**Photophysics** 

R. O. Steen, L. J. Nurkkala,

S. J. Angus-Dunne, C. X. Schmitt,

E. C. Constable, M. J. Riley,

P. V. Bernhardt,

S. J. Dunne\* ...... 1784-1794

The Role of Isomeric Effects on the Luminescence Lifetimes and Electrochemistry of Oligothienyl-Bridged Dinuclear Tris(2,2'-bipyridine)ruthenium(II) Complexes

**Keywords:** Luminescence / N ligands / Ruthenium / Cyclic voltammetry / Ligand design

# **CONTENTS**

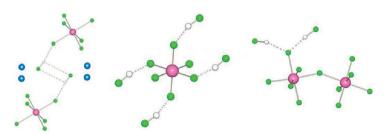
## **Ternary Fluorochromates**

Z. Mazej,\* E. Goreshnik ...... 1795-1812



Alkali Metal (Li<sup>+</sup>-Cs<sup>+</sup>) Salts with Hexafluorochromate(V), Hexafluorochromate(IV), Pentafluorochromate(IV), and Undecafluorodichromate(IV) Anions

**Keywords:** Chromium / Alkali metals / Fluorides / Crystal structures / Hydrogen fluoride



The fluorochromates  $ACrF_6$  (A = Li-Cs),  $ACrF_5$  (A = K-Cs),  $Li_2CrF_6$ ,  $A_2CrF_6$ 2HF (A = Na, K),  $A_2CrF_6$ 4HF (A = Rb, Cs),

and K<sub>3</sub>Cr<sub>2</sub>F<sub>11</sub>·2HF were prepared and characterized by single-crystal X-ray diffraction and Raman spectroscopy.

## **Strain-Suppressed Transitions**

A. Selmi, G. Corbel, S. Kojikian,

V. Voronkova, E. Kharitonova,

P. Lacorre\* ...... 1813-1821



Complex Effect of Partial Substitution of  $La^{3+}$  by  $Ca^{2+}$  on the Stability of Fast Oxide-Ion Conductor  $La_2Mo_2O_9$ 

**Keywords:** Ceramics / Phase transitions / Reversible demixing / Metastability / Temperature-controlled X-ray diffraction

4 mol-% Ca LAMOX	α phase/β phase/demixing/β phase
Ground Powder (G.P.)	heating up
G.P. annealed at 1200°C	heating up
G.P. pellet annealed at 1200°C	heating up

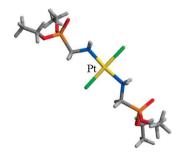
In Ca-substituted LAMOX fast oxide-ion conductors, a succession of phase transformations involving metastability and demixing/recombination phenomena has been observed and studied in powder, ceramic and single-crystal samples. These phenomena are shown to depend upon chemical composition, sample shaping and thermal history.

#### Platinum-Based MMP Inhibitors

D. Cornacchia, L. Cerasino, C. Pacifico, G. Natile\* ...... 1822–1829

Platinum(II) Complexes with the Diethyl Aminomethylphosphonate Ligand (amp): Characterization, Properties, and Unusual Solution Behavior

**Keywords:** Platinum / Diethyl aminomethylphosphonate / Antitumor agents / MMP inhibitors / Crystal structure



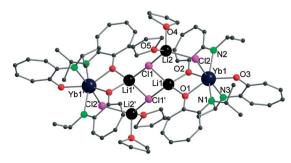
After the discovery that a platinum(II) complex with diethyl [(methylsulfinyl)-methyl]phosphonate ligand can inhibit matrix metalloproteinases (MMPs), which play a key role in the progress of metastasizing tumors, the investigation has been extended to complexes with another phosphonate ligand: diethyl aminomethylphosphonate.

#### **Lanthanide Complexes**

N. Meyer, R. Rüttinger, P. W. Roesky\* ...... 1830–1833

Lithium and Ytterbium Aminotroponate Complexes

**Keywords:** Lithium / N ligands / O ligands / Rare earths / Ytterbium

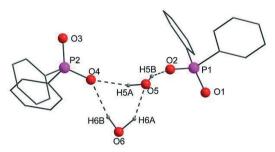


The hexameric lithium 2-(isopropylamino)-troponate complex [(*i*PrAT)Li]<sub>6</sub> and the dimeric ytterbium complex [(*i*PrAT)<sub>3</sub>-Li<sub>2</sub>Cl<sub>2</sub>Yb]<sub>2</sub>, in which the two [(*i*PrAT)<sub>3</sub>Yb]

subunits are bridged by four LiCl units, were prepared and structurally characterized.



## **Molecular Zinc Phosphates**



Reactions of zinc acetate with organic phosphates and phosphinic acids have been investigated in the presence of 1,10-phenanthroline and found to yield structurally diverse compounds. The presence of an uncoordinated P=O moiety in one of the complexes leads to the formation of water dimer aggregates.

Structural Diversity in Zinc Phosphates and Phosphinates: Observation of a Lattice Water Dimer Sandwiched Between Phosphoryl Oxygen Atoms

**Keywords:** Molecular phosphates / Zinc phosphinates / Polymers / Water clusters / X-ray diffraction

## **NLO Polymers**

Two second-order NLO complexes containing  $\mathrm{Cu^{II}}$  and  $\mathrm{Pd^{II}}$  were prepared and grafted onto poly(4-vinylpyridine). The values of  $\mu\beta$  range from (620 to 1600)  $\times$  10<sup>-48</sup> esu; a  $d_{33}$  value of 12–21 pm/V at 1500 nm and of 93–167 pm/V at 1064 nm (resonant) were measured for the grafted polymers. A maximum loss of 30% initial nonlinear response was found during thermal treatment at 80 °C.

$$R = C$$
 $N = N$ 
 $O-M-O$ 
 $N$ 
 $CH-CH_{2x} = CH-CH_{2y}$ 
 $M: Cu, Pd = R: O_{2}N$ 

Large Second-Order NLO Activity in Poly(4-vinylpyridine) Grafted with  $Pd^{II}$  and  $Cu^{II}$  Chromophoric Complexes with Tridentate Bent Ligands Containing Heterocycles

**Keywords:** Nonlinear optics / Polymers / Tridentate ligands / Copper / Palladium

Reactions of pyridyl side chain functionalized indenes with Ru<sub>3</sub>(CO)<sub>12</sub> gave a series of metal complexes with different bonding modes of the indenyl ligand.

# **Indenyl Ligand Coordination Modes**

D. Chen, S. Xu, H. Song, B. Wang\* ...... 1854–1864

Reactions of Pyridyl Side Chain Functionalized Indenes with  $Ru_3(CO)_{12}$ 

**Keywords:** Ruthenium / Carbonyl ligands / C-H activation / Coordination modes / Arene ligands / Cluster compounds

## A Manganese-Cluster-Based Polymer

C.-B. Ma, C.-N. Chen, Q.-T. Liu,\* D.-Z. Liao, L.-C. Li .............. 1865–1870

Synthesis and Characterization of a Ladder-Like Coordination Polymer Composed of Trimanganese Clusters Formed and Linked by Isophthalato Ligands

**Keywords:** Coordination polymers / Manganese / Isophthalic acid / Magnetic properties / Structure elucidation

A new isophthalatomanganese(II) coordination polymer has been prepared and characterized by single-crystal X-ray diffraction and magnetic measurements. It contains unprecedented isophthalato-

bridged trimanganese cluster building units linked by isophthalato ligands in a newly observed binding mode, forming a one-dimensional, ladder-like network. The polymer is antiferromagnetic.

# **CONTENTS**

#### Fe and Co Polymerization Catalysts

J. Cámpora,\* A. M. Naz, P. Palma, A. Rodríguez-Delgado, E. Álvarez, I. Tritto, L. Boggioni .................................. 1871–1879

Iron and Cobalt Complexes of 4-Alkyl-2,6diiminopyridine Ligands: Synthesis and Ethylene Polymerization Catalysis

**Keywords:** Iron / Cobalt / Diiminopyridine ligands / Ethylene Polymerization / Self-immobilization

$$R = Fe, Co$$

$$R = Ph, CH = CH_2,$$

$$CH_2 = CH_2$$

$$M = Fe, Co$$

$$R = Ph, CH = CH_2,$$

$$CMe_2Ph$$

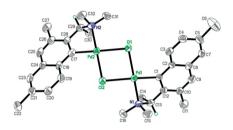
$$Polyethylene$$

Iron and cobalt diiminopyridine complexes displaying alkyl substituents at the central heterocyclic ring were synthesized and characterized. The alkyl substituent does not perturb their catalytic performance in the polymerization of ethylene, but the presence of a pending allyl group ( $R = CH = CH_2$ ) leads to a substantial increase in the polymer molecular weights.

## Palladacycle as Chiral Template

Design, Synthesis, and Stereochemical Evaluation of a Novel Chiral Amine—Palladacycle

**Keywords:** Asymmetric synthesis / Palladacycles / Chiral resolution / Cycloaddition / X-ray diffraction



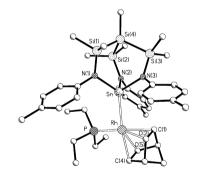
A novel chiral palladacycle was synthesized. The racemic cyclopalladated complex could be efficiently resolved through the formation of its (S)-prolinato and (S)-alaninato derivatives. With the use of the palladacycle as the chiral template, the stereoselectivity of the Diels—Alder cycloaddition between dmpp and ethyl vinyl ketone significantly improves.

## **Rh-Sn Complexes**

M. Kilian, H. Wadepohl, L. H. Gade\* ...... 1892-1900

Synthesis and Structural Characterization of New Rhodium-Tin Heterodimetallic Complexes

**Keywords:** Rhodium / Tin / Triamidostannates / Heterodimetallic complexes

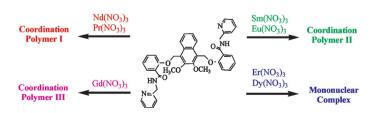


Large cone angles and strong bonding to transition metals make triamidostannates suitable ancillary ligands for transition metals as shown in the synthesis of a series of 16- and 18-electron rhodium(I) complexes.

#### **Luminescent Ln Complexes**

Structure Variation and Luminescence Properties of Lanthanide Complexes Incorporating a Naphthalene-Derived Chromophore Featuring Salicylamide Pendant Arms

**Keywords:** Lanthanide coordination polymers / Salicylamide /  $\pi-\pi$  Stacking / Hydrogen bonds / Luminescence properties



This work not only demonstrates that the supramolecular structure of lanthanide complexes with a naphthalene-derived chromophore, featuring salicylamide pendant arms, can be tuned by the nature of metal ions, but also offers interesting perspectives for the development of efficient luminescent stains.



## **Chelate Vinyl Complexes**

$$P = P(OEt)_3; R = Ph, Me$$

$$P = P(OEt)_4; R = Ph, Me$$

$$P = P(OEt)_4; R = Ph, Me$$

The preparation of vinyl chelate complexes  $[M\{\eta^2\text{-}C(=CH_2)\text{CPh}(R)\text{OH}(M-O)\}$ - $P_4]\text{BPh}_4$  (M = Ru, Os) and  $[Os\{\eta^2\text{-}CH=C(H)\text{CPh}(R)\text{OH}(Os-O)\}P_4]\text{BPh}_4$  [P =  $P(OEt)_3$ ; R = Ph, Me] and their reactivity

with terminal alkynes  $R^1C \equiv CH$ , which yields enynyl derivatives  $[Ru(\eta^3 - R^1C_3 - CHR^1)P_4]BPh_4$  are reported. The preparation of the allenylidene complex  $[Os(=C=C=CPh_2)P_5](BPh_4)_2$  is described.

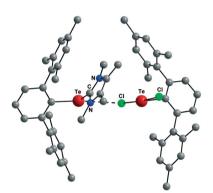
G. Albertin,\* S. Antoniutti, A. Bacchi, G. Pelizzi, G. Zanardo .......... 1913–1920

Reactions of Hydride Complexes of Ruthenium and Osmium with Propargylic Alcohols: Preparation of Chelate Vinyl Derivatives

**Keywords:** Hydrides / Alkene ligands / Alcohols / Ruthenium / Osmium / Vinyl complexes

#### **Aryltellurenyl Cation**

The syntheses and molecular structures of  $[2,6\text{-Mes}_2C_6H_3\text{Te}(CR'_2)]^+$   $(2,6\text{-Mes}_2C_6H_3$ . TeCl<sub>2</sub>)<sup>-</sup> (4) and  $[2,6\text{-Mes}_2C_6H_3\text{Te}(CR'_2)]^+$  I<sup>-</sup> (6) are reported. These compounds are rare examples of a well-defined  $\sigma$ -donor-stabilized aryltellurenyl cation (CR'<sub>2</sub> = 1,3,4,5-tetramethylimidazol-2-ylidene).



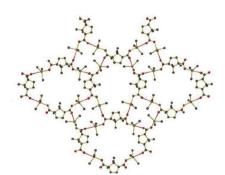
J. Beckmann,\* P. Finke, S. Heitz, M. Hesse ...... 1921–1925

Aryltellurenyl Cation [RTe(CR'<sub>2</sub>)]<sup>+</sup> Stabilized by an N-Heterocyclic Carbene

**Keywords:** Tellurium / Halides / Carbenes / Cations

## **Chiral Camphoric Acid**

A series of chiral triorganotin complexes based on chiral (+)-(1R,3S)-camphoric acid and *meso-cis*-4-cyclohexene-1,2-dicarboxylic acid ligands have been synthesized. Both the spectra and crystal structures show that when (+)-(1R,3S)-camphoric acid and *meso-cis*-4-cyclohexene-1,2-dicarboxylic acid react with triorganotin compounds they can form dinuclear, 1D polymeric chain, and 2D network polymers with metal—organic structures.



C. Ma,\* Q. Wang, R. Zhang ...... 1926–1934

Self-Assembly of Triorganotin Complexes: Syntheses, Characterization, and Crystal Structures of Dinuclear, 1D Polymeric Chain, and 2D Network Polymers Containing Chiral (+)-(1*R*,3*S*)-Camphoric Acid and *meso-cis*-4-Cyclohexene-1,2-dicarboxylic Acid Ligands

**Keywords:** Triorganotin complexes / Chiral camphoric acid / *meso-cis-*4-Cyclohexene-1,2-dicarboxylic acid

If not otherwise indicated in the article, papers in issue 10 were published online on March 18, 2008