## **CONTENTS**



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.

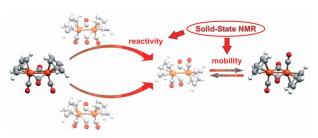
# **COVER PICTURE**

The cover picture shows the logo of the centenary year of the Società Chimica Italiana (SCI) superimposed on the view of the bay of Naples from Sorrento, where the SCI XXIII National Congress celebrating this anniversary will take place. The Società Chimica Italiana was one of the first to amalgamate its journal, Gazzetta Chimica Italiana, with those of other European Chemical Societies to form the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry with the far-sighted vision to create out of the national journals a high-quality international forum for the dissemination of research in chemistry in the broadest sense. The conglomerate of European Chemical Societies, now called Chem-PubSoc Europe, publishes a family of highquality journals based wherever possible on previously existing journals. Thus ChemPubSoc Europe has turned two other journals previously owned by the Società Chimica Italiana into the highly successful ChemMedChem (formerly Il Farmaco) and ChemSusChem (Annali di Chimica).





# **MICROREVIEW**



The key question of the influence of the mobility on the solid-state reactivity is the occasion for presenting several selected examples of dynamics and reactivity of transition metal complexes as seen by advanced solid-state NMR techniques.

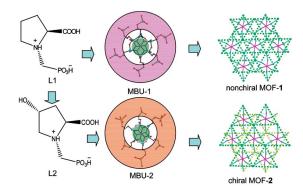
#### Solid-State NMR

M. R. Chierotti, R. Gobetto\* ... 2581-2597

Solid-State NMR Investigation of Ligand Mobility and Reactivity in Transition Metal Complexes

**Keywords:** Solid-state NMR / Solid-state mobility / Solid-state reactivity / Transition metal complexes / Ligand fluxionality / Solid-solid reactions / Solid-gas reactions

# SHORT COMMUNICATION



By introducing an additional chiral site into the original ligand (H<sub>3</sub>L1), we achieved the transformation of a MOF

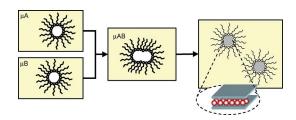
from a nonchiral to a chiral structure, which provides a new strategy for designing chiral compounds.

#### Chiral Metal-Organic Frameworks

A Chiral Metal-Organic Framework Based on Heptanuclear Zinc Cores

**Keywords:** Chirality / Metal—organic frameworks / Cluster compounds / Molecular building units

# **FULL PAPERS**



MgAl, NiAl and ZnAl hydrotalcite-like compounds (HTlcs) were prepared as colloidal dispersions of nanoparticles using water-in-oil microemulsions. Nanoparticle sizes and shapes were examined by transmission electron microscopy and atomic force microscopy. HTlc nanocrystals recovered from the reaction medium were characterized with chemical and thermogravimetric analyses, X-ray powder diffraction, BET surface analysis and porosity and scanning electron microscopy.

## Hydrotalcite-Like Nanoparticles

F. Bellezza, A. Cipiciani,\* U. Costantino, M. Nocchetti, T. Posati ........ 2603–2611

Hydrotalcite-Like Nanocrystals from Waterin-Oil Microemulsions

**Keywords:** Microreactors / Micelles / Nanostructures / Layered compounds / Hydrotalcite-like compounds

# **CONTENTS**

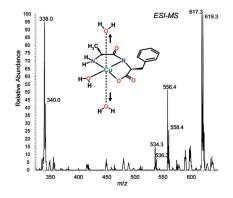
### Copper(II)—Dipeptide Systems

G. Maccarrone,\* R. Caruso, A. Contino, A. Giuffrida, M. Messina,

V. Cucinotta ...... 2612-2620

The Contribution of Electrospray Mass Spectrometry to the Study of Metal Complexes: The Case of Copper(II)—Dipeptide Systems

**Keywords:** Copper / Coordination modes / Mass spectrometry / Peptides / UV/Vis spectroscopy



By investigating the copper(II) complexes of a series of dipeptides it was ascertained that the in-plane coordinated water molecule was not removed in ESI-MS experiments.

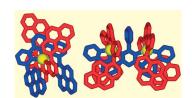
### **Metallosupramolecular Chemistry**

M. Barboiu,\* Y.-M. Legrand, L. Prodi,\* M. Montalti, N. Zaccheroni, G. Vaughan, A. van der Lee, E. Petit,

J.-M. Lehn\* ...... 2621-2628

Modulation of Photochemical Properties in Ion-Controlled Multicomponent Dynamic Devices

**Keywords:** Fluorescence / Molecular devices / Structural switching / Metallosupramolecular complexes / Terpyridine / Zinc



The pyrene-terpyridine-pyrene-based receptor 1 converts from a W to a U shape upon ion-metal cation complexation. The U form of 1 is capable of substrate binding through insertion between the lateral donor-pyrene arms of acceptor-terpyridine-type systems, with the participation of the metal ions, simultaneously coordinating the binding units of such multicomponent dynamic devices.

#### **Mixed-Valent Co Complexes**

L. Mechi, P. Siega, R. Dreos,\*

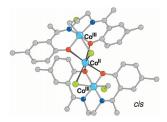
E. Zangrando,

L. Randaccio\* ...... 2629-2638

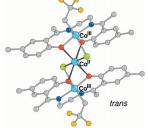


Crystal Structures and Solution Behavior of Paramagnetic, Trinuclear, Mixed-Valent Cobalt Complexes with Salen-Type Ligands

**Keywords:** Mixed-valent compounds / Cobalt / N,O ligands / Solid-state structures / NMR spectroscopy



Three new trinuclear mixed-valent cobalt complexes, which show different configurations (*cis* or *trans*) in the solid state, have been synthesized and fully characterized.



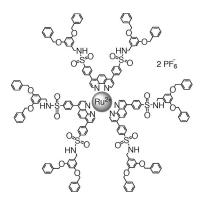
The isotropically shifted <sup>1</sup>H NMR spectra show that both the *cis* and *trans* isomers are present in solution, with interconversion being slow on the NMR time-scale.

#### Luminescent Dendrimers

U. Hahn,\* F. Vögtle,\* G. De Paoli, M. Staffilani, L. De Cola\* .... 2639–2646

Long-Lived Luminescent Dendrimers with a [Ru(dpp)<sub>3</sub>]<sup>2+</sup>-Type Core: Synthesis and Photophysical Properties

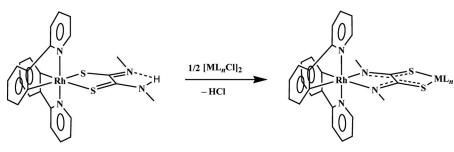
**Keywords:** Dendrimers / Dioxygen quenching / Luminescence / N ligands / Ruthenium



Four metallodendrimers with a photoactive luminescent [Ru(dpp)<sub>3</sub>]<sup>2+</sup>-type core were prepared. The photophysical characterisation revealed a dendritic effect on the excited-state lifetimes, which were found to increase with growing size of the surrounding dendritic shell.



### **Multitopological Ligands**



The metalloligand [Rh(2-phenylpyridine)<sub>2</sub>- $\{H(isoamyl)_2C_2N_2S_2 \ \kappa$ -S,S-Rh $\}$ ] changes the coordination mode of the binucleating

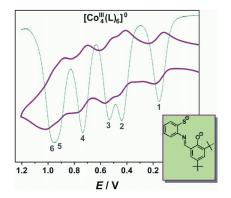
dithiooxamide when linked to a soft metal fragment  $ML_n$  [ $ML_n = Rh(cod)$ ,  $Pd(\eta^3-allyl)$ , PdCl(n-propylphosphane)].

Metalloligands: Rhodium(III) Cyclometallated Compounds Containing Multitopological Binucleating Ligands

**Keywords:** Rhodium / Metalloligands / Heterometallic complexes / Coordination modes / NMR spectroscopy

### **Ligand Radicals**

Polynuclear complexes of Cu, Pd, Pt, and Co were prepared by using a N,O,S-donor Schiff base ligand, 2-[(*E*)-2-mercaptophenylimino]methyl-4,6-di-*tert*-butylphenolate. The tetrameric Co and Pd complexes show multiple reversible redox processes. The oxidation was found to be ligand-based, leading to compounds with coordinated phenoxyl radical ligands.

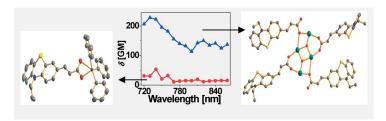


N. Roy, S. Sproules, E. Bothe, T. Weyhermüller, K. Wieghardt\* ...... 2655–2663

Polynuclear Complexes Containing the Redox Noninnocent Schiff Base Ligand 2-[(*E*)-2-Mercaptophenylimino]methyl-4,6-di-*tert*-butylphenolate(2-)

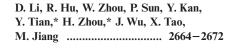
**Keywords:** Schiff bases / Polynuclear complexes / Electrochemistry / Radicals / Density functional calculations

#### **Organostannoxanes**



(*E*)-3-(10-ethylphenothiazine-3-yl)acrylic acid (LCOOH) and two organostannoxanes have been synthesized and fully characterized. Their structures were solved

by single-crystal X-ray diffraction determination. The two-photon absorption properties of the compounds are much more enhanced than that of LCOOH.

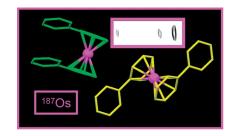


Synthesis, Structures, and Photophysical Properties of Two Organostannoxanes from a Novel Acrylic Acid Derived from Phenothiazine

**Keywords:** Tin / Photophysics / Structure—activity relationship / Charge transfer

## **Sandwich Complexes**

The osmium biphenyl sandwich complex has both staggered and eclipsed configurations in its X-ray crystal structure, in contrast to the ruthenium complex. The use of inverse heteronuclear multiple bond correlation spectroscopy allows facile observation of the <sup>187</sup>Os resonance despite the extreme insensitivity of <sup>187</sup>Os to NMR spectroscopic detection by normal methods.



J. C. Gray, A. Pagelot, A. Collins, F. P. A. Fabbiani, S. Parsons, P. J. Sadler\* ...... 2673–2677

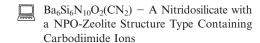
Organometallic Osmium(II) and Ruthenium(II) Biphenyl Sandwich Complexes: X-ray Crystal Structures and <sup>187</sup>Os NMR Spectroscopic Studies in Solution

**Keywords:** Osmium / Ruthenium / Sandwich complexes / Arenes / NMR spectroscopy / Structure elucidation

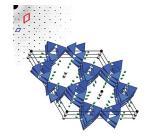
# **CONTENTS**

#### **NPO-Zeolite Nitridosilicate**

S. Pagano, O. Oeckler, T. Schröder, W. Schnick\* ...... 2678-2683



Keywords: Solid-sate structures / Nitridosilicates / Precursor / Zeolites



A new precursor approach employing amorphous "Si(CN2)2" led to the NPOzeolite analogous nitridosilicate Ba<sub>6</sub>Si<sub>6</sub>N<sub>10</sub>-O<sub>2</sub>(CN<sub>2</sub>) with channels containing carbodiimide ions. The latter is the first nitridosilicate incorporating carbodiimide ions and the partially ordered integration leads to the formation of a superstructure.

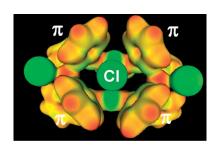
### **Supramolecular Interactions**

P. de Hoog, A. Robertazzi,\* I. Mutikainen, U. Turpeinen, P. Gamez,\*

J. Reedijk ...... 2684-2690



**Keywords:** Supramolecular chemistry 1,3,5-Triazine rings / Anion recognition / Density functional calculations / Copper(II) compounds / Host-guest systems

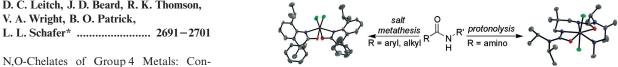


An electron-deficient cavity formed by four coordinated pyridine rings is capable of hosting a chloride anion or a water mole-

### N,O-Chelating Ligands

D. C. Leitch, J. D. Beard, R. K. Thomson,

L. L. Schafer\* ...... 2691-2701



trasting the Use of Amidates and Ureates in the Synthesis of Metal Dichlorides

Keywords: Chelates / Titanium / Zirconium / Amidate / Ureate / N,O ligands

Group 4 dichloride complexes with amidate or ureate ancillary ligands, while potentially useful as starting materials or precatalysts, have been largely been overlooked in the literature. Here, several examples of

these compounds have been prepared. A modified salt metathesis procedure is used to synthesize amidate dichlorides, while protonolysis is effective with electron-rich ureate ligands.

#### **Ruthenium Nitrosyl Complexes**

P. De, B. Sarkar, S. Maji, A. K. Das, E. Bulak, S. M. Mobin, W. Kaim,\*

G. K. Lahiri\* ...... 2702-2710



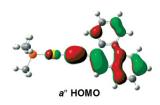
The co-ligands trpy and bik in [(bik)(trpy)- $Ru^{II}(NO)]^{n+}$  [4]<sup>n+</sup> facilitate the stabilization of both NO+ and NO+ redox states and primarily "NO"-based electron-transfer has been reflected by a 300 cm<sup>-1</sup> lower shift in v(NO) frequency on reduction of  $[4]^{3+}$  to  $[4]^{2+}$  while the v(C=O) of bik remains unaltered. The photocleavage of the Ru-NO+ bond is much faster than that of the Ru-NO· bond.

Stabilization of {RuNO}<sup>6</sup> and {RuNO}<sup>7</sup> States in  $[Ru^{II}(trpy)(bik)(NO)]^{n+}$  {trpy = 2,2':6',2''-terpyridine, bik = 2,2'-bis(1methylimidazolyl) ketone} - Formation, Reactivity, and Photorelease of Metal-Bound Nitrosyl

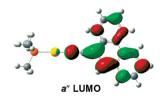
Keywords: Ruthenium / Nitrosyl / N,O ligands / Redox chemistry / EPR spectroscopy / Photolysis / Radicals



#### Calixarene Probe for Anion



A series of new alkynylgold(I) complexes has been synthesized; the luminescence of (arylalkynyl)gold complexes is characterized. The structures of ligand-centered



and metal-centered triplet excited states have been optimized within the densityfunctional theory. L. Gao, D. V. Partyka, J. B. Updegraff III, N. Deligonul, T. G. Gray\* ...... 2711–2719

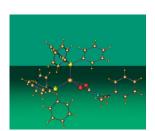
Synthesis, Structures, and Excited-State Geometries of Alkynylgold(I) Complexes



**Keywords:** Gold / Alkynyl complexes / Luminescence / Triplet states / Density-functional theory

### **Copper Complexes**

The facile synthesis, crystal structures of [{Cu(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(piperzdtc)] (1) and [{Cu(PPh<sub>3</sub>)<sub>2</sub>}(BzMedtc)] (2), interpretation of the NLO property of asymmetrical 2 by DFT using the finite-field perturbation method and electronic absorptions by TD-DFT calculations and conducting properties of 1 and 2 are reported.



A. Kumar, H. Mayer-Figge, W. S. Sheldrick, N. Singh\* .... 2720–2725

Synthesis, Structure, Conductivity, and Calculated Nonlinear Optical Properties of Two Novel Bis(triphenylphosphane)copper(I) Dithiocarbamates



**Keywords:** Copper / Dithiocarbamate / Density functional calculations / Semiconductivity / Nonlinear optics

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

If not otherwise indicated in the article, papers in issue 17 were published online on May 27, 2009

<sup>\*</sup> Author to whom correspondence should be addressed.