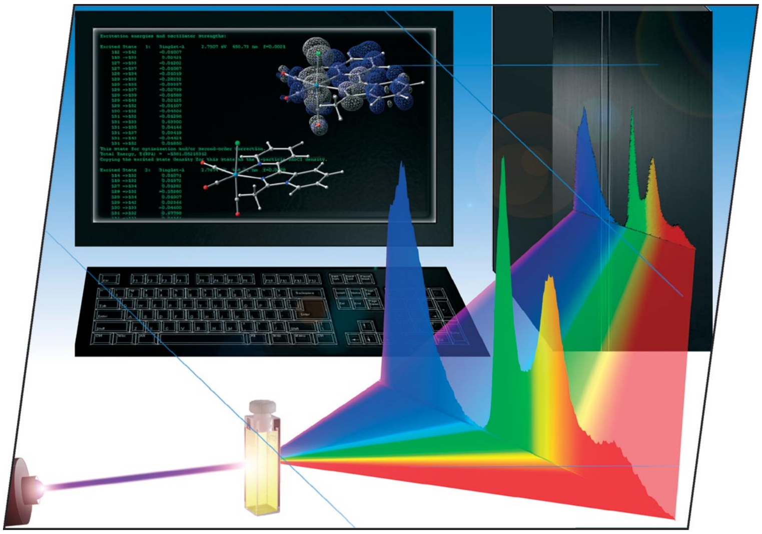
COVER PICTURE

The cover picture shows a representation of the mixed theoretical and experimental method employed by inorganic chemists in the study of structural and photophysical properties of luminescent molecules. The combination of time-dependent density functional theory and spectroscopy is crucial for determining the nature of excited states in metal complexes and thus their absorption and emission features. New dual-emitting ReL(CO)$_3$Cl complexes and their 1-(2-pyridyl)imidazo[1,5-*a*]pyridine ligands were successfully studied by using such a hybrid approach. Details are discussed in the Short Communication by R. Gobetto et al. on p. 3587ff.



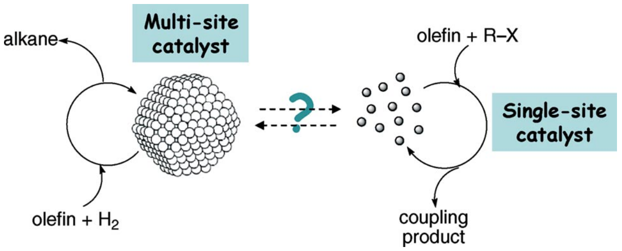
MICROREVIEW

Palladium Nanocatalysts

J. Durand, E. Teuma,
M. Gómez* 3577–3586

An Overview of Palladium Nanocatalysts: Surface and Molecular Reactivity

Keywords: Palladium / Nanoparticles / Homogeneous catalysis / Heterogeneous catalysis



From a mechanistic point of view, the use of nanoparticles as catalysts requires analysis of the catalytically active species in terms of their agglomeration and the leaching of the molecular species. This aspect becomes crucial for work under "wet" catalytic conditions. The present review focuses on the nature of palladium nanoparticle catalysts that are either preformed or generated in situ.

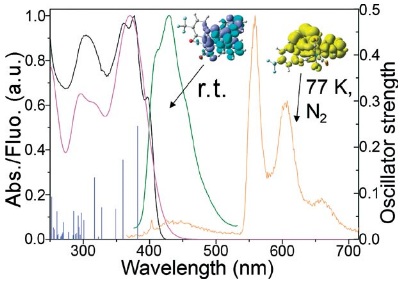
SHORT COMMUNICATIONS

Luminescent Rhenium Complexes

C. Garino, T. Ruiu, L. Salassa,
A. Albertino, G. Volpi, C. Nervi,
R. Gobetto,* K. I. Hardcastle ... 3587–3591

Spectroscopic and Computational Study on New Blue Emitting ReL(CO)$_3$Cl Complexes Containing Pyridylimidazo[1,5-*a*]pyridine Ligands

Keywords: Rhenium / X-ray structure / TDDFT / UV/Vis spectroscopy / Luminescence



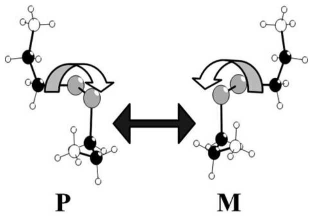
Synthesis, characterization, and photophysical properties of new Re(CO)$_3$Cl complexes containing 1-pyridylimidazo[1,5-*a*]pyridine ligands are presented. The complexes display high-energy singlet emissions arising from a $\pi \rightarrow \pi^*$ ligand-centered state and intense ligand-centered triplet emission in oxygen-free acetonitrile solutions. The nature of the excited states was analyzed by using TDDFT methods.

Hybrid Materials

N. Louvain, N. Mercier,* J. Luc,
B. Sahraoui 3592–3596

Example of Disulfide Conformational Change in the Solid State: Preparation, Optical Properties, and X-ray Studies of a Cystamine-Based Iodoplombate Hybrid

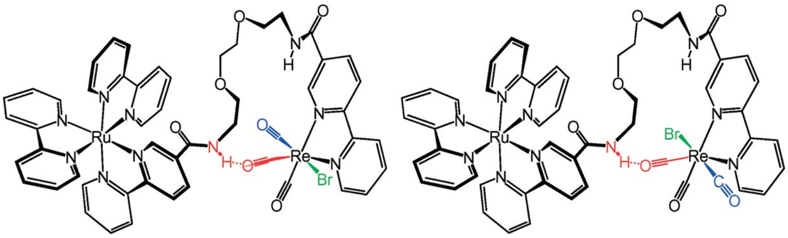
Keywords: Cystamine / Iodometalate / Organic–inorganic hybrid composites / Disulfides / Nonlinear optics / Polymorphism



An organic–inorganic hybrid was found to undergo reversible structural transition under moderate conditions leading to a polymorph phase. Conformational changes in the disulfide molecules in the solid state resulted in an abrupt decrease in the second harmonic generation (SHG) intensity; thus, this material can be considered as an SHG switch controlled by temperature.

FULL PAPERS

Luminescent Heterometallic Complexes



A new stepwise route to heteronuclear tricarbonylrhenium(I)–tris(bipyridine)ruthenium(II) complexes has been explored with the product exhibiting an unusual configurational arrangement attributed to a hydrogen-bonding interaction between an Re–CO group and an amide proton.

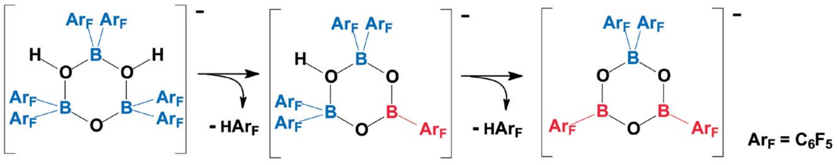
D. Pelleteret, N. C. Fletcher* 3597–3605

A Modular Approach to Luminescent Dinuclear Ruthenium(II) and Rhenium(I) Complexes

Keywords: Rhenium / Ruthenium / 2,2′-Bipyridine / Bridging ligands / Heterometallic complexes

---

Arylboroxinates



Addition of bis(dimethylamino)naphthalene to CH$_2$Cl$_2$ solutions of (C$_6$F$_5$)$_2$BOH causes instantaneous trimerization to the hexaaryl anion [(C$_6$F$_5$)$_6$B$_3$O$_3$H$_2$]$^-$, accompanied by stepwise dearylation, with elimination of pentafluorobenzene and formation at first of the pentaaryl anion [(C$_6$F$_5$)$_5$B$_3$O$_3$H]$^-$ and then of the tetraaryl anion [(C$_6$F$_5$)$_4$B$_3$O$_3$]$^-$.

D. Donghi, D. Maggioni, T. Beringhelli, G. D'Alfonso* 3606–3613

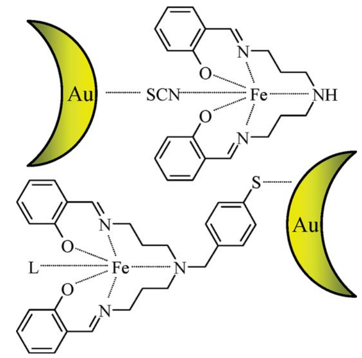
^{19}F NMR Spectroscopic Investigation of the Reaction of Bis(pentafluorophenyl)borinic Acid with a "Proton Sponge": Deprotonation, Trimerization and Stepwise Dearylation

Keywords: Fluoroarylboranes / Cyclooligomerization / Hydrodeboration / Proton sponge / NMR spectroscopy

---

Functionalized Gold Nanoparticles

Iron(III) complexes of a series of salten derivative ligands [H$_2$salten = bis(3-salicylideneaminopropyl)amine] have been used to efficiently stabilize and functionalize gold nanoparticles. The connection between the gold surface and the iron complex was ensured either by the ambidentate thiocyanate ligand or by a thiol pendant group.



C. R. Mayer, G. Cucchiaro, J. Jullien, F. Dumur, J. Marrot, E. Dumas,* F. Sécheresse 3614–3623

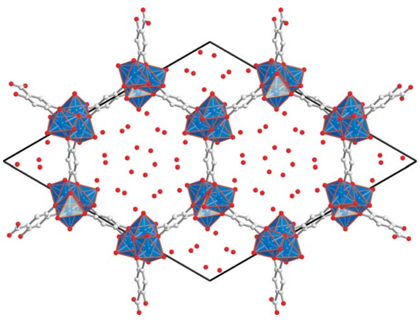
Functionalization of Gold Nanoparticles by Iron(III) Complexes Derived from Schiff Base Ligands

Keywords: Gold nanoparticles / Schiff base ligands / Iron / Isothiocyanate

---

Microporous MOFs

Two coordination polymers based on the light-weight metal magnesium were prepared by solvothermal synthesis. One of these is microporous with a large pore volume, high apparent surface area, and potentially accessible metal sites. Framework, thermal stability, and behavior upon dehydration and re-hydration indicate that it is a suitable adsorbent.



P. D. C. Dietzel,* R. Blom, H. Fjellvåg 3624–3632

Base-Induced Formation of Two Magnesium Metal-Organic Framework Compounds with a Bifunctional Tetratopic Ligand

Keywords: Microporous materials / Coordination polymers / Metal-organic frameworks / Organic-inorganic hybrid composites / Adsorption / Magnesium / X-ray diffraction / Hydrothermal synthesis / 2,5-Dihydroxyterephthalic acid

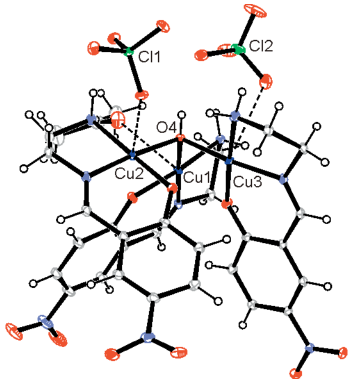
CONTENTS

Oligonuclear Copper Complexes

L. Rigamonti, A. Cinti, A. Forni,*
A. Pasini,* O. Piovesana* 3633–3647

Copper(II) Complexes of Tridentate Schiff Bases of 5-Substituted Salicylaldehydes and Diamines – The Role of the Substituent and the Diamine in the Formation of Mono-, Di- and Trinuclear Species – Crystal Structures and Magnetic Properties

Keywords: ridentate ligands / Copper / Magnetic interactions / Dinuclear complexes / Trinuclear complexes



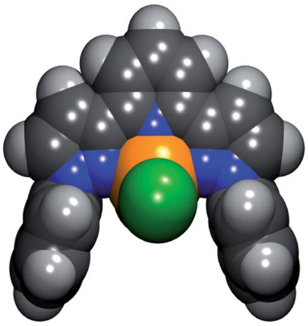
We report the selective syntheses of mono-, di- and trinuclear μ_3-OH complexes of Cu^{II} with tridentate Schiff bases derived by the condensation of 5-G-salycilaldehyde and ethylenediamine or 1,3-diaminopropane. The trinuclear derivatives represent a case of spin frustration.

Post-Metallocenes

D. Zabel, A. Schubert, G. Wolmershäuser,
R. L. Jones Jr, W. R. Thiel* 3648–3654

Iron and Cobalt Complexes of Tridentate N-Donor Ligands in Ethylene Polymerization: Efficient Shielding of the Active Sites by Simple Phenyl Groups

Keywords: Polyethylene / Iron / Cobalt / Pyridine / Pyrazole



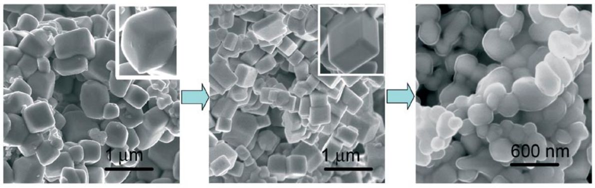
Due to the geometry of the five-membered pyrazole rings in the tridentate N-donor ligand, the iron and cobalt centres of the derived complexes are already efficiently shielded by simple phenyl groups, which results in the generation of high-molecular-weight polyethylene.

Molten Salt Perovskite Synthesis

J. Chen, R. Yu, L. Li, C. Sun, T. Zhang,
H. Chen, X. Xing* 3655–3660

Structure and Shape Evolution of $Bi_{1-x}La_xFeO_3$ Perovskite Microcrystals by Molten Salt Synthesis

Keywords: Bismuth / Iron / Synthesis design / Perovskite phases / Crystal growth



$Bi_{0.8}La_{0.2}FeO_3$ $Bi_{0.4}La_{0.6}FeO_3$ $Bi_{0.2}La_{0.8}FeO_3$

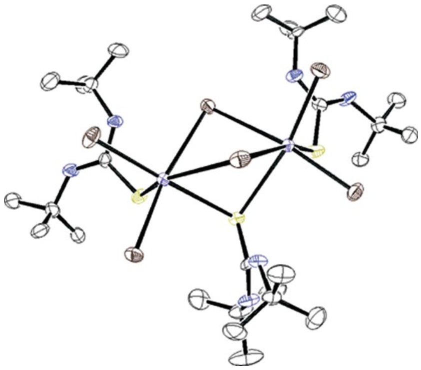
$Bi_{1-x}La_{xFeO3}$ microcrystals were prepared by molten salt synthesis. The particle shape (cubic, tetragonal, and semi-sphere crystallite) evolves with composition. The growth of $Bi_{1-x}La_xFeO_3$ crystals was revealed to follow the Ostwald ripening mechanism by investigation of the particle size distribution and by high-resolution TEM.

Antimony Thiourea Complexes

N. A. Barnes, S. M. Godfrey,*
R. G. Pritchard, S. Ratcliffe 3661–3667

The Reaction of *N,N'*-Di-*tert*-butylthiourea (dtbtu) with Antimony(III) Halides – Formation of the Triply Bridged [(dtbtu)-$SbX_2(\mu\text{-}X)_2(\mu\text{-dtbtu})SbX_2$(dtbtu)] (X = Cl, Br) Dimers

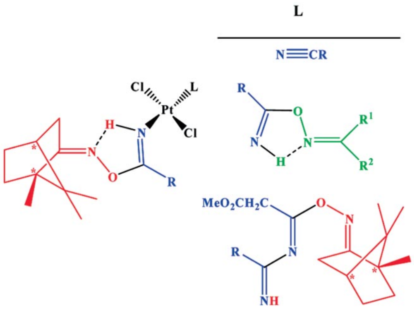
Keywords: Main group elements / S ligands / Antimony / Thioureas



The reactions of *N,N'*-di-*tert*-butylthiourea (dtbtu) with SbX_3 (X = Cl, Br) result in the formation of triply bridged dimers, [(dtbtu)$SbX_2(\mu\text{-}X)_2(\mu\text{-dtbtu})SbX_2$(dtbtu)], with one bridging dtbtu ligand and two bridging halides. The geometry at antimony is distorted octahedral, with evidence for a stereochemically active lone pair. The reaction of SbI_3 with dtbtu produces a 1:1 complex, [SbI_3(dtbtu)].

Additions to Platinum Organonitriles

Optically active unsymmetric mixed-ligand imine-nitrile, bis(imine), or imine-diazadiene platinum(II) complexes have been prepared by sequential nucleophilic additions of (R*)-camphor oxime, ketoximes, or chiral diimino esters to *trans*-[$PtCl_2(NCR)_2$] or *trans*-(R*)-[$PtCl_2\{NH{=}C(R)ON{=}C(C_9H_{16})\}(NCR)$].



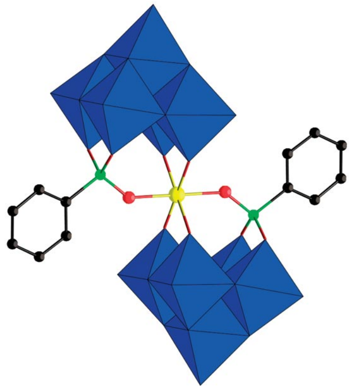
J. Lasri,* M. F. C. Guedes da Silva, M. A. J. Charmier, A. J. L. Pombeiro* .... **3668−3677**

Optically Active Mixed Unsymmetric Imine Platinum(II) Complexes − Utilization of the Liberated Imines for Further Syntheses of Mixed Imine-Diazadiene Complexes and of (*E*)-Cyanoalkenes

Keywords: (R*)-Camphor oxime / Optically active complexes / (*E*)-Cyanoalkenes / Platinum / Microwave irradiation

Hybrid Polyoxometalates

A series of organophosphono polyoxoniobotungstates [$NbW_{10}O_{38}(RP)_2$]$^{3-}$ {R = Me (**1**), Et (**2**), Pr (**3**), *n*Bu (**4**), Hex (**5**), Hep (**6**), Cy (**7**), Ph (**8**), All (**9**)} has been prepared by the reaction of (nBu_4N)$_3$-[NbW_5O_{19}] with organophosphono dichlorides. The anions [$NbW_{10}O_{38}(RP)_2$]$^{3-}$ are made up of two W_5O_{18} subunits, which can be viewed as monovacant derivatives of the niobotungstate precursor linked by a {$Nb(OPR)_2$} group.



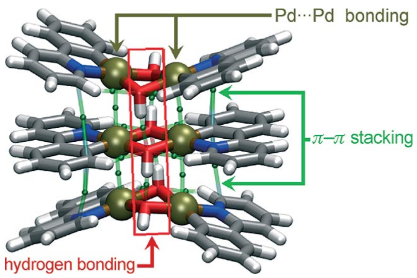
H. Driss, K. Boubekeur, M. Debbabi,* R. Thouvenot* .... **3678−3686**

Synthesis and Spectroscopic Characterization of Organophosphono Derivatives of Lindqvist Niobotungstates − X-ray Crystal Structures of (nBu_4N)$_3$[$NbW_{10}O_{38}(RP)_2$] (R = *n*Bu, Hep and Ph)

Keywords: Polyoxometalates / Organic−inorganic hybrid composites / Organophosphono groups / Niobium / Tungsten

ortho-Palladated Complexes

Crystal structures of two *ortho*-palladated complexes have been elucidated by X-ray powder diffraction. Some unprecedented features in the crystal packing are analyzed by DFT calculations.



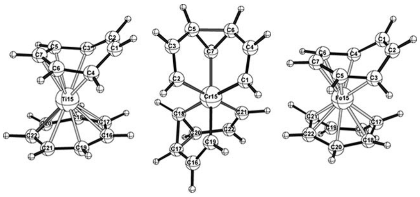
J. Pérez,* A. Espinosa,* J. M. Galiana, E. Pérez, J. L. Serrano, A. Cabeza, M. A. G. Aranda .... **3687−3697**

Crystal Packing in Di-(μ-OH)-*ortho*-palladated Complexes − A DFT Insight into the Molecular Structure and Solid-State Interactions

Keywords: Palladium complexes / X-ray powder diffraction / Density functional calculations / Hydrogen bonds / Stacking interactions

Sandwich Complexes

The preferred structures of the $(C_7H_7)_2M$ (M = Ti, V, Cr, Mn, Fe, Co, Ni) sandwich compounds have been studied by density functional theory.



$(C_7H_7)_2Ti$ $(C_7H_7)_2Cr$ $(C_7H_7)_2Fe$

H. Wang,* Y. Xie, R. B. King,* H. F. Schaefer III .... **3698−3708**

Bis(cycloheptatrienyl) Derivatives of the First-Row Transition Metals: Variable Hapticity of the Cycloheptatrienyl Ring

Keywords: Cycloheptatrienyl derivatives / Sandwich compounds / Density functional theory

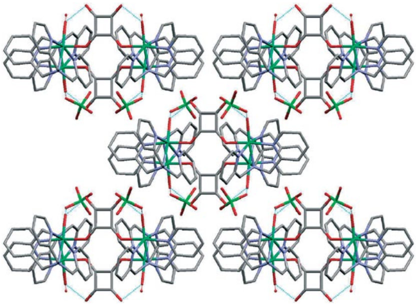
CONTENTS

Squarato Complexes

S. S. Massoud,* F. A. Mautner, R. Vicente, F. R. Louka **3709–3717**

μ-1,3- (*trans*) and μ-1,2- (*cis*) Bonding in Squarato-Bridged Dinuclear Copper(II) and Nickel(II) Complexes Derived from Polypyridyl Amines

Keywords: Copper / Nickel / Dinuclear complexes / Squarato bridges / Crystal structures / Magnetic properties



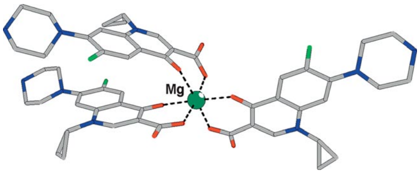
The dinuclear squarato-bridged copper(II) and nickel(II) complexes $[Cu_2(TPA)_2(\mu_{1,3}\text{-}C_4O_4)](ClO_4)_2\cdot 4H_2O$ (**1**), $[Cu_2(MeDPA)_2(\mu_{1,3}\text{-}C_4O_4)(H_2O)_4](ClO_4)_2$ (**2**) and $[Ni_2(TPA)_2(\mu_{1,2}\text{-}C_4O_4)(H_2O)_2](ClO_4)_2$ (**3**) were synthesized, and structurally and magnetically characterized.

Ciprofloxacin Magnesium Complexes

I. Turel,* P. Živec, A. Pevec, S. Tempelaar, G. Psomas* **3718–3727**

💻 Compounds of Antibacterial Agent Ciprofloxacin and Magnesium – Crystal Structures and Molecular Modeling Calculations

Keywords: Magnesium / Quinolone / Antibiotics / Crystal structure / Molecular modeling



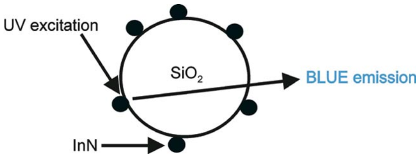
Crystal structures of isolated Mg complexes of the quinolone antibacterial drug ciprofloxacin (metal–ligand ratio 1:2 and 1:3) were determined. A bidentate O,O′-bonding was found for both complexes. The crystal structures of several Mg–ciprofloxacin complexes were analyzed. Additionally, molecular modeling calculations in these systems were performed.

Blue-Emitting Nanomaterials

P. Munusamy, V. Mahalingam, F. C. J. M. van Veggel* **3728–3732**

$InN@SiO_2$ Nanomaterials as New Blue Light Emitters

Keywords: Hybrid nanomaterials / Blue photoluminescence / Indium nitride / Silica



Blue photoluminescence (≈ 450 nm) was obtained upon excitation of a $InN@SiO_2$ nanomaterial with UV light. These hybrid nanomaterials were prepared by a simple precipitation reaction followed by a solid-state reaction.

---

* Author to whom correspondence should be addressed.

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