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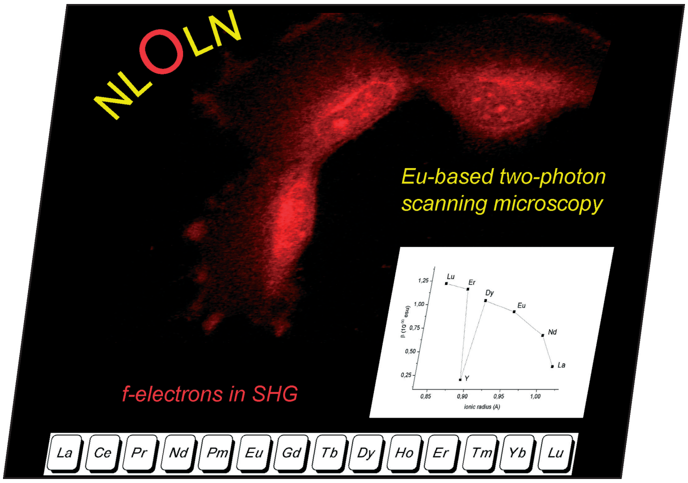
A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows two of the most striking results of the use of lanthanide complexes for non-linear optical applications: (i) the design of lanthanide-based bioprobes for two-photon scanning microscopy and (ii) the direct contribution of *f* electrons to the quadratic hyperpolarisability. In their Microreview on p. 4357ff, C. Andraud and O. Maury propose an exhaustive description of the state-of-the-art of this emerging but also challenging field of research.



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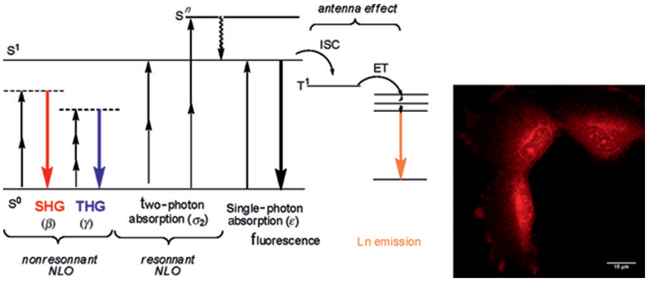
MICROREVIEW

NLO of Lanthanide Complexes

C. Andraud, O. Maury* 4357–4371

Lanthanide Complexes for Nonlinear Optics: From Fundamental Aspects to Applications

Keywords: Lanthanides / Nonlinear optics / Bioimaging / Luminescence / Second harmonic generation / Two-photon absorption



Whereas magnetic and luminescence properties of lanthanide complexes have been extensively studied, their potentialities in nonlinear optics (NLO) have been less explored. In the last ten years, the latter properties have become an emerging field of research from the point of view of both fundamental aspects and bioimaging applications.

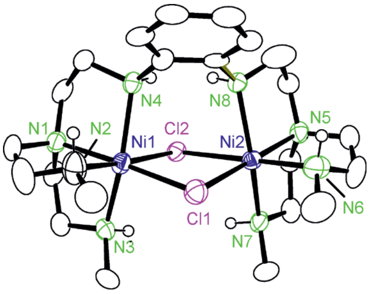
SHORT COMMUNICATION

Amine Complexes

F. E. Hahn,* H. Schröder,
T. Pape 4373–4377

Halido-Bridged Dinuclear Nickel and Zinc Complexes with a Bis(tripodal) Octaamine Ligand – Unusual Coordination Mode of an *ortho*-Phenylenediamine

Keywords: Nickel / Zinc / Dimetallic complexes / Tripodal ligands / Coordination modes



The *ortho*-phenylenediamine bridging unit in dinuclear polyamine complexes coordinates in an unprecedented fashion as a monodentate donor to each of the two metal centers.

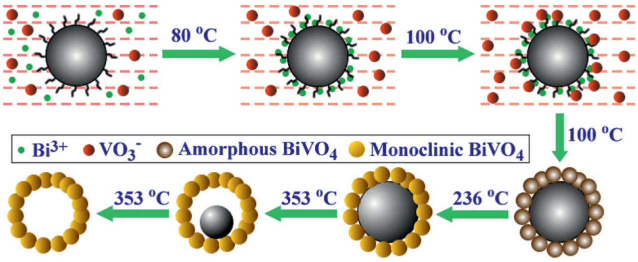
FULL PAPERS

Hollow Structures

W. Yin, W. Wang*, M. Shang, L. Zhou,
S. Sun, L. Wang 4379–4384

$BiVO_4$ Hollow Nanospheres: Anchoring Synthesis, Growth Mechanism, and Their Application in Photocatalysis

Keywords: Bismuth / Vanadates / Nanostructures / Template synthesis / Photochemistry



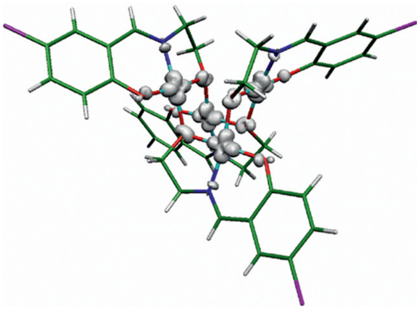
An anchoring method was developed to synthesize $BiVO_4$ hollow nanospheres by employing colloidal carbon spheres (CCSs) as hard templates. The detailed mechanism of this anchoring method was revealed. Considering the general adsorption of metal ions on the surface of the CCSs, this anchoring method could be extended to synthesize other hollow-structured multicomponent oxides.

Magnetic and Catalytic Properties

S. Thakurta, P. Roy, R. J. Butcher, M. Salah El Fallah,* J. Tercero, E. Garribba, S. Mitra* 4385–4395

Ferromagnetic Coupling in a New Copper(II) Schiff Base Complex with Cubane Core: Structure, Magnetic Properties, DFT Study and Catalytic Activity

A new tetranuclear copper(II) Schiff base complex with μ_3-alkoxo-bridged Cu_4O_4 cubane core was synthesized and characterized. Magnetic studies reveal prominent ferromagnetic interaction and the coupling constants determined by DFT calculations can be nicely correlated with the structural parameters. Moreover, the complex behaves as an active catalyst in the peroxidative oxidation of cycloalkanes.



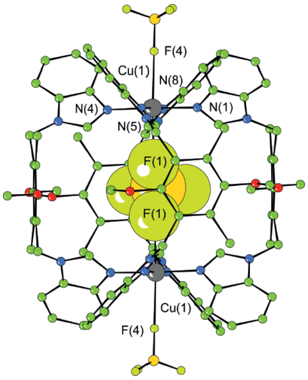
Keywords: Cluster compounds / Metallocluster / Copper / Ferromagnetic interaction / Density functional calculations / Oxidation / Magnetic properties / Schiff bases

Metallomacrocycles

C. Desmarets, C. Policar, L.-M. Chamoreau, H. Amouri* 4396–4400

Design, Self-Assembly, and Molecular Structures of 3D Copper(II) Capsules Templated by BF_4^- Guest Anions

Two new 3D M_2L_4 copper(II) capsules, $\{[BF_4\subseteq(CH_3CN)_2Cu_2(L^1)_4][BF_4]_3\}$ (**1**) and $\{[BF_4\subseteq(BF_4)_2Cu_2(L^1)_4][BF_4]\}$ (**2**), were prepared by using the semirigid exobidentate ligand 1,3-bis(benzimidazol-1-ylmethyl)-2,5-dimethoxy-4,6-dimethylbenzene (L^1). Remarkably, in both metallocages the weakly coordinated BF_4^- anion acts as a template and interacts with the metal center through a weak Cu···F contact.

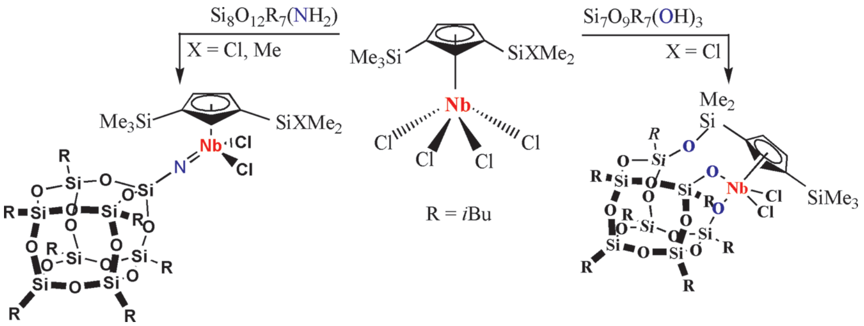


Keywords: Copper / Encapsulation / Self-assembly / Host–guest systems / Cage compounds

Niobium(V) Complexes

C. García, M. Gómez,* P. Gómez-Sal, J. M. Hernández 4401–4415

Monocyclopentadienyl(niobium) Compounds with Imido and Silsesquioxane Ligands: Synthetic, Structural and Reactivity Studies



Chlorido-, alkylchlorido- and dialkylimido, chlorido(silsesquioxanylimido)-, chloridosilsesquioxanyl- and alkylsilsesquioxanyl-monocyclopentadienyl(niobium) complexes were prepared, and their reactivity was studied in insertion processes. Interesting details of the structural and chemical behaviour of these complexes are discussed.

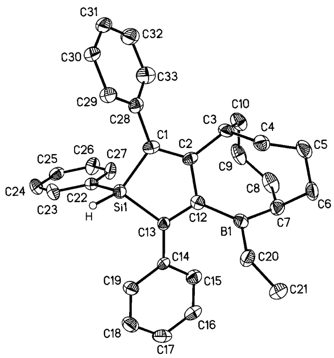
Keywords: Niobium / Silsesquioxane / Cyclopentadienyl ligands / Insertion / Structure–activity relationships

Silole Chemistry

E. Khan, S. Bayer, R. Kempe, B. Wrackmeyer* 4416–4424

Synthesis and Molecular Structure of Silole Derivatives Bearing Functional Groups on Silicon: 1,1-Organoboration of Dialkynylsilanes

Dialkynylsilanes bearing Si–H or SiCl functions in addition to the alkynyl groups react with an excess of triethylborane or 9-ethyl-9-borabicyclo[3.3.1]nonane after heating at 100–110 °C for several days to give Si-functional substituted siloles. Similarly, the reactions with afford polycyclic compounds containing the silole ring.



Keywords: Main group elements / Silicon / Boron / Alkynes / Heterocyclic compounds

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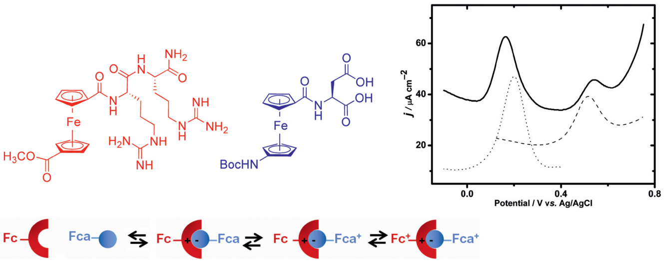
Ferrocene Peptide Conjugates

A. Lataifeh, C. R. Bondy,
H.-B. Kraatz* 4425–4432

Ferrocene Conjugates Containing Diarginine and Aspartic Acid: Salt Bridge Interactions in Water

Keywords: Molecular recognition / Peptide conjugates / Amino acids / Bioorganic chemistry / Metallocenes / Electrochemistry



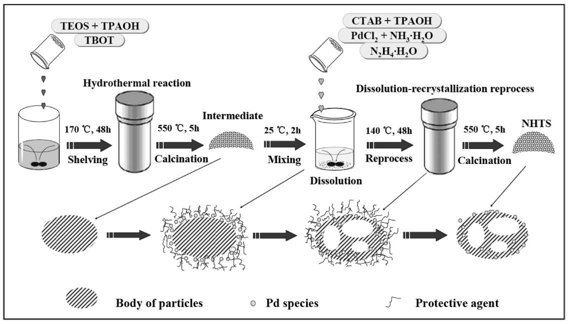
Ferrocene conjugates of diarginine and aspartic acid bind in water as a 1:1 associate. The process is driven by the formation of a salt bridge. The association affects the electronic properties of the ferrocene centres as well as the conformation of the peptide ligands.

Intra-Particle Voids

C. Shi, B. Zhu, M. Lin,*
J. Long* 4433–4440

NHTS: A Hollow, Noble-Metal-Modified Titanium Silicalite

Keywords: Heterogeneous catalysis / Palladium / Oxidation / Hydrothermal synthesis / Zeolites



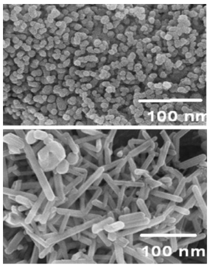
A new hollow titanium silicalite (NHTS) containing intra-particle voids and with bifunctional catalytic properties has been synthesized by a semi-in-situ hydrothermal method. NHTS has a very ordered MFI topology, with a noble metal stably incorporated into the framework, and a hollow structure, which makes it a good alternative for catalytic oxidations.

Thulium(3+)-Doped Nanocrystals

M. K. Devaraju,* S. Yin,
T. Sato 4441–4445

Tm^{3+}-Doped Y_2O_3 Nanocrystals: Rapid Hydrothermal Synthesis and Luminescence

Keywords: Hydrothermal synthesis / Nanostructures / Luminescence / Lanthanides / Thulium / Yttrium



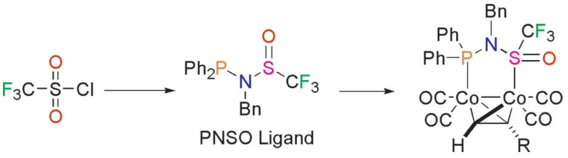
The hydrothermal synthesis of Tm^{3+}-doped Y_2O_3 nanocrystals in batch reactors at 220 and 250 °C was carried out under high autogenous pressure within short reaction time. Two kinds of product morphologies were obtained: nanospheres and nanorods with monodispersed morphology.

Sulfinyl–Metal Bonding

M. Revés, A. Riera,*
X. Verdaguer* 4446–4453

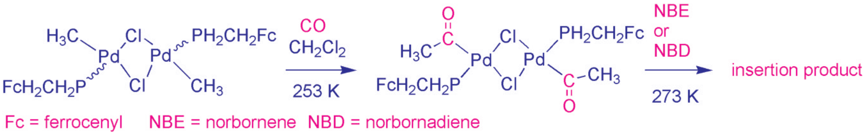
PNSO Ligands as a Tool to Study Metal Bonding of Electron-Deficient Sulfinyl Groups

Keywords: S ligands / Electron-deficient compounds / Cobalt / Cycloaddition



The S binding capacity of different sulfinyl groups was examined on the basis of stretching frequencies of CO ligands in PNSO-bridged Co_2–alkyne complexes. This allowed the ranking of these groups on the basis of their π acidity. Additional X-ray and Pauson–Khand reactivity studies confirmed that electron-deficient sulfinyl groups provide enhanced metal bonding.

Primary Phosphanes



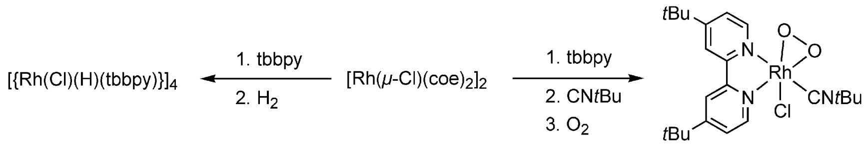
This paper reports the synthesis and reactivity towards the insertion of CO and strained olefins of the new primary phosphane-ligated methylpalladium complex $[Pd(PH_2CH_2Fc)(CH_3)(\mu\text{-}Cl)]_2$ (**3**). After chloride abstraction, the activity of complex **3** as precatalyst for the vinyl addition polymerization of norbornene and for the copolymerization of CO/norbornene was investigated.

M. M. Dell'Anna, D. Giardina-Papa, S. Ibáñez, A. Martín, P. Mastrorilli,* C. F. Nobile, M. Peruzzini **4454–4463**

Insertion of CO and Strained Olefins into Organometallic (Ferrocenylmethyl)phosphane Palladium Complexes

Keywords: Phosphanes / Palladium / Insertion / Alkenes / Polymerization / Carbonylation

Peroxido Complexes



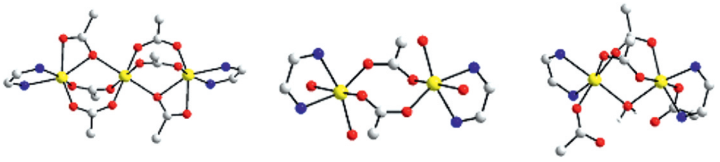
Unique rhodium bipyridine compounds were synthesized starting from $[Rh(\mu\text{-}Cl)(coe)_2]_2$ (coe = cyclooctene) and 4,4′-di-*tert*-butyl-2,2′bipyridine (tbbpy). The new complexes include the Rh^{II} cluster $[\{Rh(Cl)(H)(tbbpy)\}]_4$ and the Rh^{III} peroxido complex $[Rh(Cl)(O_2)\text{-}(tbbpy)(CNtBu)]$. The latter was prepared in the solid state by using O_2.

A. Penner, T. Schröder, T. Braun,* B. Ziemer **4464–4470**

Synthesis, Structure, and Reactivity of Rhodium Bipyridine Compounds: Formation of a Rh^{II} Hydrido Cluster and a Rh^{III} Peroxido Complex

Keywords: Rhodium / Cluster compounds / N ligands / Peroxido ligands

Polynuclear Manganese Compounds



Five polynuclear Mn^{II} compounds with four different coordination modes of the chlorobenzoato ligands were obtained. All of the compounds display weak antiferromagnetic coupling, which depends on the number of bridges and the conformation of the carboxylate bridge. Each type of compound shows a characteristic EPR spectrum at 4 K.

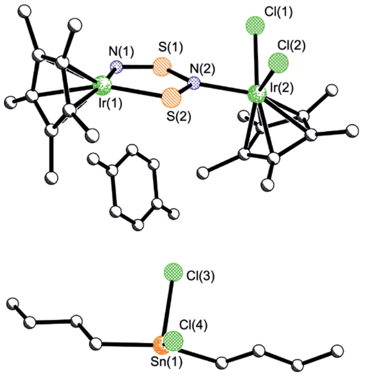
V. Gómez,* M. Corbella **4471–4482**

Versatility in the Coordination Modes of *n*-Chlorobenzoato Ligands: Synthesis, Structure and Magnetic Properties of Three Types of Polynuclear Mn^{II} Compounds

Keywords: Manganese / Carboxylate ligands / Coordination modes / Magnetic properties / EPR spectroscopy

Metallasulfur–Nitrogen Chemistry

Metallasulfur–nitrogen chemistry continues to surprise theoreticians and synthetic chemists. During the synthesis of a simple MS_2N_2 complex we obtained a binuclear complex.



V. Matuska, K. Tersago, P. Kilian, C. Van Alsenoy, F. Blockhuys, A. M. Z. Slawin, J. D. Woollins* **4483–4490**

Molecular and Crystal Structures of $Cp^*M(S_2N_2)$ (M = Co, Rh, Ir) and Related Compounds

Keywords: Metallacycles / Rhodium / Structure elucidation / Density functional calculations

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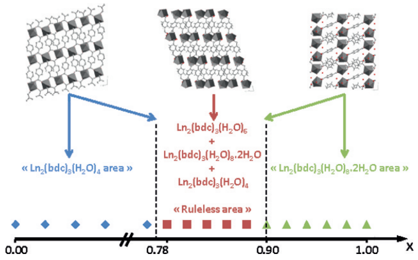
Luminescent Coordination Polymers

V. Haquin, F. Gumy, C. Daiguebonne,*
J.-C. Bünzli, O. Guillou .... 4491−4497

Structural and Near-IR Luminescent Properties of Erbium-Containing Coordination Polymers

Keywords: Heterometallic complexes / Lanthanides / X-ray diffraction / Luminescence / Polymers



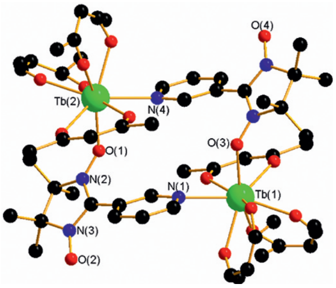
The near-IR luminescence properties of two Er^{III}-containing coordination polymers were investigated with the aim of testing their potential use as optical materials. Because both present relatively small quantum yields and short excited-state lifetimes, factors influencing their luminescent properties were deciphered in an effort to improve their luminescent properties.

Lanthanide-Radical Clusters

H. X. Tian, R.-N. Liu, X.-L. Wang,
P.-P. Yang, Z.-X. Li, L.-C. Li,*
D.-Z. Liao .... 4498−4502

Magnetic Slow Relaxation in Cyclic Tb^{III}-Nitronyl Nitroxide Radical Complexes

Keywords: Radicals / Nitronyl nitroxide / Lanthanides / Terbium / Magnetic properties / Single molecule magnet



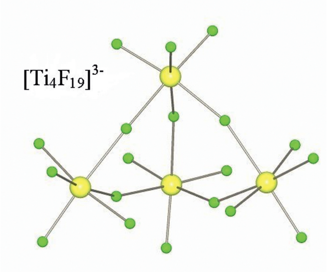
Two new radical-Tb^{III} complexes have been synthesized by using pyridyl-substituted nitronyl nitroxide radicals. These two complexes show similar cyclic structure in which each pyridyl-substituted radical links two different metal ions through the oxygen of nitroxide group and the pyridine nitrogen, but the different magnetic relaxation phenomenon was observed.

Discrete [Ti(IV)F] Anions

Z. Mazej,* E. Goreshnik .... 4503−4506

Synthesis and Characterisation of $[XeF_5]_3[Ti_4F_{19}]$ Containing a Discrete $[Ti_4F_{19}]^{3-}$ Anion

Keywords: Titanium / Xenon / Fluorine / Structure elucidation / Vibrational spectroscopy



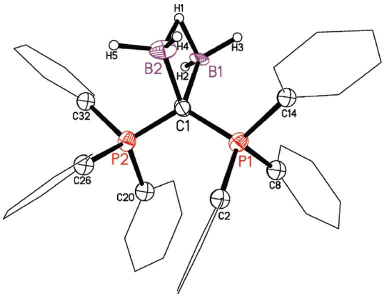
The crystal structure of $[XeF_5]_3[Ti_4F_{19}]$ differs from the previously reported ones in XeF_6/MF_4 systems {i.e., $[XeF_5]_2[MF_6]$ (M = Pd, Ni), XeF_5CrF_5, $[XeF_5CrF_5]_4{\cdot}XeF_4$ and XeF_5GeF_5}. It represents a unique case containing discrete $[M_4F_{19}]^{3-}$ anions.

Carbon(0) Complexes

W. Petz,* F. Öxler, B. Neumüller,*
R. Tonner, G. Frenking* .... 4507−4517

Carbodiphosphorane $C(PPh_3)_2$ as a Single and Twofold Lewis Base with Boranes: Synthesis, Crystal Structures and Theoretical Studies on $[H_3B\{C(PPh_3)_2\}]$ and $[\{(\mu\text{-}H)H_4B_2\}\{C(PPh_3)_2\}]^+$

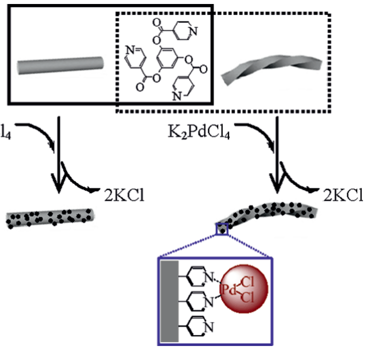
Keywords: Boranes / Density functional calculations / Donor-acceptor systems / Bond energy / Ab initio calculations



Reaction of the carbodiphosphorane $C(PPh_3)_2$ with B_2H_6 yields the monoadduct $[H_3B\{C(PPh_3)_2\}]$. Treatment of the latter with DME gives $[\{(\mu\text{-}H)H_4B_2\}\{C(PPh_3)_2\}][B_2H_7]$, which has been characterized by X-ray structure analysis. This compound is the first complex of a carbodiphosphorane where the carbon donor atom binds with its two-electron lone pairs to two main-group Lewis acids larger than protons.

Morphology Manipulation

For tri-*O*-isonicotinoylphloroglucinol, the formation and control of uniform helix and stick morphologies shows subtle external sonication media effects. The first control of submicrohelices versus submicrosticks by sonication without any additives seems to be a function of conformational isomers. The present approach to loading $PdCl_2$ nanoparticles from K_2PdCl_4 on the morphologies is a conceptually advanced method of metal-surface–donor interaction.

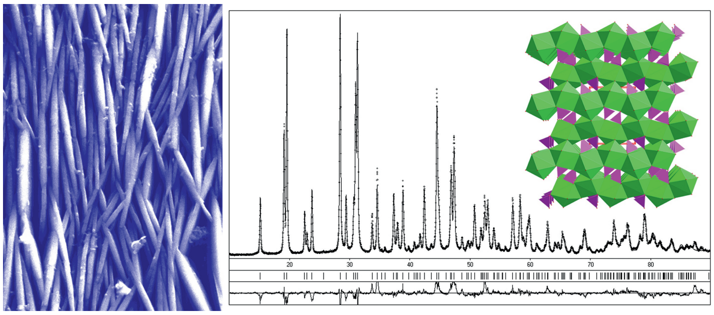


T. H. Noh, S. A. Kim, S. Y. Lee, O.-S. Jung* 4518–4521

Submicrosticks versus Submicrohelices by Sonication – Assembly of $PdCl_2$ Nanoparticles on Those Morphologies

Keywords: Palladium / Sonication / Submicrohelix / Submicrostick / Surface chemistry

Lanthanum Phosphite Microspheres



Lanthanum phosphite {La(HO)(HPO_3)} microspheres with crusts consisting of well-orientated submicron-sized rods were prepared under hydrothermal conditions. Their structure was solved by ab initio methods from X-ray powder diffraction analysis. Possible mechanisms of formation were proposed. Ce^{3+} doped samples show intensive broad emission bands with a maximum around 364 nm under UV excitation.

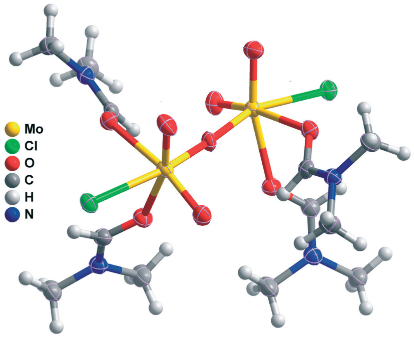
D.-B. Xiong, Y.-F. Zhao, L. D. Gulay, J.-T. Zhao 4522–4527

Lanthanum Phosphite Microspheres: Hydrothermal Synthesis, Ab Initio Structure Determination, Morphology and Photoluminescence of La(HO)(HPO_3)

Keywords: Lanthanum phosphite / Ab initio calculations / Microspheres / Self-assembly / Structure elucidation / Luminescence

Catalytic Olefin Epoxidation

The mononuclear complexes [MoO_2Cl_2-($RCONR'_2$)$_2$] containing different *N*,*N*-dialkylamide ligands exhibit very high initial activities in the epoxidation of *cis*-cyclooctene with *tert*-butylhydroperoxide. Decreases in reaction rates in subsequent runs are mainly due to the formation of binuclear species with a structure related to that determined for [$Mo_2O_4(\mu_2\text{-}O)Cl_2$-(dmf)$_4$].



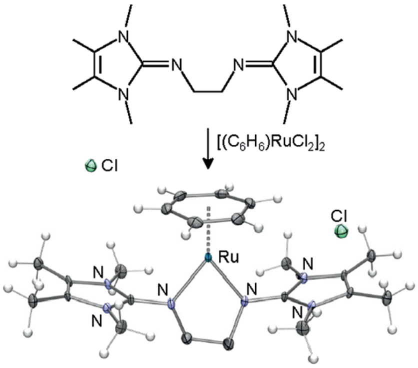
S. Gago, P. Neves, B. Monteiro, M. Pessêgo, A. D. Lopes, A. A. Valente, F. A. Almeida Paz, M. Pillinger, J. Moreira, C. M. Silva, I. S. Gonçalves* 4528–4537

Synthesis and Catalytic Properties in Olefin Epoxidation of Octahedral Dichloridodioxidomolybdenum(VI) Complexes Bearing *N*,*N*-Dialkylamide Ligands: Crystal Structure of [$Mo_2O_4(\mu_2\text{-}O)Cl_2(dmf)_4$]

Keywords: Molybdenum / O ligands / Homogeneous catalysis / Epoxidation / Kinetics

Coordinative Unsaturation

The syntheses of stable mono- and dicationic 16-electron (arene)ruthenium half-sandwich complexes bearing bis(imidazolin-2-imine) ligands are presented and their stabilities ascribed to the strong π-electron release capability of the imine ligands, leading to a weak propensity of the Ru atom to coordinate other π-basic ligands such as chloride.



T. Glöge, D. Petrovic, C. Hrib, P. G. Jones, M. Tamm* 4538–4546

16-Electron (Arene)ruthenium Complexes with Superbasic Bis(imidazolin-2-imine) Ligands and Their Use in Catalytic Transfer Hydrogenation

Keywords: Ruthenium / Arene ligands / N ligands / Coordinative unsaturation / Hydrogenation

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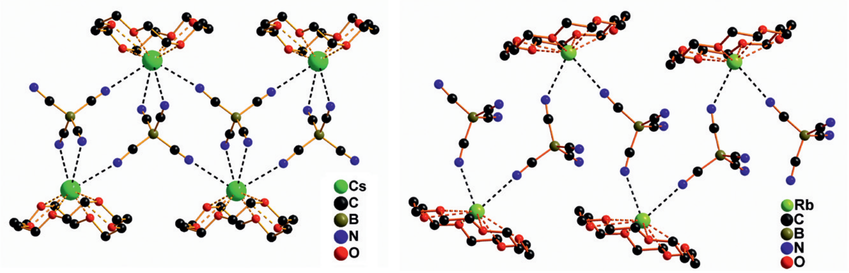
Tetracyanidoborato-Linked Chains

A. Bernsdorf, M. Köckerling* ... 4547–4553

Chains of Alkaline Metal Cations and Tetracyanidoborato Anions – Syntheses, Structures and Properties of the New $[A^I(18\text{-crown-6})][B(CN)_4]$ (A^I = Cs, Rb)

Keywords: Alkali metals / Borates / Structure elucidation / Crown compounds



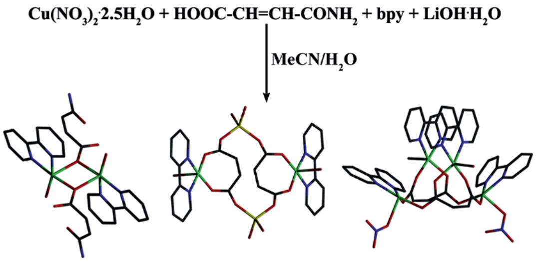
The structures of the two new compounds $[A^I(18\text{-crown-6})][B(CN)_4]$ (A^I = Cs, Rb) consist of unprecedented double-row chains of alkaline metal cations interconnected by $[B(CN)_4]^-$ ions, with two completely different connectivity modes for the two compounds.

Cu(II) Maleamate/Maleate Complexes

K. N. Lazarou, A. K. Boudalis, S. P. Perlepes, A. Terzis, C. P. Raptopoulou* ... 4554–4563

💻 Maleamate(−1) and Maleate(−2) Copper(II)–2,2′-Bipyridine Complexes: Synthesis, Reactivity and Structural and Physical Studies

Keywords: Amides / Hydrolysis / Copper / Magnetic properties



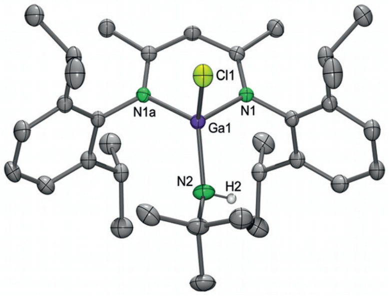
The reactions of $Cu(NO_3)_2{\cdot}2.5H_2O$ with the maleamate(−1) ligand, in the presence of 2,2′-bipyridine, give dinuclear and tetranuclear complexes; in some cases, an interesting Cu^{II}-assisted/promoted transformation of the maleamate(−1) ion to the maleate(−2) ligand is observed.

Gallium Amides

D. Solis-Ibarra, A. P. Gómora-Figueroa, N. Zavala-Segovia, V. Jancik* 4564–4571

β-Diketiminate Gallium Amides: Useful Synthons in Gallium Chemistry

Keywords: Gallium / Amides / O ligands / Aluminum



β-Diketiminate gallium amides with a general formula of either $LGa(NHR)_2$ (L = $[HC\{C(Me)N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)\}_2]^-$, R = Et, *i*Pr, *n*Bu, Ph) or LGa(NHR)Cl (R = *t*Bu, Et) were prepared. $LGa(NHEt)_2$ was used for the preparation of $LGa(OEt)_2$ and $LGa(OH)_2$ in quantitative yields. Furthermore, LGa(OEt)Cl can be obtained by ethanolysis of LGa(NH*t*Bu)Cl.

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