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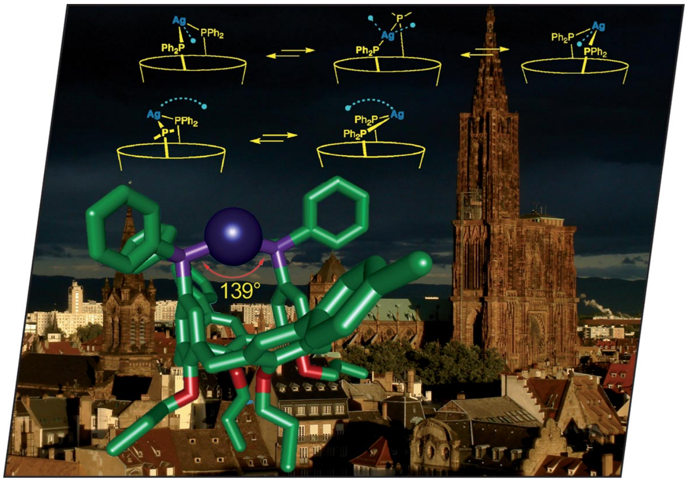
COVER PICTURE

The cover picture shows the structure of a calix[4]arene-based ligand with an unusually large bite angle. Calix[4]arenes constitute versatile macrocyclic compounds, which can be obtained by condensation of phenols with formaldehyde. The so-called CALDIPs, which are diphosphanes built upon such a skeleton, have recently found applications in a variety of C–C bond-forming reactions, including polymerisation reactions. In the presence of group 8–10 transition metals, CALDIP ligands form straightforwardly dynamic chelate complexes, in which the ligand bite angle undergoes periodic variation. In the article by C. Jeunesse, D. Matt et al. on p. 4917ff, a new chelate complex is described in which a CALDIP ligand adopts an unexpectedly large bite angle of 139°, which thus illustrates the great flexibility of the calix[4]arene core. The key ligand is depicted as superimposed over the sky of Strasbourg city (photo courtesy of Dr. R. Ruppert, UdS). Phenol–formaldehyde condensation products were already synthesised in Strasbourg by A. Baeyer in 1872.



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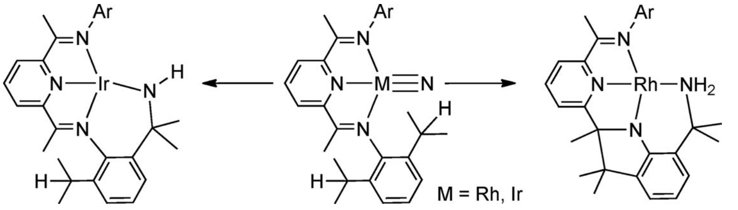
SHORT COMMUNICATION

Tuck-in Complexes

J. Schöffel, N. Šušnjar, S. Nückel, D. Sieh, P. Burger* **4911–4915**

4d vs. 5d – Reactivity and Fate of Terminal Nitrido Complexes of Rhodium and Iridium

Keywords: C–H activation / Rhodium / Iridium / Nitrido complexes / Dinitrogen complexes



C–H activation by terminal nitrido complexes of rhodium and iridium: Different reactivities of Rh– and Ir–azido complexes are observed upon thermally induced N_2 extrusion.

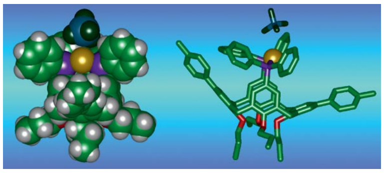
FULL PAPERS

Calixarene Chelator

S. Sameni, C. Jeunesse,* M. Awada, D. Matt,* R. Welter **4917–4923**

Unusually Large Bite Angle of a Distally Diphosphanylated Calix[4]arene Chelator

Keywords: Calixarenes / Diphosphane / Nickel / Silver / Chelates / Strained ligands



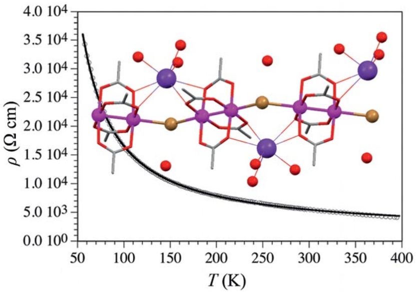
An upper-rim, distally diphosphanylated calix[4]arene readily forms a complex with $AgBF_4$. In the solid state the ligand displays an unexpectedly large bite angle of 138.8°, which reflects the flexibility of the calixarene skeleton. In solution the silver atom moves rapidly between two positions lying on either side of the calixarene axis.

Conductor Dirhodium Polymers

P. Amo-Ochoa, R. Jiménez-Aparicio,* M. R. Torres, F. A. Urbanos, A. Gallego, C. J. Gómez-García **4924–4932**

MMX Chains and Molecular Species Containing Rh_2^{n+} (n = 4, 5, and 6) Units: Electrical Conductivity in Crystal Phase of MMX Polymers

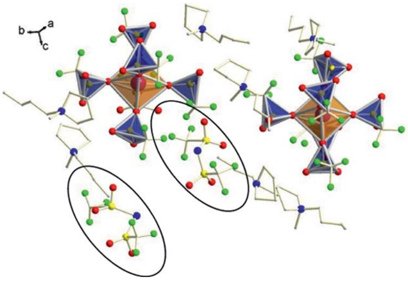
Keywords: Rhodium / Polymers / Conducting materials / Metal-metal interactions / Molecular wires / Electrical properties / Metal-organic frameworks / Paddle-wheel compounds



The first polymeric tetracarboxylato derivatives containing the Rh_2^{4+} core and a molecular species of Rh_2^{6+}, are presented, together with two new examples of tetracarboxylato complexes with mixed valence (Rh_2^{5+}). The isolation on surface of single chain fibres, and the detected electrical conductivity in some of the reported species make them suitable as molecular wires.

Ligand Exchange in Ionic Liquids

Solvation and ligand exchange reactions of ytterbium(III) as a model for the later trivalent lanthanides have been studied in triflate and bistriflylamide ionic liquids (ILs) with the purpose of contributing to a wider understanding of organometallic catalysis, as well as separation and nuclear fuel reprocessing, in ILs.



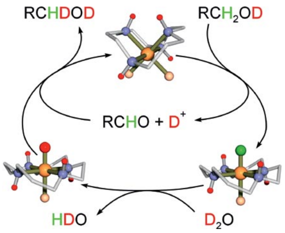
A. Babai, S. Pitula,
A.-V. Mudring* **4933–4937**

Structural and Electrochemical Properties of Yb^{III} in Various Ionic Liquids

Keywords: Lanthanides / Ionic liquids / Solvation / Structure elucidation / Ytterbium

Primary Alcohols

The catalytic H/D exchange in primary alcohol substrates, promoted by a macrocyclic rhodium(III) complex, occurs by a reversible redox reaction that gives aldehyde and a rhodium–hydride complex. Hydride exchange in the latter complex promotes the introduction of solvent hydrogen in the primary alcohol formed by the reverse reaction.



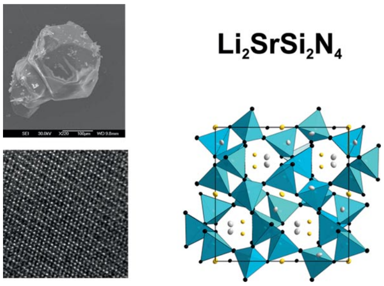
J. Eriksen, L. Mønsted, O. Mønsted,*
C. E. Olsen,
S. J. C. Schäffer **4938–4944**

Initial Stages in the Rhodium(III)-Catalyzed C–H Bond Activation of Primary Alcohols in Aqueous Solution

Keywords: Homogeneous catalysis / Rhodium / C–H activation / Alcohols / Aqueous media

Lithium Nitridosilicates

The crystal structures of the novel framework lithium nitridosilicates $Li_2MSi_2N_4$ (M = Ca, Sr) have been determined. $Li_2MSi_2N_4$ consists of a three-dimensional corner sharing $[SiN_4]$ network with the metal ions in the voids. The ^7Li and ^{29}Si solid-state NMR spectra of $Li_2SrSi_2N_4$ are reported. EELS measurements gave a deeper insight into the lithium surrounding.



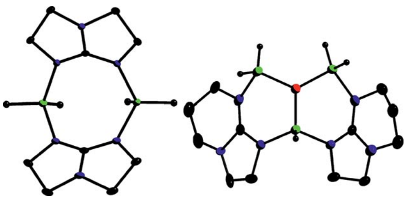
M. Zeuner, S. Pagano, S. Hug, P. Pust,
S. Schmiechen, C. Scheu,
W. Schnick* **4945–4951**

$Li_2CaSi_2N_4$ and $Li_2SrSi_2N_4$ – a Synthetic Approach to Three-Dimensional Lithium Nitridosilicates

Keywords: Solid-state reactions / Lithium / Nitridosilicates / Solid-state NMR

Gallium Hydrides

Reaction between $Me_3N{\cdot}GaH_3$ and the bicyclic guanidine htbo affords a new binuclear Ga hydride which eliminates further H_2 already at room temp. in solution. In the presence of H_2O trinuclear Ga hydrides are formed.



D. Rudolf, E. Kaifer,
H.-J. Himmel* **4952–4961**

Novel Bi- and Trinuclear Gallium Halides and Hydrides with Acyclic and Bicyclic Guanidinate Substituents: Synthesis and Reactivity

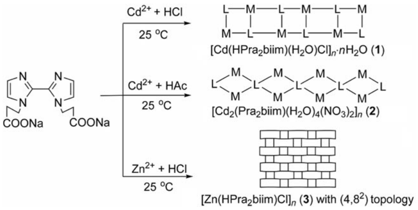
Keywords: Gallium / Guanidines / Hydrides / Binuclear compounds

Inorganic–Organic Polymers

R.-L. Sang, L. Xu* 4962–4968

Construction of a Series of 1D and 2D Inorganic–Organic Hybrid Coordination Polymers Based on 1,1′-Bis(propionic acid)-2,2′-biimidazole

Keywords: Organic-inorganic hybrid composites / Coordination polymers / Polymers / N ligands / Cadmium / Zinc



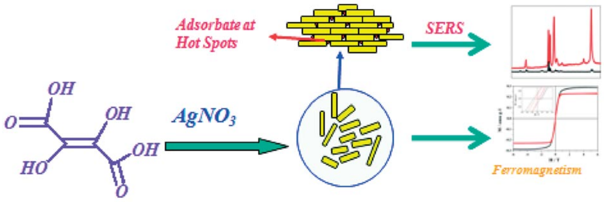
Three novel coordination polymers of d^{10} metal ions and the newly designed Pra_2biim^{2-} with three different coordinating modes have been synthesized and characterized by X-ray crystallography and luminescence spectroscopy.

Silver Nanorods

S. Mohapatra, S. Siddhanta,
D. R. Kumar, C. Narayana,*
T. K. Maji* 4969–4974

Facile and Green Synthesis of SERS Active and Ferromagnetic Silver Nanorods

Keywords: 2,3-Dihydroxyfumaric acid / Nanostructures / Silver / Ferromagnetism / Surface-enhanced Raman scattering / Hot spots



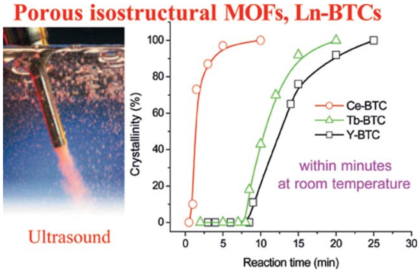
We have developed a novel method employing a new reducing agent for the synthesis of silver nanorods having excellent SERS sensitivity and trace detection of the adsorbate molecules (thiophenol and Rhodamine 6G) up to picomolar concentrations.

Metal-Organic Frameworks

N. A. Khan, M. M. Haque,
S. H. Jhung* 4975–4981

Accelerated Syntheses of Porous Isostructural Lanthanide–Benzenetricarboxylates (Ln–BTC) Under Ultrasound at Room Temperature

Keywords: Metal-organic frameworks / Lability / Ultrasound / Synthetic methods / Kinetics



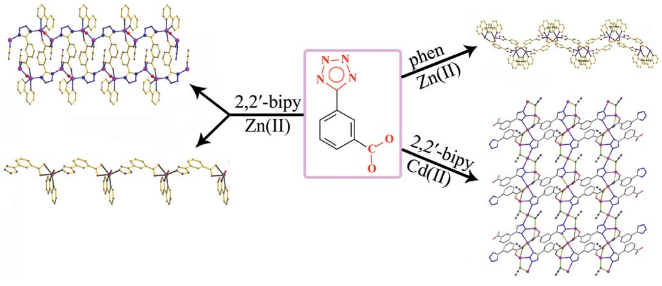
Isostructural Ln–BTCs (Ln: Ce, Tb, and Y) with a small size and high porosity are synthesized under ultrasound within minutes under ambient conditions. The synthesis rates of the Ln–BTCs are $r_{Ce-BTC} > r_{Tb-BTC} > r_{Y-BTC}$, which shows the importance of lability/inertness of the metal ions in the synthesis kinetics.

Structures and Luminescence

F. Chen, M.-F. Wu, G.-N. Liu,
M.-S. Wang, F.-K. Zheng,* C. Yang,
Z.-N. Xu, Z.-F. Liu, G.-C. Guo,*
J.-S. Huang 4982–4991

Zinc(II) and Cadmium(II) Coordination Polymers Based on 3-(5*H*-Tetrazolyl)benzoate Ligand with Different Coordination Modes: Hydrothermal Syntheses, Crystal Structures and Ligand-Centered Luminescence

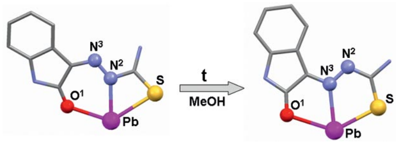
Keywords: Cadmium / Zinc / Hydrothermal synthesis / Photochemistry / Luminescence



Four Zn^{II}/Cd^{II} coordination polymers based on the 3-(5*H*-tetrazolyl)benzoate ($3-tzba^{2-}$) ligand exhibit various polymeric frameworks with the introduction of different auxiliary ligands. The $3-tzba^{2-}$ ligand displays flexible coordination modes. Ligand-centered photoluminescent emissions are active in these polymers and can be altered by changing the organic ligands in the polymer.

Thiosemicarbazone Lead Complexes

Solid state and solution studies indicated that, in the title derivatives, the thiosemicarbazone chain is initially bound by N^2,S coordination, but evolves with time to form the N^3,S-linkage isomer.



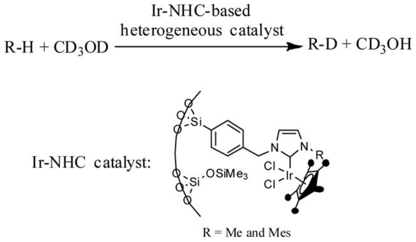
J. S. Casas,* N. Casanova, M. S. García-Tasende, A. Sánchez, J. Sordo, Á. Touceda, S. Vázquez 4992–5004

Back to the Coordination Modes of the Thiosemicarbazonate Chain: New Insights from Diorganolead(IV) and Lead(II) Derivatives of Isatin-3-thiosemicarbazone

Keywords: Lead / Coordination modes / Thermodynamics

Molecular Catalytic Material

Highly active and single-site Ir–NHC-containing materials have been synthesized and characterized. Their catalytic performances in C–H bond activation of several substrates have been studied, and it has been shown that the local confinement around the metal centre (size of the NHC ligand, proximity to the surface and size of the passivating groups), and not the pore size, has a major effect.



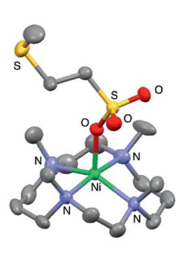
T. K. Maishal, M. Boualleg, M. Bouhrara, C. Copéret, E. Jeanneau, L. Veyre, C. Thieuleux* 5005–5010

Domination of Local Environment Over Pore Confinement Effects on the Catalytic Performances of Single-Site Cp*Ir^{III}-NHC Heterogeneous vs. Homogeneous H/D Exchange Catalysts

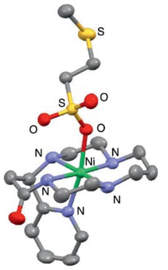
Keywords: Iridium / Mesoporous materials / Heterogeneous catalysis / Homogeneous catalysis / C-H activation

Enzyme Models

A series of tetraazamacrocyclic nickel(II) complexes coordinated by methyl coenzyme M (MeSCoM), coenzyme M (HSCoM), and 3-methylthiopropionate (Metp) have been synthesized as structural models of the active site of methyl coenzyme M reductase in the oxidized MCR_{silent} state.



RSRS-[Ni(tmc)(MeSCoM)]$^+$



[Ni(pyc)(MeSCoM)]$^+$

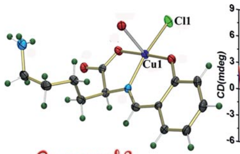
J. Nishigaki, T. Matsumoto, K. Tatsumi* 5011–5017

Coordination of Coenzyme M and Its Derivatives on Ni^{II}(tetraazacycle) Complexes: A Model for the Active Site of Methyl Coenzyme M Reductase

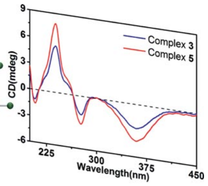
Keywords: Enzyme models / Nickel / Tetraazamacrocycle / Methanogenesis / Methane

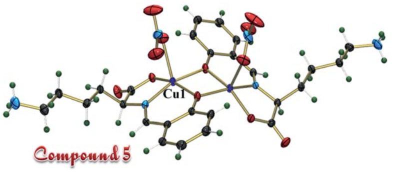
Mono- and Dicopper(II) Complexes

Five new copper(II) complexes (three mono and two dinuclear) were synthesized by a one-pot method in which the Schiff-base ligands were formed in situ and characterized by various spectroscopic techniques and single-crystal X-ray diffraction.



Compound 3





Compound 5

S. Khatua, J. Kang, K. Kim, J. O. Huh, J. Lee, C. S. Hong, D. G. Churchill* 5018–5026

Crystal Structures and Magnetic Properties of Newly Synthesized Mono- and Dinuclear Cu^{II} Schiff-Base Complexes

Keywords: Copper / Schiff bases / Magnetic properties / Hydrogen bonds

CONTENTS

Lead(II) Cryptates

D. Esteban-Gómez, T. Enríquez-Pérez, R. Ferreirós-Martínez, M. Mato-Iglesias, C. Platas-Iglesias, A. de Blas,* T. Rodríguez-Blas* .... **5027−5034**

Lead(II) Complexes of Lateral Macrobicyclic Receptors That Incorporate a Crown Moiety and a Pyridine Head Unit

Keywords: Macrocycles / N,O ligands / Lead / Crown compounds / Cryptands

The coordinative properties towards lead(II) of two lateral macrobicyclic receptors that incorporate either a 1,10-diaza-[15]crown-5 (**L**^{7}) or a 4,13-diaza-[18]crown-6 (**L**^{8}) fragment are reported. Their protonation constants as well as the stability constants of their Pb^{II} complexes have been investigated by using potentiometric titrations.

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* Author to whom correspondence should be addressed.

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