CONTENTS

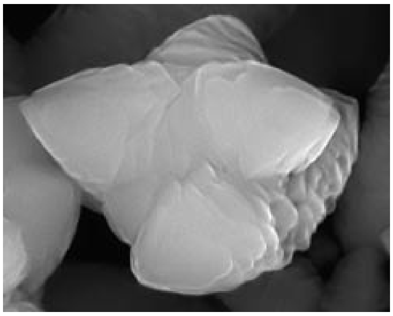
FULL PAPERS

Biominerals

M. Neumann, M. Epple* 1953–1957

Monohydrocalcite and Its Relationship to Hydrated Amorphous Calcium Carbonate in Biominerals

Keywords: EXAFS spectroscopy / Biomineralisation / Materials science / Monohydrocalcite / Bioinorganic chemistry



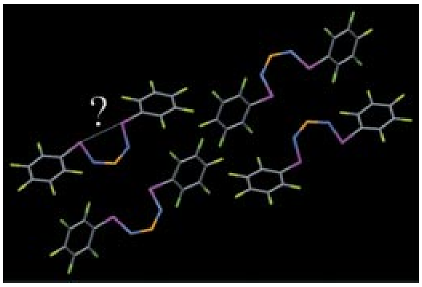
Hydrated amorphous calcium carbonate (ACC) is often postulated as an intermediate and final phase in biomineralisation. The crystalline phase monohydrocalcite ($CaCO_3{\cdot}H_2O$) is prepared, characterised and compared to biogenic calcium carbonate phases.

Chalcogen-Nitrogen Compounds

K. Tersago, I. Yu. Bagryanskaya,
Yu. V. Gatilov, S. A. Gromilov,
A. Yu. Makarov, M. Mandado,
C. Van Alsenoy, A. V. Zibarev,*
F. Blockhuys* 1958–1965

Insight Into the Intermolecular Factors Responsible for the *Z*,*Z* Configuration of Ar–X–N=S=N–X–Ar (X = S, Se) Derivatives in the Solid State

Keywords: Chalcogen-nitrogen chains / Crystal packing / Density functional theory / Molecular configurations / X-ray diffraction



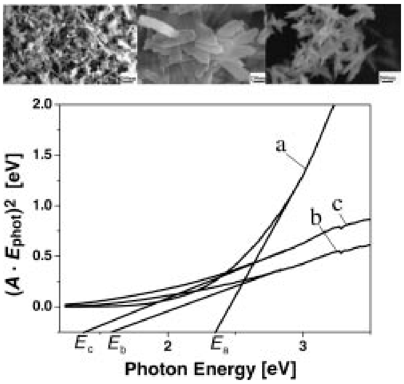
For derivatives of Ph–X–N=S=N–X–Ph (X = S, Se) the predominance of the *Z*,*Z* configuration in the solid state can not be explained by intramolecular stereoelectronic effects. Calculation of the packing energies and densities reveals that the crystal packing of the structures in the *Z*,*Z* configuration has a systematic preference over the corresponding packing in the *Z*,*E* configuration. As a result, packing forces are most likely responsible for the dominance of the *Z*,*Z* configuration in the crystal.

CuO Nanostructures

H.-M. Xiao, S.-Y. Fu,* L.-P. Zhu,
Y.-Q. Li, G. Yang 1966–1971

Controlled Synthesis and Characterization of CuO Nanostructures through a Facile Hydrothermal Route in the Presence of Sodium Citrate

Keywords: Hydrothermal synthesis / Nanostructures / Sodium citrate / Copper complexes



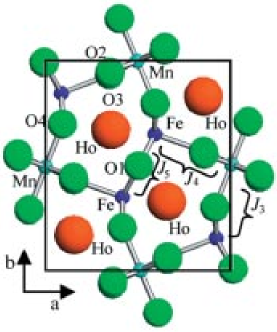
1D, 2D, and 3D CuO nanostructures have been synthesized by a hydrothermal process in the presence of sodium citrate. The bandgap energies of the nanostructures have been determined by ultraviolet absorption spectroscopy.

Ferrimagnets

A. Muñoz,* J. A. Alonso,
M. J. Martínez-Lope,
J. L. Martínez 1972–1979

Synthesis and Study of the Crystallographic and Magnetic Structure of $HoFeMnO_5$

Keywords: Ferrimagnetic structure / Superexchange interactions / Neutron diffraction / High oxygen pressure



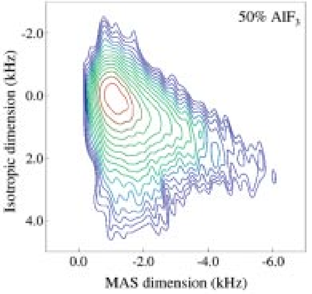
$HoFeMnO_5$ has been obtained by replacing Mn^{3+} cations by Fe^{3+} in $HoMn_2O_5$. $HoFeMnO_5$ adopts a collinear ferrimagnetic structure below $T_C \approx 153$ K; the magnetic moments are oriented along the *c* direction. There is a frustration concerning the long-range ordering of the Ho^{3+} moments at low temperature.

^{27}Al NMR Spectroscopy

M. Body,* C. Legein, J.-Y. Buzaré, G. Silly **1980–1988**

The Relationship Between ^{27}Al Quadrupolar Parameters and AlF_6^{3-} Octahedron Connectivity in Crystalline and Glassy Fluoroaluminates

Keywords: Glasses / Fluorides / ^{27}Al NMR spectroscopy / Quadrupolar parameters



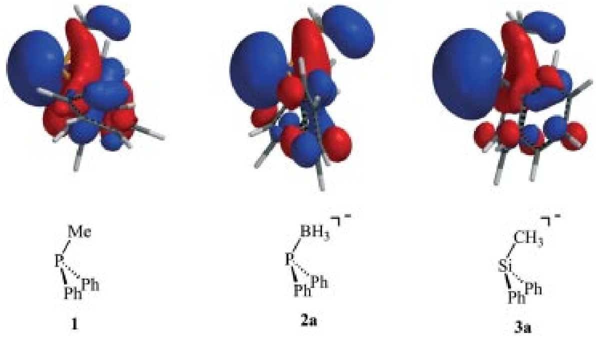
Correlation of ^{27}Al NMR results for glassy and crystalline phases enables an accurate picture to be gained of the glass network through the dependence of the quadrupolar parameters on the octahedron connectivity.

Ligand Donor Properties

T. I. Kückmann, F. Dornhaus, M. Bolte, H.-W. Lerner, M. C. Holthausen,* M. Wagner* **1989–2003**

Broadening the Scope of Ancillary Phosphane-Type Ligands: A Systematic Comparison of PR_3, $PR_2BH_3^-$, and SiR_3^- and Their Chalcogen Derivatives

Keywords: Isoelectronic analogs / P ligands / Si ligands / Ligand design / Boron



Phosphane derivatives are ubiquitous ligands in coordination chemistry. It is demonstrated that key properties of this ligand system can be further developed by using corresponding isolobal, negatively charged phosphanyl borohydride ($PR_2BH_3^-$) and silyl (SiR_3^-) derivatives to generate a broad spectrum of related species with smoothly varying donor capacities.

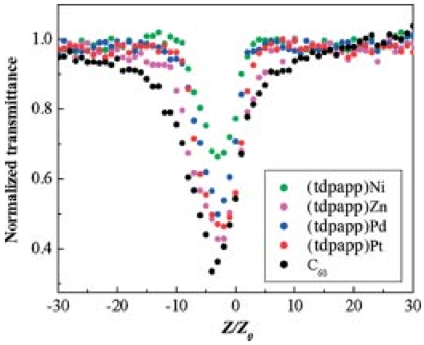
Optical Limiting

S. Fu, X. Zhu, G.-J. Zhou, W.-Y. Wong, C. Ye, W.-K. Wong,* Z. Li* **2004–2013**

Synthesis, Structures and Optical Power Limiting of Some Transition Metal and Lanthanide Monoporphyrinate Complexes Containing Electron-Rich Diphenylamino Substituents

Keywords: Lanthanides / Optical limiting / Photoluminescence / Porphyrins / Transition metals

The synthesis, structural characterization and optical limiting properties of a series of transition metal and lanthanide monoporphyrinate complexes functionalized with diphenylamino units are described. The performance of these optical power limiters is compared with those of benchmark materials.



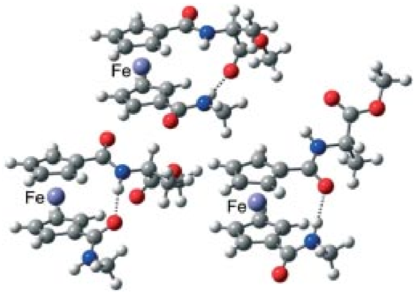
Ferrocene Amides

J. Lapić, D. Siebler, K. Heinze,* V. Rapić* **2014–2024**

Conformational Analysis of Heteroannularly Substituted Ferrocene Oligoamides

Keywords: Conformation analysis / Density functional calculations / Hydrogen bonds / Metallocenes / Molecular modelling

^{1}H NMR spectroscopic variation ratio analysis of asymmetrically substituted ferrocene derivatives suggests that an increase in the steric demand of the amino acid side chains favours conformations with hydrogen-bonded FnCO*NH*Me groups. CD spectroscopy of chiral derivatives reveals that (*P*)-helical conformations predominate in solution.



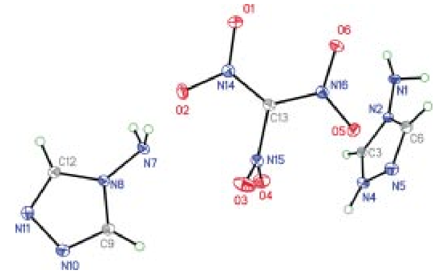
CONTENTS

Energetic Salts

Y. Huang, H. Gao, B. Twamley,
J. M. Shreeve* .... 2025−2030

Synthesis and Characterization of New Energetic Nitroformate Salts

Keywords: Nitroform / Energetic salt / Oxygen balance



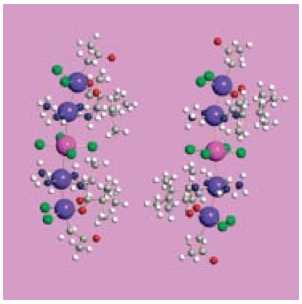
Energetic nitroformates with high-nitrogen cations were synthesized and characterized. Theoretical performance calculations indicate that these materials have properties which compare favorably with hydrazinium nitroformate, TNT and Tetryl suggesting potential applications as eco-friendly oxidizers.

Mixed-Valent PtPd Chains

S. Arai, M. Ochiai, K. Ishihara,*
K. Matsumoto* .... 2031−2039

Mixed-Valent Linear Chain Pt_2PdPt_2 Complexes

Keywords: Platinum / Palladium / Chain structures / Metal−metal interactions / Mixed-valent compounds



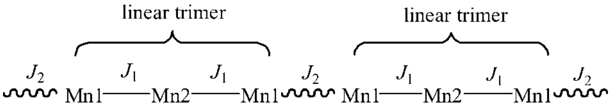
Pentanuclear linear-chain PtPd complexes composed of a monomeric Pd^{II} complex sandwiched by two amidato-bridged dimeric Pt^{III} units were synthesized. The PtPd complexes have either an arch or a sigmoid backbone structure, depending on the solvent used. The UV/Vis/NIR spectra clearly show the existence of quite rare charge transfer from Pd to Pt in the PtPd complexes.

Mn^{II} Ferrocenecarboxylato Complexes

Z.-L. Chen, Y.-S. Ma, F.-P. Liang,*
Z.-H. Zhou .... 2040−2045

Synthesis, Crystal Structure, and Magnetic Properties of Two Manganese(II) Polymers Bearing Ferrocenecarboxylato Ligands

Keywords: Manganese / Crystal structure / Ferrocenecarboxylato / Magnetic properties



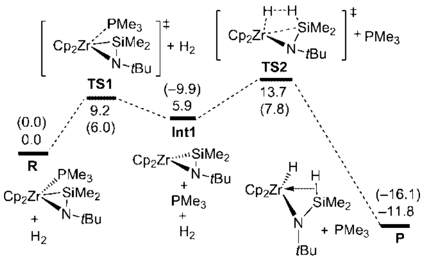
Two Mn^{II} polymers bearing ferrocenecarboxylato ligands and having repeating linear trinuclear $-Mn-(\mu_2\text{-COO})_n-Mn-(\mu_2\text{-COO})-Mn-(\mu_2\text{-COO})-Mn-(\mu_2\text{-COO})_n-Mn-$ (n = 4 and 2 for **1** and **2**, respectively) building blocks were prepared and characterized. Magnetic susceptibility measurements revealed a weak antiferromagnetic coupling for both complexes with an unprecedented $J_1-J_1-J_2$ (AF1−AF1−AF2) repeating sequence.

Insertion Mechanisms

S. Bi,* S. Zhu, Z. Zhang .... 2046−2054

Mechanisms of H_2, $H_2C=CH_2$, and $O=CH_2$ Insertion into $Cp_2Zr(\eta^2\text{-}SiMe_2=N\mathit{t}Bu)(PMe_3)$

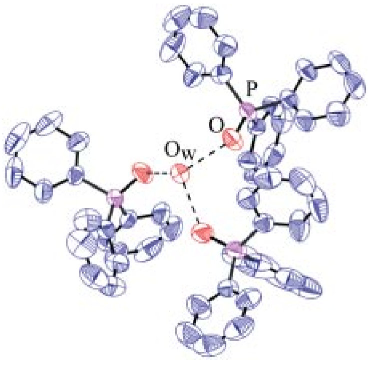
Keywords: Zirconium / Silanimines / Insertion / Mechanism



Mechanisms of H_2, $H_2C=CH_2$, and $O=CH_2$ insertion into $Cp_2Zr(\eta^2\text{-}SiMe_2=N\mathit{t}Bu)(PMe_3)$ are theoretically investigated with the aid of DFT calculations. The regiochemistry for $O=CH_2$ insertion has been theoretically explored.

Hydrogen Bonding

The new cluster compounds $[H_3O(Ph_3PO)_3]_2[Mo_6Cl_{14}]$ and $[H(Ph_3PO)_2]_2[Re_6S_6Br_8]$ have been studied by single-crystal X-ray diffraction and solid-state NMR and luminescence spectroscopy; strong hydrogen bonds are found in the complex cations.

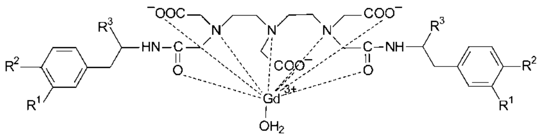


Z. S. Kozhomuratova, Y. V. Mironov, M. A. Shestopalov, I. V. Drebushchak, N. K. Moroz, D. Y. Naumov, A. I. Smolentsev, E. M. Uskov, V. E. Fedorov* **2055–2060**

Synthesis, Structures and Properties of Cluster Complexes $[H_3O(Ph_3PO)_3]_2[Mo_6Cl_{14}]$ and $[H(Ph_3PO)_2]_2[Re_6S_6Br_8]$

Keywords: Cluster compounds / Molybdenum / Rhenium / Triphenylphosphane oxide / Crystal structure / NMR spectroscopy / Hydrogen bonding

MRI Contrast Agents



Three new potential MRI contrast agents, gadolinium complexes of DTPA-bis(tyramide), DTPA-bis(3-hydroxytyramide) and DTPA-bis(phenylalanine ethyl ester), were studied in vitro by ^{17}O NMR spectroscopy and by nuclear magnetic relaxation dispersion (NMRD) measurements. In view of the data, the best candidate is the Gd complex of DTPA-bis(tyramide).

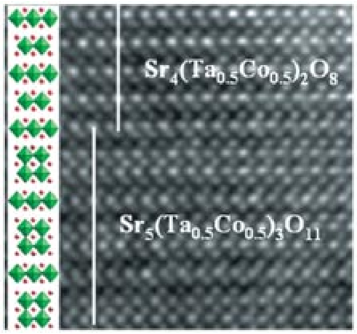
S. Laurent, T. N. Parac-Vogt,* K. Kimpe, C. Thirifays, K. Binnemans, R. N. Muller, L. Vander Elst* **2061–2067**

Bis(phenylethylamide) Derivatives of Gd-DTPA as Potential Receptor-Specific MRI Contrast Agents

Keywords: Lanthanides / MRI contrast agents / N,O ligands / NMRD / ^{17}O NMR spectroscopy

Layered Perovskites

An example of a noninteger member in the Ruddlesden–Popper series is found in a layered perovskite. The crystal is constituted by two structurally different domains; one corresponds to the n = 1 Sr_4CoTaO_8 Ruddlesden–Popper phase whereas the other corresponds to the n = 1.5 term and is associated to a chemical composition of $Sr_5(Co_{0.5}Ta_{0.5})_3O_{11}$.

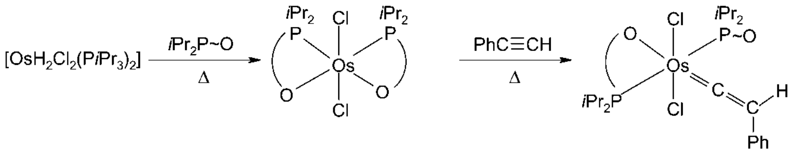


K. Boulahya, M. Parras, J. M. González-Calbet* **2068–2071**

Structural Chemistry of an n = 1 Member of the Ruddlesden–Popper $Sr_{n+1}(Co_{0.5}Ta_{0.5})_nO_{3n+1}$ Homologous Series: Sr_4CoTaO_8

Keywords: Electron diffraction / X-ray diffraction / Electron microscopy / Magnetic properties

Hemilabile Ligands



With the highly reactive dihydridoosmium(IV) compound $[OsH_2Cl_2(PiPr_3)_2]$ as the starting material, a series of osmium(II) and osmium(IV) complexes with phosphane–ethers, –esters, and –amines as mono- and bidentate ligands were prepared. The hemilabile nature of the functionalized phosphanes was illustrated by the reactions with CO, CN*t*Bu, and phenylacetylene, the latter yielding (vinylidene)osmium(II) complexes, which in solution at room temperature are fluxional on the NMR timescale.

B. Weber, H. Werner* **2072–2082**

Osmium(II) and Osmium(IV) Complexes with Phosphane–Ethers, –Esters, and –Amines as Mono- and Bidentate Ligands

Keywords: Osmium / Phosphane–Ethers / Phosphane–Esters / Phosphane–Amines / Vinylidene complexes

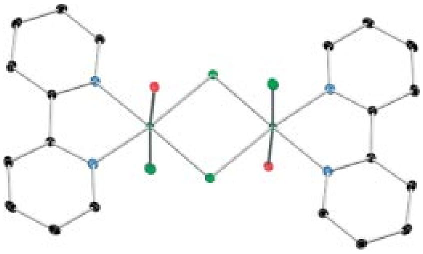
CONTENTS

Ferromagnetic Dimers

O. F. Ikotun, W. Ouellette, F. Lloret, M. Julve,* R. P. Doyle* 2083–2088

Synthesis, X-ray Structure, Thermal and Magnetic Behavior of $[(bipy)_2Ni_2(\mu\text{-}Cl)_2Cl_2(H_2O)_2]$: The First Neutral Ferromagnetically Coupled Six-Coordinate Dichlorido-Bridged Nickel(II) Dimer

Keywords: Crystal structures / Nickel complexes / Ferromagnetic coupling / Thermal analysis



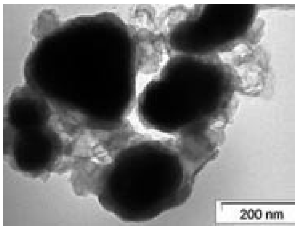
$[(bipy)_2Ni_2(\mu\text{-}Cl)_2Cl_2(H_2O)_2]$ (C = black; N = blue; Ni = green, small; Cl = green, large; O = red) exhibits the strongest ferromagnetism for a dichlorido-bridged dinuclear nickel(II) complex reported to date.

Core-Shell Nanostructures

S. V. Pol, V. G. Pol, I. Felner, A. Gedanken* 2089–2096

The Thermal Decomposition of Three Magnetic Acetates at Their Autogenic Pressure Yields Different Products. Why?

Keywords: Decomposition / Acetates / Magnetic properties / Core-shell nanostructures



The reproducible and straightforward approach for the synthesis of fullerene-like Ni@C, Co@C and Fe_3O_4@C core-shell nanostructures is reported. Although identical reaction parameters are employed with the three acetate precursors, graphitic carbon is coated on nanosized metallic Ni and Co cores, while metallic Fe is not formed. Fe_3O_4 forms but maintains the same core-shell morphology.

If not otherwise indicated in the article, papers in issue 13 were published online on April 16, 2007