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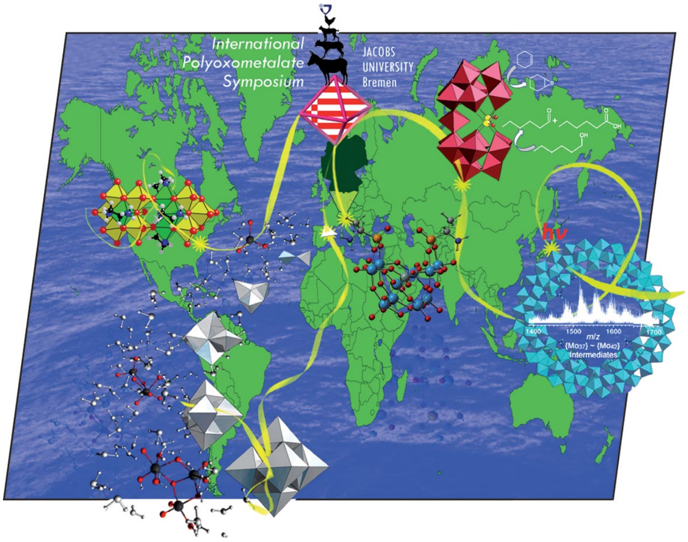
A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further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

COVER PICTURE

The cover picture depicts not only the internationality of the polyoxometalate community, well-reflected at the International Polyoxometalate Symposium (Jacobs University, Bremen July 28–August 1, 2009) on which this cluster issue is based, but also the huge scope of these compounds. The diversity of aspects in this issue is highlighted on the cover by a selection of graphics placed over the country of origin of the authors. Structural features (M. T. Pope et al.), mechanisms of formation (J. Poblet et al.), homogeneous oxidation catalysis (O. Kholdeeva et al.), design of enantioselective catalysts (M. Bonchio et al.) and photochemistry-based analytical techniques (T. Yamase et al.) are some of the topics you will find. Mr Rami Al-Oweini (Jacobs University) is thanked for his creative design.



CONTENTS

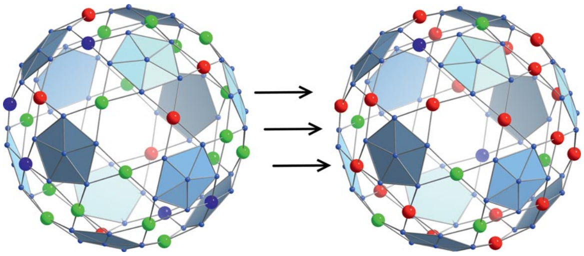
SHORT COMMUNICATIONS

Giant Molybdate Molecular Magnets

B. Botar,* A. Ellern, M. T. Sougrati, P. Kögerler* 5071–5074

Removing Compositional Boundaries in Mixed-Linker Keplerate Clusters

Keywords: Cluster compounds / Molybdenum / Iron / Vanadium / Polyoxometalates / Metal-metal interactions / Molecular magnetism



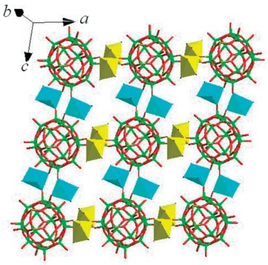
Controlling the reducing conditions in the self-assembly condensation process of molybdates with iron(II) and vanadyl heteroions affords a mixed-linker Keplerate with an unprecedentedly high Fe/V ratio. This new synthetic approach directly addresses the linker composition and thus the electronic and magnetic properties of such mixed-spin clusters.

Polyoxometalate Networks

J. Zhou, S.-T. Zheng, W.-H. Fang, G.-Y. Yang* 5075–5078

A New 2-D Network Containing $\{As_4V_{16}O_{42}(H_2O)\}$ Cluster Units

Keywords: Hydrothermal synthesis / Polyoxometalates / Arsenic / Vanadium / Cluster compounds



A new 2-D As–V–O network are built by rare $\{As_4V_{16}O_{42}(H_2O)\}$ cluster units and two types of Cd complex bridges, showing the special sql type net with double edges.

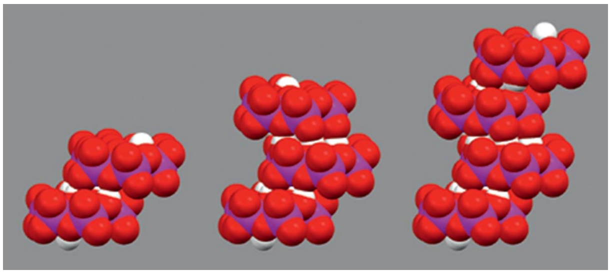
FULL PAPERS

Polyoxometalate Stacks

V. W. Day,* J. C. Goloboy, W. G. Klemperer,* 5079–5087

Synthesis and Solid State Structures of the Hydrogen-Bonded Hexamolybdoplatinate(IV) Tetramer $[(PtMo_6O_{24})_4H_{23}]^{9-}$ and the Hexamolybdoplatinate(IV) Trimers $[(PtMo_6O_{24})_3H_{16}]^{8-}$ and $[(PtMo_6O_{24})_3H_{14}]^{10-}$

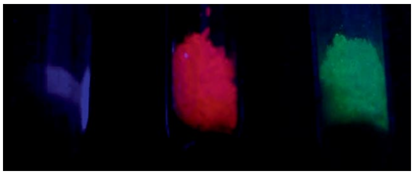
Keywords: Polyoxometalates / Hydrogen bonds / Platinum / Molybdenum



The $[(PtMo_6O_{24})_2H_9]^{7-}$, $[(PtMo_6O_{24})_3H_{16}]^{8-}$, and $[(PtMo_6O_{24})_4H_{23}]^{9-}$ anions form a homologous series of hydrogen-bonded stacks of protonated 1:6 platinomolybdate ions.

Lanthanopolyoxometalate Hybrids

Organic−inorganic hybrid materials were prepared by combining Wells−Dawson-derived lanthanopolyoxometalate clusters and the 3-hydroxypicolinate ligand. Photoluminescent properties resulting from a synergetic combination of both organic and inorganic moieties were observed. The Eu^{III} inorganic moiety (left) and Eu and Tb^{III} hybrid materials, under 366 nm radiation, are pictured.



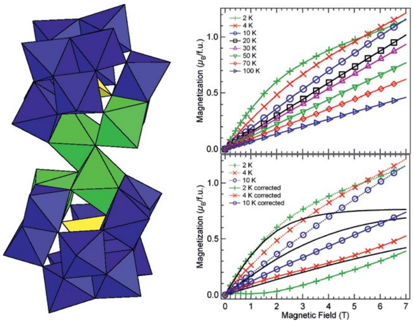
C. M. Granadeiro, R. A. S. Ferreira, P. C. R. Soares-Santos, L. D. Carlos, H. I. S. Nogueira* .... **5088−5095**

Lanthanopolyoxometalates as Building Blocks for Multiwavelength Photoluminescent Organic−Inorganic Hybrid Materials

Keywords: Polyoxometalates / Lanthanides / Organic-inorganic hybrid composites / Luminescence

Ni-Containing Tungstogermanates

The dimeric, tetranickel(II)-containing 20-tungsto-2-germanate $[\{\beta\text{-}GeNi_2W_{10}O_{36}(OH)_2(H_2O)\}_2]^{12-}$ (**1**) was synthesized by reaction of the dilacunary polyanion precursor $[\gamma\text{-}GeW_{10}O_{36}]^{8-}$ with Ni^{2+} ions in aqueous medium. Polyanion **1** was isolated in the solid state as $K_{10}Ni[\{\beta\text{-}GeNi_2W_{10}O_{36}(OH)_2(H_2O)\}_2]\cdot 28H_2O$ (KNi-**1**), which revealed antiferromagnetic coupling of the Ni_4 core.

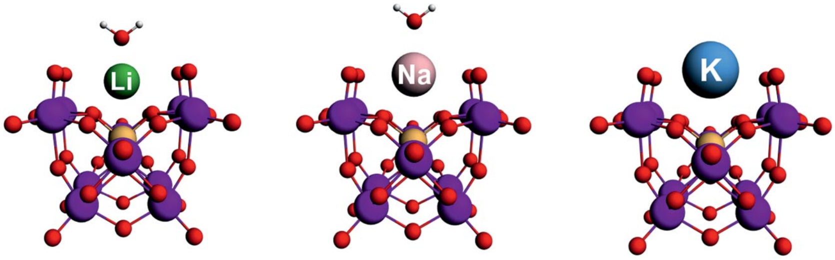


N. H. Nsouli, M. Prinz, N. Damnik, M. Neumann,* E. Talik, U. Kortz* .... **5096−5101**

Dimeric Nickel(II) Containing Tungstogermanate $[\{\beta\text{-}GeNi_2W_{10}O_{36}(OH)_2(H_2O)\}_2]^{12-}$

Keywords: Polyoxometalates / Tungsten / Nickel / Magnetic properties

NMR of Polyoxometalates



A DFT approach incorporating relativistic corrections and solvent treatment is used for calculations of ^{51}V and ^{183}W chemical shifts for a series of POMs. Dilacunary polyoxotungstates with a counterion specifically included in the lacuna are modelled, and the computed ^{183}W NMR spectra are presented. In the case of a relatively small counterion the explicit location of a water molecule in its vicinity is shown to improve the correlation between computed and experimental shifts.

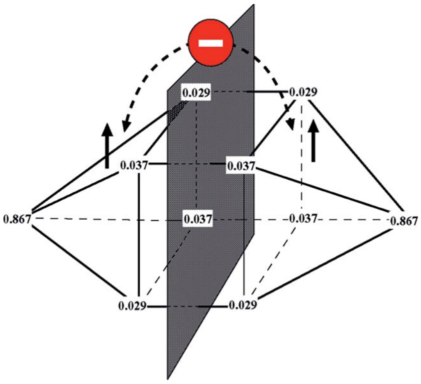
N. Vankova,* T. Heine, U. Kortz .... **5102−5108**

NMR Chemical Shifts of Metal Centres in Polyoxometalates: Relativistic DFT Predictions

Keywords: Density functional calculations / NMR spectroscopy / Polyoxometalates / Vanadium / Tungsten

A Two-Electron-Reduced POM

The magnetic properties of a mixed-valence $[GeV_{14}O_{40}]^{8-}$ polyoxometalate reduced by two electrons have been investigated. In contrast to what happens in other two-electron-reduced polyoxometalates, this compound does not show any magnetic coupling between the two unpaired electrons. The reason for this behavior is that each unpaired electron is trapped in a different half of the polyoxovanadate.



N. Suaud,* Y. Masaro, E. Coronado, J. M. Clemente-Juan, N. Guihéry .... **5109−5114**

Origin of the Paramagnetic Properties of the Mixed-Valence Polyoxometalate $[GeV_{14}O_{40}]^{8-}$ Reduced by Two Electrons: Wave Function Theory and Model Hamiltonian Calculations

Keywords: Polyoxometalates / Mixed-valent compounds / Ab initio calculations / Electron transfer / Magnetic properties

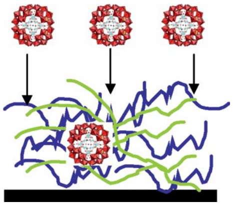
CONTENTS

Polyoxometalates in Thin Films

V. Ball,* F. Bernsmann, S. Werner, J.-C. Voegel, L. F. Piedra-Garza, U. Kortz 5115–5124

Polyoxometalates in Polyelectrolyte Multilayer Films: Direct Loading of $[H_7P_8W_{48}O_{184}]^{33-}$ vs. Diffusion into the Film

Keywords: Polyoxometalates / Polyelectrolyte multilayer films / Electrochemistry



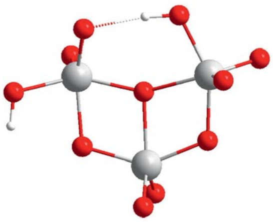
Two methods to incorporate polyoxometalates (POM) into polyelectrolyte multilayer films were investigated and compared. The first comprises the alternate deposition of a polycation and the POM. The second method has never been used to load POMs into thin films: a polyelectrolyte multilayer film is plunged into the POM solution to allow its passive diffusion into the PEM film.

Lindqvist Anion Formation

L. Vilà-Nadal, A. Rodríguez-Fortea,* J. M. Poblet* 5125–5133

Theoretical Analysis of the Possible Intermediates in the Formation of $[W_6O_{19}]^{2-}$

Keywords: Polyoxometalates / Density functional calculations / Molecular dynamics / Solvation methods / Anions



Planar W_3 building blocks

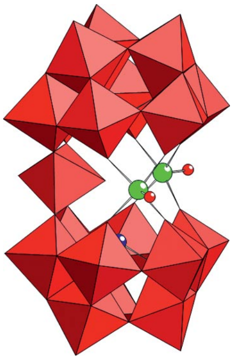
Expansion of the coordination sphere of W^{VI} ions is observed as a consequence of the interaction of the W ions with solvent molecules (water); the possible di- and trinuclear intermediates may result in the formation of the Lindqvist anion. Common structural motifs ("building blocks") are also identified for structures with higher nuclearities.

Hydrogen Peroxide Activation

O. A. Kholdeeva,* B. G. Donoeva, T. A. Trubitsina, G. Al-Kadamany, U. Kortz 5134–5141

Unique Catalytic Performance of the Polyoxometalate $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$: The Role of 5-Coordinated Titanium in H_2O_2 Activation

Keywords: Reaction mechanisms / Homogeneous catalysis / Polyoxometalates / Oxidation / Titanium



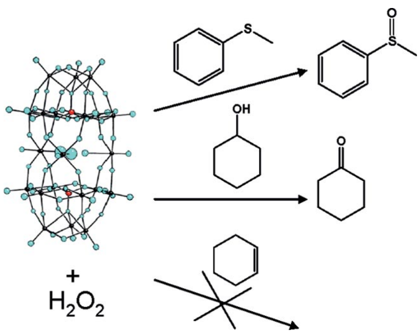
Tetra-*n*-butylammonium salts of the dititanium sandwich-type 19-tungstodiarsenate(III) $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**) containing two square-pyramidal $[Ti(OH)]^{3+}$ groups catalyze efficiently the selective oxidation of organic compounds with aqueous hydrogen peroxide by heterolytic routes.

Peroxide Activation by Tungsten

B. G. Donoeva, T. A. Trubitsina, G. M. Maksimov, R. I. Maksimovskaya, O. A. Kholdeeva* 5142–5147

Catalytic Properties and Stability of the Heteropolytungstate $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ in H_2O_2-Based Oxidations

Keywords: Heteropolytungstates / Hydrogen peroxide / Homogeneous catalysis / Oxidation / Polyoxometalates



The sandwich-type heteropolytungstate $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ catalyzes the selective oxidation of thioethers and alcohols with aqueous H_2O_2 but is not active in alkene epoxidation. The stability of this compound towards solvolytic destruction under turnover conditions was confirmed by using ^{31}P NMR, IR, and Raman spectroscopic techniques.

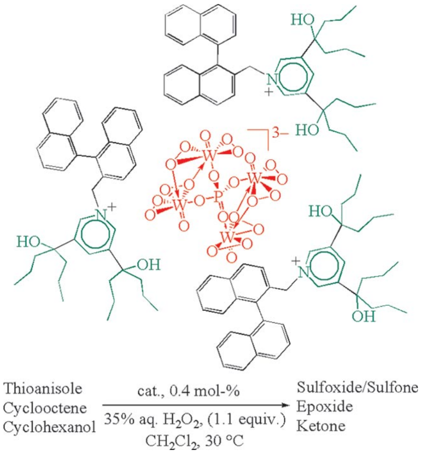
1,1′-Binaphthyl–POM Catalysts

C. Jahier, F.-X. Felpin, C. Méliet, F. Agbossou-Niedercorn, J.-C. Hierso, S. Nlate* **5148–5155**

1,1′-Binaphthyl-2-methylpyridinium-Based Peroxophosphotungstate Salts: Synthesis, Characterization, and Their Use as Oxidation Catalysts

Keywords: Dendrimers / Polyoxometalates / Oxidation / Homogeneous catalysis

A series of 1,1′-binaphthyl-2-methylpyridinium-based polyoxometalate salts was prepared in their racemic form and tested as recoverable catalysts in the oxidation of thioanisole, cyclooctene, and cyclohexanol with H_2O_2. The racemic salts were prepared with the goal of extending this synthetic route to enantiomerically pure dendritic 1,1′-binaphthyl-based POM frameworks.



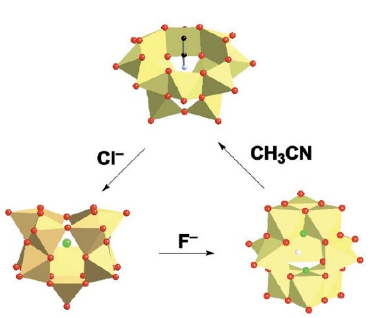
Lacunary Polyoxovanadates

K. Okaya, T. Kobayashi, Y. Koyama, Y. Hayashi,* K. Isobe **5156–5163**

Formation of V^V Lacunary Polyoxovanadates and Interconversion Reactions of Dodecavanadate Species

Keywords: Polyoxometalates / Vanadium / Host-guest systems / Template synthesis

Lacunary-type polyoxovanadates with fluoride, chloride, and bromide anion guests were isolated, and the oxidation state of all vanadium atoms was V^V. The first V^V spherical polyoxovanadates with lacunary units were produced in nonpolar solvents, and the interconversion reactions of the dodecavanadate frameworks were observed by reaction with anions.



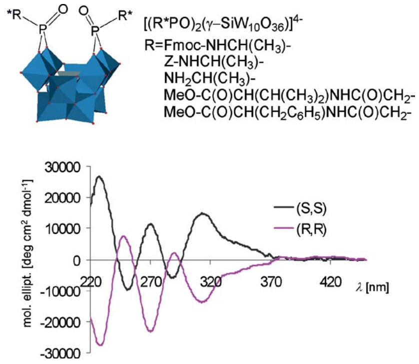
Chiral Molecular Hybrids

M. Carraro,* G. Modugno, A. Sartorel, G. Scorrano, M. Bonchio* **5164–5174**

Optically Active Polyoxotungstates Bearing Chiral Organophosphonate Substituents

Keywords: Polyoxometalates / Chirality / Organic–inorganic hybrid composites / Phosphorus / Circular dichrois

Chiral organophosphonates were covalently grafted onto divacant Keggin-type decatungstosilicates. Spectroscopic analysis revealed the integrity of both the organic and inorganic domain, as well as the effect of the pendant arm on the optical activity and on the structural features of the polyoxometalate.



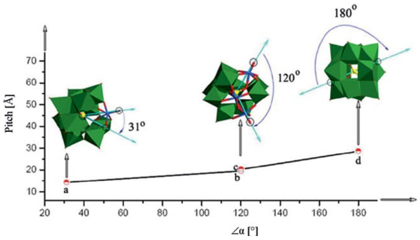
Helical Compounds

H.-j. Pang, C.-j. Zhang, J. Peng,* Y.-h. Wang, J.-q. Sha, A.-x. Tian, P.-p. Zhang, Y. Chen, M. Zhu, Z.-m. Su* **5175–5180**

Two New Helical Compounds Based on Pitch-Tunable Keggin Clusters

Keywords: Polyoxometalates / Helical structures / Luminescence / Electrochemistry

Two new compounds possess the left- and right-handed helical chains with Keggin polyoxometalates as connectors, which verify the pitch tunableness of the Keggin polyoxometalates.



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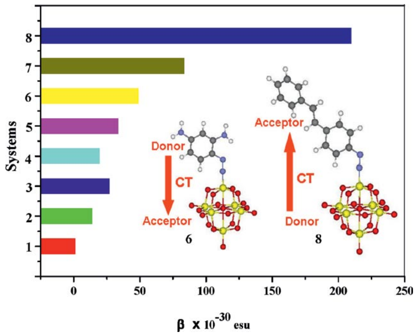
Aryldiazenido Hexamolybdates

M. R. S. A. Janjua, W. Guan, C. G. Liu,
S. Muhammad, L. Yan,
Z. Su* 5181–5188

A Quantum Mechanical Study of the Second-Order Nonlinear Optical Properties of Aryldiazenido-Substituted Hexamolybdates: A Surprising Charge Transfer

Keywords: Polyoxometalates / Organic–inorganic hybrid composites / Molybdenum / Charge transfer / Density functional calculations / Nonlinear optics



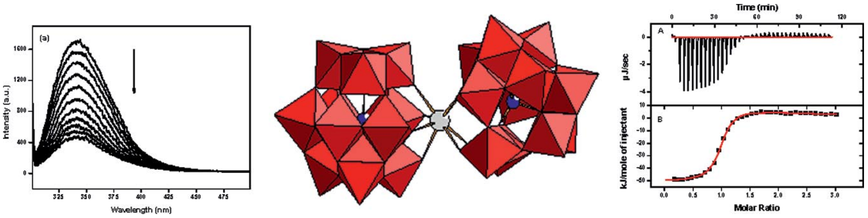
The nonlinear optical properties of aryldiazenido hexamolybdates were studied by DFT analysis. An electron donor in the aryldiazenido ligand enhanced the first hyperpolarizability, and the NLO properties could be improved strikingly by increasing the conjugation path of the ligand. Thus, the NLO behavior of aryldiazenido hexamolybdates can be tuned for the design of high-performance NLO materials.

Gd–POM Binding Protein

L. Zheng, Y. Ma, G. Zhang,* J. Yao,*
B. S. Bassil, U. Kortz, B. Keita,*
P. de Oliveira, L. Nadjo, C. T. Craescu,
S. Miron 5189–5193

Molecular Interaction between a Gadolinium–Polyoxometalate and Human Serum Albumin

Keywords: Gadolinium / Polyoxometalates / Fluorescence / Energy transfer / Protein structures



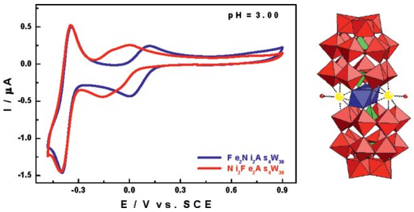
The interaction between a Gd–polyoxometalate (Gd–POM) and human serum albumin (HSA) was studied to elucidate, at the molecular level, the mechanism of action of POMs as potential therapeutic agents. The POM forms a 1:1 complex with HSA, and its binding significantly alters the secondary structure of the protein. Energy transfer between the POM and HSA was also found to occur.

Fe–Ni Sandwich-Type POMS

I. M. Mbomekalle,* P. Mialane,
A. Dolbecq, J. Marrot, F. Sécheresse,
P. Berthet, B. Keita,
L. Nadjo 5194–5204

Rational Synthesis, Structure, Magnetism and Electrochemistry of Mixed Iron–Nickel-Containing Wells–Dawson-Fragment-Based Sandwich-Type Polyoxometalates

Keywords: Polyoxometalates / Sandwich complexes / Nickel / Iron / Magnetic properties / Electrochemistry



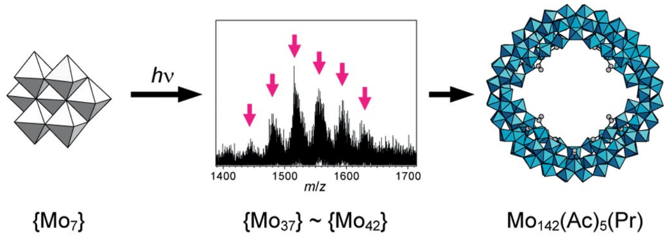
We report on some novel nickel- and/or iron-containing Wells–Dawson sandwich-type polyoxoanions that were synthesized for the first time. These species are stable in solution, and their magnetic and redox behaviours were studied. The six complexes presented in this study are effective in the electrocatalytic reduction of nitrite, dioxygen and hydrogen peroxide.

MS of POM Intermediates

T. Ito, T. Yamase* 5205–5210

Investigation of Intermediates Involved in the Photochemical Formation of Mo-Blue Nanoring by Capillary Electrophoresis–Mass Spectrometry

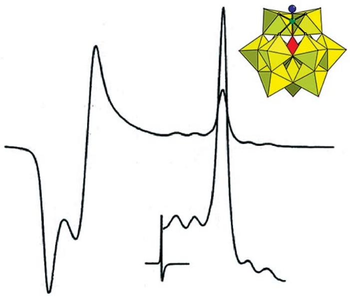
Keywords: Polyoxometalates / Mass spectrometry / Electrophoresis / Photolysis / Reactive intermediates



The photoinduced self-assembly of $[Mo_7O_{24}]^{6-}$ into $Mo_{142}(Ac)_5(Pr)$ Mo-blue nanoring was investigated by capillary electrophoresis (CE) coupled with electrospray ionization mass spectrometry (ESI-MS). The intermediates involved in the photolysis were successfully detected and assigned as species with moderate nuclearity: $\{Mo_{37}\}$ to $\{Mo_{42}\}$.

Polytungstate-Imposed Ligand Fields

Analysis of the EPR spectra of three $[PW_{11}O_{39}Ru^{III}(L)]^{4-}$ anions provides detailed descriptions of the axial and rhombic components of the ligand field imposed upon the Ru cation by the lacunary polytungstate structure.



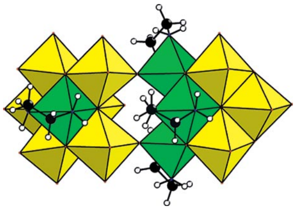
C. C. Rong, H. So,*
M. T. Pope* **5211–5214**

Electron Paramagnetic Resonance Investigation of Some 11-Tungstoruthenate(III) Polyoxoanions

Keywords: Polyoxometalates / Ruthenium / EPR spectroscopy / Ligand field parameters

Chelate Centers in Polymolybdates

Two polymolybdate anions that incorporate multiple $\{Co(en)\}^{3+}$ groups confirm that monochelated transition-metal centers can act as topological analogs of the *cis*-$\{MO_2\}^{2+}$ motifs frequently observed in polyoxometalate structures. The possible resulting hybrid structures offer new properties and applications.



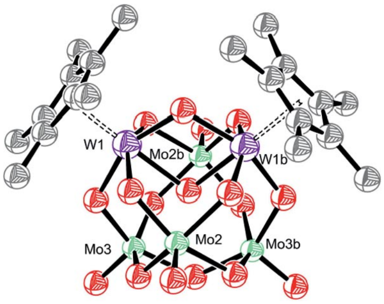
N. Belai, P. N. Kapoor, M. H. Dickman,
R. J. Butcher,* M. T. Pope* ... **5215–5218**

Fusion of Coordination- and Polyoxometalate Chemistry – Chelated Cobalt(III) Centers as Structural Components of Polyoxomolybdates – $[\{Co(en)\}_4Mo_{10}O_{38}]^{4-}$ and Macrocyclic $[\{Co^{II}(H_2O)_2\}\text{-}\{Co(en)\}_8\text{-}\{Mo_{20}O_{76}\}]^{6-}$

Keywords: Polyoxometalates / Molybdenum / Cobalt / Chelates

Mixed-Metal Organometallic Oxides

Room-temperature assembly of the organometallic $Cp^*{}_2M_2O_5$ and the inorganic $M'O_4{}^{2-}$ under aqueous acidic conditions readily and selectively yields the organometallic oxides $Cp^*{}_2M_2M'{}_4O_{17}$ (M, M′ = Mo, W) with a Lindqvist-type structure.

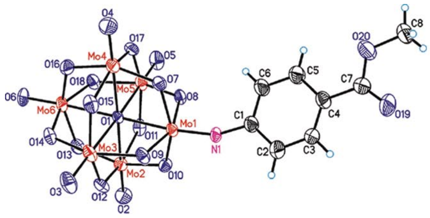


G. Taban-Çalışkan, D. Agustin,*
F. Demirhan,* L. Vendier,
R. Poli* **5219–5226**

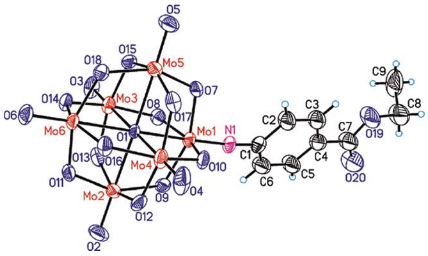
Rational, Facile Synthesis and Characterization of the Neutral Mixed-Metal Organometallic Oxides $Cp^*{}_2Mo_xW_{6-x}O_{17}$ ($Cp^* = C_5Me_5$, $x = 0, 2, 4, 6$)

Keywords: Organometallic oxides / Tungsten / Molybdenum / Polyoxometalates / Density functional calculations / X-ray diffraction

Biological Applications of POMS



Two new aromatic ester derivatives of hexamolybdate were obtained from $[\alpha\text{-}Mo_8O_{26}]^{4-}$ aromatic amine hydrochlorides.



The products are labile in basic solutions; this behaviour potentially offers access to new drugs for controlled release of agents.

Q. Li, P. Yin, L. Shi,
Y. Wei* **5227–5232**

Syntheses, Crystal Structures, and Spectroscopic Studies of Aromatic Ester Derivatives of Hexamolybdate

Keywords: Polyoxometalates / Hexamolybdate / Organic and inorganic hybrids / Drug delivery / Hydrogen bonds

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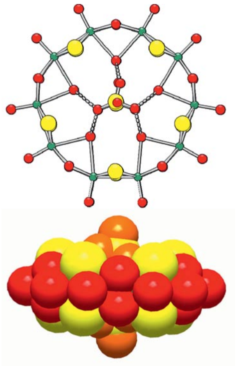
Molybdenum Rings

J.-F. Lemonnier, S. Floquet,* J. Marrot, E. Cadot* .... 5233−5239

Polyoxothiomolybdenum Wheels as Anionic Receptors for Recognition of Sulfate and Sulfonate Anions

Keywords: Molybdenum / Polyoxometalates / Sulfur / Molecular recognition / Self-assembly



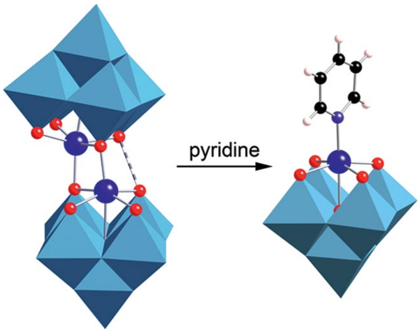
In the presence of sulfate or sulfonate anions in aqueous media, the $[Mo_2O_2S_2]^{2+}$ oxothiocations self-assemble to give two new Mo_{10} rings that interact with the template anions through hydrogen-bonding networks.

CoW_5 Polyoxometalates

R. J. Errington,* G. Harle, W. Clegg, R. W. Harrington .... 5240−5246

Extending the Lindqvist Family to Late 3d Transition Metals: A Rational Entry to CoW_5 Hexametalate Chemistry

Keywords: Polyoxometalates / Lindqvist structures / Tungsten / Cobalt / Mass spectrometry



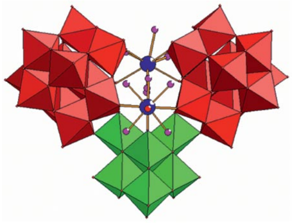
Lindqvist-type MW_5 polyoxometalates $[\{CoW_5O_{18}H\}_2]^{6-}$ and $[(py)CoW_5O_{18}H]^{3-}$ have been prepared from a “virtual” $W_5O_{18}{}^{6-}$ precursor and characterised by single-crystal X-ray diffraction and electrospray mass spectrometry.

Stabilization of POMs by Ln Ions

A. H. Ismail, B. S. Bassil, A. Suchopar, U. Kortz* .... 5247−5252

Synthesis and Structural Characterization of the 28-Isopolytungstate Fragment $[H_2W_{28}O_{95}]^{20-}$ Stabilized by Two External Lanthanide Ions $[Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-}$

Keywords: Cluster compounds / Polyoxometalates / Tungsten / Lanthanides / Structure elucidation



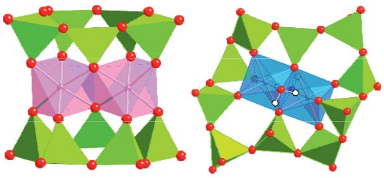
The V-shaped lanthanide-containing isopolyanions of type $[Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-}$ have been synthesized and fully characterized in the solid state as the hydrated salts. The polyanions are composed of a novel $\{W_{28}\}$ isopolyanion unit comprising two undeca $\{W_{11}\}$ and one hexa $\{W_6\}$ fragment coordinated to two external lanthanide ions.

Polyoxovanadate Complexes

S. Inami, M. Nishio, Y. Hayashi,* K. Isobe, H. Kameda, T. Shimoda .... 5253−5258

Dinuclear Manganese and Cobalt Complexes with Cyclic Polyoxovanadate Ligands: Synthesis and Characterization of $[Mn_2V_{10}O_{30}]^{6-}$ and $[Co_2(H_2O)_2V_{10}O_{30}]^{6-}$

Keywords: Polyoxometalates / Oxido ligands / Vanadates / Cobalt / Manganese

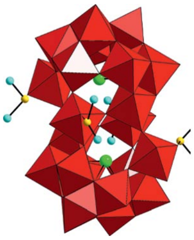


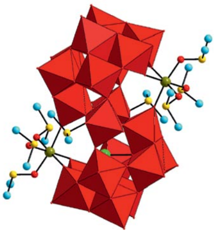
$[Mn_2(V_5O_{15})_2]^{6-}$ $[Co_2(H_2O)_2V_{10}O_{30}]^{6-}$

A ferrocene-like dinuclear manganese complex sandwiched by biscyclopentavanadate and a dinuclear cobalt complex with a crown-ether-type macrocyclic decavanadate was synthesized and characterized.

dmso-Coordinated POMs

Addition of $[Ru(bpy)_3]^{2+}$ to the dmso/H_2O mixed solutions containing $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ or $[Sb_2W_{20}Fe_2O_{70}(H_2O)_6]^{8-}$ results in the dmso-coordinated tungstoantimonates and -bismuthates of $[X_2W_{22}(dmso)_4O_{72}]^{6-}$ and $[X_2W_{20}Fe_2(dmso)_8O_{68}]^{9-}$ (X = Sb, Bi).





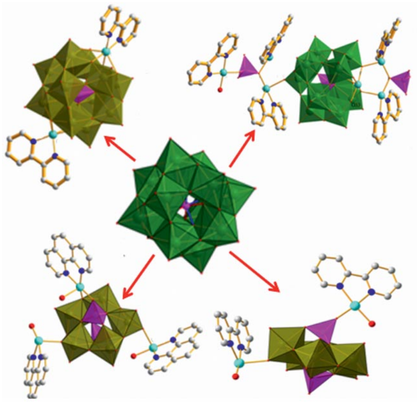
L.-H. Bi,* G.-F. Hou, Y.-Y. Bao, B. Li, L.-X. Wu,* Z.-M. Gao, T. McCormac, S. S. Mal, M. H. Dickman, U. Kortz 5259–5266

Syntheses and Crystal Structures of dmso-Coordinated Tungstoantimonates(III) and -bismuthates(III) 💻

Keywords: Dimethyl sulfoxide / Polyoxometalates / Antimony / Bismuth / Tungsten

Polyoxophosphometalate Hybrids

Organo-polyoxophosphometalate hybrid materials with magnetic properties, photoluminescence, or EPR activities are made by introducing copper complex subunits with phen and bpy ligands. The polymerization of the POMs is modified by adjusting the pH of the reaction using diluted HCl, and the valence of Mo is reduced by reductant oxalic acid.



X. Lu,* X. Shi, Y. Bi, C. Yu, Y. Chen, Z. Chi 5267–5276

The Assembly of Phosphometalate Clusters with Copper Complex Subunits 💻

Keywords: Polyoxometalates / Organic–inorganic hybrid composites / Solvothermal synthesis / Copper / Molybdenum / Tungsten

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