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POLYHEDRON

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1982–2002. 21 Years of Polyhedron: a Celebration

Papers

Catherine M.G. Judkins, Kevin A. Knights, Brian F.G. Johnson, Yolanda R. de Miguel

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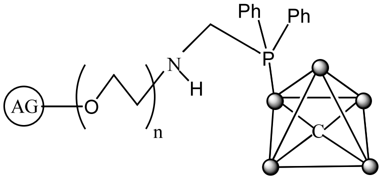
Gas sensor activity of ArgoGel resin-supported pentaruthenium clusters

A new sensor bead has been prepared by coordination of $[Ru_5C(CO)_{15}]$ to phosphine ligands supported on ArgoGel resins. These cluster containing beads exhibit characteristic colour changes and FTIR shifts when treated with the gases H_2S, SO_2 and CO, demonstrating an important use for such supported metals in gas sensing devices.



Laura H. van Poppel, Simon G. Bott, Andrew R. Barron

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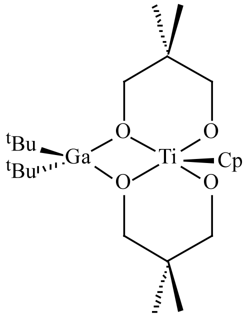
Reaction of $[Ga_2({}^tBu)_4(neol\text{-}H)]_2$ with early transition metal chlorides and amides

Reaction of $[Ga_2({}^tBu)_4(neol\text{-}H)_2]$ with $Ti(NMe_2)_4$ yields $[({}^tBu)_2Ga(\mu\text{-}NMe_2)]_2$, $[Ti(NMe_2)_2(neol)_2]$ and $[Ti(neol)_2]$ via the intermediates $[({}^tBu)_2Ga(neol)_2Ti(NMe_2)]$ and $[({}^tBu)_2Ga(neol)_2]_2Ti(NMe_2)_2$. The reactions proceed through amine elimination and amide/alkoxide exchange reactions. Reaction with $CpTi(NMe_2)_3$ yields $[({}^tBu)_2Ga(neol)_2TiCp]$ and $[({}^tBu)_2Ga(\mu\text{-}NMe_2)]_2$.



Matthew L. Clarke, Alexandra M.Z. Slawin, J. Derek Woollins

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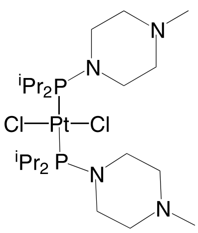
Platinum complexes of tertiary amine functionalised phosphines

The ability of several tertiary amine functionalised phosphines to chelate to platinum has been studied. An example of how subtle differences in ligand structure alter the coordination modes observed are the complexes **9** and **12** shown on the left, which were formed under the same reaction conditions (equimolar reaction with $[Pt(COD)Cl_2]$). The crystal structure of **12** is reported.



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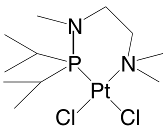

(12)

Erzsébet Kiss, Attila Bényei, Tamás Kiss

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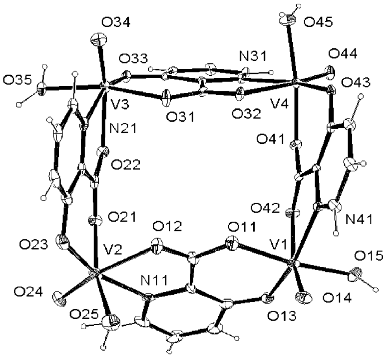
VO(IV) complexes of 3-hydroxypicolinic acid: a solution study and the structure of a supramolecular assembly in the solid state

3-Hydroxypicolinic acid was found to form an interesting tetranuclear complex with VO(IV) in aqueous solution through the tridentate (N, COO^-, O^-) coordination of the ligand; the carboxylate behaves as bridging group. The complex was characterized crystallographically in the solid state and by EPR in solution; the binding mode was found to be identical in both phases. The binding properties of the ligand are compared with those of other substituted picolinic acid derivatives. A possible relationship between the insulin-mimetic activity and the structure of these complexes is discussed.



Ashti Rampaul, Ivan P. Parkin,
Shane A. O'Neill, Juilio DeSouza,
Andrew Mills, Nickolas Elliott

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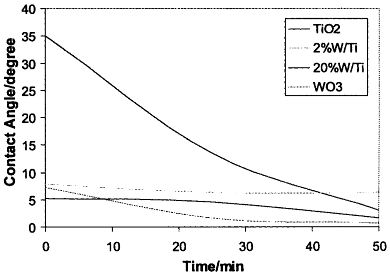
Titania and tungsten doped titania thin films on glass; active photocatalysts

Titania, tungsten oxide and TiO_2/WO_3 thin films were produced on glass substrates by annealing dip-coated fims. The annealed films showed low contact angle measurements and significant photoactivity for the destruction of a stearic acid overlayers. The 2% WO_3 doped TiO_2 films were shown to be the most effective photocatalysts.



Clint A. Sharrad, Lawrence R. Gahan

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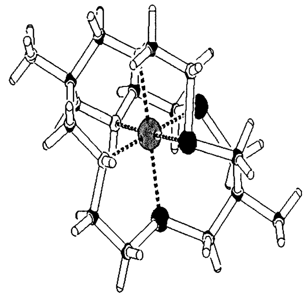
Characterization of $[Fe(AMN_3S_3sarH)]^{3+}$ — a rigorously low-spin iron(II) complex

The characterization of the rigorously low-spin iron(II) complex of the encapsulating ligand AMN_3S_3sar is reported. The short Fe(II)–S(thiaether) bond lengths contribute to both stabilization of the low-spin condition, and to resistance to metal centered oxidation.



José S. Casas, Alfonso Castiñeiras,
Félix Condori, María D. Couce,
Umberto Russo, Agustín Sánchez,
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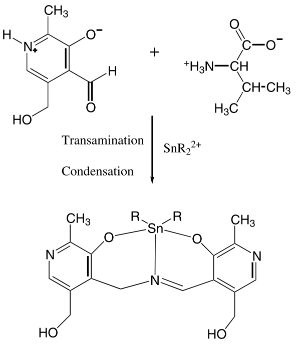
Diorganotin(IV)-promoted deamination of amino acids by pyridoxal: SnR_2^{2+} complexes of pyridoxal 5′-phosphate and of the Schiff base pyridoxal-pyridoxamine (PLPM), and antibacterial activities of PLPM and $[SnR_2(PLPM\text{-}2H)]$ (R = Me, Et, Bu, Ph)

Diorganotin(IV) complexes of types $[SnR_2(PLP\text{-}2H)]$ (PLP = pyridoxal 5′-phosphate) and $[SnR_2(PLPM\text{-}2H)]$ (PLPM = the Schiff base pyridoxal–pyridoxamine) were prepared and characterized. The former are polymeric complexes with hexacoordinated tin atoms. The latter, which in the case of R = Me, Et were isolated from reaction mixtures containing PL, $SnR_2(OAc)_2$ and valine or glicine (see Scheme), consist of molecules in which the metal atom is pentacoordinated. The Schiff base PLPM and its complexes show intense antibacterial activity against *Pseudomonas aeruginosa* (ATCC27853).



Arunashree Panda, Matthias Stender,
Marilyn M. Olmstead, Peter Klavins,
Philip P. Power

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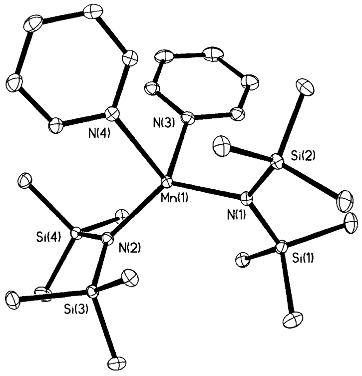
Reactions of M$\{N(SiMe_3)_2\}_2$ (M = Mn, Fe or Co) with pyridine and 4,4′-bipyridyl: structural and magnetic studies

The reaction of pyridine with silyamides of Mn, Fe or Co produced two and three coordinate adducts, whereas the reaction with 4,4′-bipyridyl afforded 1:1 adducts which had polymeric, zig-zag chain structures.



Harry Adams, David E. Fenton,
Paul E. McHugh

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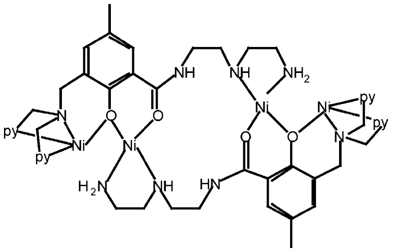
Di- and tetra-nuclear nickel(II) complexes of an unsymmetric compartmental ligand bearing a terdentate linear arm and a terdentate dipodal arm

The unsymmetric compartmental proligand HL^{O} gives the homodinuclear complex [$Ni_2(\mathbf{L^O})(AcO)(SCN)_2$] (**3**), whereas HL^{N} gives the tetranuclear complexes [$Ni_4(\mathbf{L^1})_2(OAc)_4$][X]$_2$,(**4a**, X = PF_6; **4b**, X = BF_4), in which ligand modification has occurred such that the iminic pendant arm of the proligand has been converted into an amidic pendant arm. The crystal structure of (**4b**)$_2\cdot 3CH_3OH\cdot 2H_2O$ is reported.



Larissa M. Fostiak, Isabel García,
John K. Swearingen, Elena Bermejo,
Alfonso Castiñeiras, Douglas X. West

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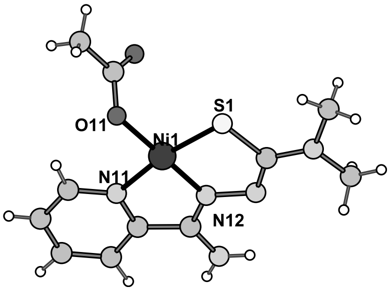
Structural and spectral characterization of transition metal complexes of 2-pyridineformamide N(4)-dimethylthiosemicarbazone

A total of 13 new complexes of 2-pyridineformamide N(4)-dimethylthiosemicarbazone with iron(III), cobalt(III), nickel(II), copper(II), palladium(II) and platinum(II) have been prepared and characterized. The single-crystal structure analysis of [Ni(Am4DM)(OAc)], [Ni(Am4DM)(CH_3CN)]ClO_4, [Cu(Am4DM)(OAc)] and [Pt(Am4DM)-(DMSO)]$Cl\cdot 2H_2O$ shows the coordination of the anionic thiosemicarbazone ligand is via the pyridyl nitrogen, imine nitrogen and thiolato sulfur atoms.



Edwin C. Constable,
Catherine E. Housecroft,
Markus Neuburger, Ingo Poleschak,
Margareta Zehnder

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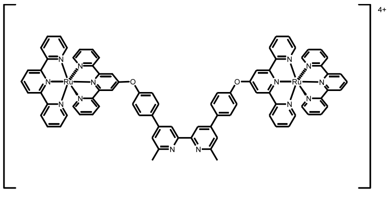
Functionalised 2,2′-bipyridine ligands for the preparation of metallostars; X-ray structures of free ligands and preparation of copper(I) and silver(I) complexes

2,2-Bipyridine ligands with aryl substituents have been prepared and subsequently ruthenated at the periphery to give precursors to multinuclear metallostars. Copper(I) and silver(I) complexes of 4,4′-di(methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine have been prepared and structurally characterised as have the ligands 4,4′-di(methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine and 4,4′-di(methoxyphenyl)-2,2′-bipyridine.



Jason A. Kautz, Thomas D. McGrath, F. Gordon A. Stone

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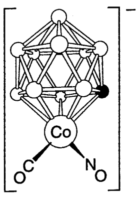
Nitrosyl-cobalt monocarbollide complexes

The cobalt(carbonyl)(nitrosyl) anion [2-CO-2-NO-*closo*-2,1-$CoCB_{10}H_{11}]^-$ (shown), and CO substituted derivatives, are reported. These anions react with Me^+ in donor solvents L to give zwitterionic B–L substituted species, and with $\{M(PPh_3)\}^+$ (M = Cu, Ag, Au) forming bimetallic complexes containing Co–M bonds.



William J. Evans, Matthew A. Johnston, Michael A. Greci, Tammy S. Gummersheimer, Joseph W. Ziller

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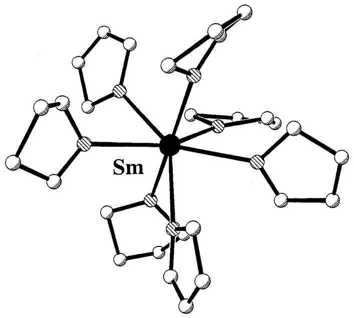
Divalent lanthanide complexes free of coordinating anions: facile synthesis of fully solvated dicationic $[LnL_x]^{2+}$ compounds

Divalent lanthanide cations ligated only by THF or acetonitrile have been prepared by protonation of amide, indenyl, and cyclopentadienyl precursors. Pentagonal bipyramidal $[Sm(THF)_7]^{2+}$ is shown here.



Stéphane Daniele, Liliane G. Hubert-Pfalzgraf, Jacqueline Vaissermann

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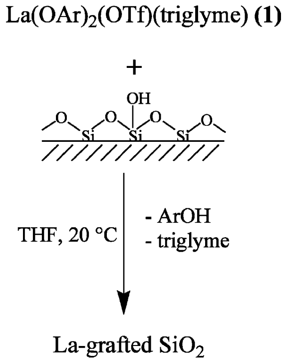
Synthesis, characterisation and grafting onto silica of alkoxide–triflate lanthanum complexes. Molecular structure of $La(OC_6H_3\text{-}2,6\text{-}Me_2)_2(\eta^1\text{-}O_3SCF_3)(tetraglyme)$

Reactions between $La(OTf)_3(LL^x)$ (OTf = O_3SCF_3; LL^1 = triglyme, LL^2 = tetraglyme] and 2 equiv. of LiOAr (Ar = C_6H_3-2,6-Me_2) in THF lead to $La(OTf)(OC_6H_3\text{-}2,6\text{-}Me_2)_2(LL^x)$ [LL^1 = triglyme (**1**); LL^2 = tetraglyme (**2**)] derivatives. The grafting of **1** onto silica led to an hybrid material which was used as hydroxymethylation catalyst of silyl enol ether in mild conditions.



Anastasios J. Tasiopoulos, Nicholas C. Harden, Khalil A. Abboud, George Christou

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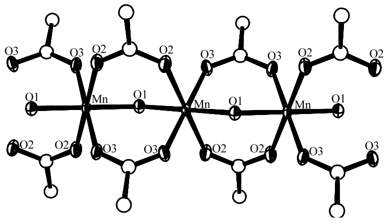
Preparation and crystal structures of Mn^{II}, mixed-valent Mn^{II}/Mn^{III}, and Mn^{III} polymeric compounds

The preparation and properties are reported of three polymeric Mn compounds at the Mn^{II}, mixed-valent Mn^{II}/Mn^{III}, and Mn^{III} oxidation levels. They all contain chains, with inter-chain linkages varying from essentially none to strongly covalent via bridging acetate groups.



Malcolm H. Chisholm, Ernest R. Davidson, Kristine B. Quinlan

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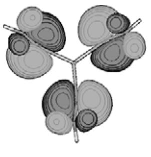
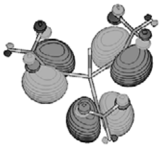
An investigation into the relative influence of alkoxide and thiolate ligands on the metal–carbon triple bond in $X_3M{\equiv}CH$ compounds, where M = Cr, Mo and W and X = OH, SH, OCH_3, SCH_3, OCF_3 and SCF_3 from electronic structure calculations

Electronic structure calculations using density functional theory have been carried out on the model Group 6 alkylidyne complexes $X_3M{\equiv}CH$, where M = Cr, Mo and W and X = OH, SH, OCH_3, SCH_3, OCF_3 and SCF_3. These calculations show the influence of the metal and ancillary ligands on the frontier molecular orbitals.



$W(CH)(SCH_3)_3$



$W(CH)(SCF_3)_3$

Garth R. Giesbrecht, John C. Gordon, David L. Clark, Cybele A. Hijar, Brian L. Scott, John G. Watkin

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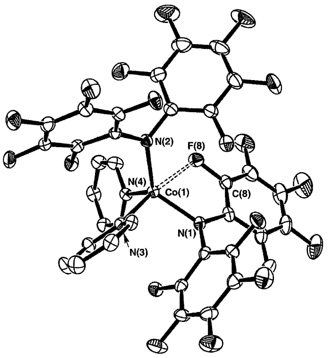
Neutral and anionic transition metal complexes supported by decafluorodiphenylamido ligands: X-ray crystal structures of $\{Na(THF)_2\}\{Ti[N(C_6F_5)_2]_4\}$, $\{K(\eta^6\text{-}C_6H_5\text{-}Me)_2\}\{ZrCl_2[N(C_6F_5)_2]_3\}$, $K\{VCl[N(C_6F_5)_2]_3\}$, $Fe[N(C_6F_5)_2]_2(THF)_2$ and $Co[N(C_6F_5)_2]_2(py)_2$

The electron-withdrawing decafluorodiphenylamido ligand is easily introduced to a wide variety of transition metals (Ti, Zr, V, Fe, Co) by simple metathetical synthetic procedures. ^{19}F NMR is a convenient probe for characterizing the molecules in solution, and in the solid state, this ligand displays a marked tendency to form secondary interactions between the central metal ion and *ortho*-fluorine atoms on the fluorophenyl substituent.



David J. Price, Stuart R. Batten, Kevin J. Berry, Boujemaa Moubaraki, Keith S. Murray

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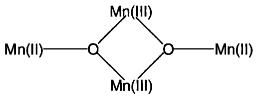
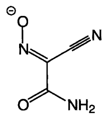
Structure and magnetism of trinuclear and tetranuclear mixed valent manganese clusters from dicyanonitrosomethanide derived ligands

Two new mixed valent trinuclear and tetranuclear Mn(II)/Mn(III) complexes containing pseudochalcogenide-derived chelating oximate ligands are described. Linear trinuclear Mn(II)Mn(III)Mn(II) and planar rhomboidal Mn(lI)OMn(III)Mn(III)OMn(II) core structures lead to antiferromagnetic coupling with some unusual S_T ground state effects with other states close by.





Randy S. Rarig, Jr., Jon Zubieta

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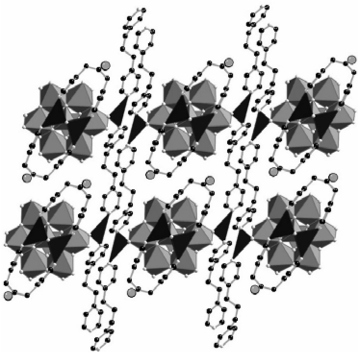
Octamolybdate subunits as building blocks in the hydrothermal synthesis of organically templated mixed metal oxides: the synthesis and X-ray characterization of $[Cu_2Mo_4O_{13}(3,3'\text{-bipy})_2]\cdot H_2O$, $[CuMo_4O_{13}(Hdipyreth)]$, and $[Cu(dpp)]_2[Cu_2(\alpha\text{-}Mo_8O_{26})(dpp)_2]\cdot 2H_2O$ (3,3′-bipy = 3,3′-bipyridine; dipyreth = 1,2-bis(2-pyridyl)ethylene; dpp = 4,4′-trimethylenedipyridine)

The hydrothermal reactions of MoO_3, an appropriate Cu(II) source, and a dipodal nitrogen donor ligand yielded a series of bimetallic oxides $[Cu_2Mo_4O_{13}(3,3'\text{-bipy})_2]\cdot H_2O$ (**1**·H_2O), $[CuMo_4O_{13}(Hdipyreth)]$ (**2**), and $[Cu(dpp)]_2[Cu_2(\alpha\text{-}Mo_8O_{26})(dpp)_2]\cdot 2H_2O$ (**3**·$2H_2O$). (3,3′-bipy = 3,3′-bipyridine; dipyreth = 1,2-bis(2-pyridyl)ethylene; dpp = 4,4′-trimethylenedipyridine). The materials **1**·H_2O and **2** are constructed from octamolybdate clusters linked through copper-ligand subunits, while **3**·$2H_2O$ exhibits fused octamolybdate building blocks in a two-dimensional molybdate chain.



Eric W. Ainscough, Andrew M. Brodie, Andreas Derwahl

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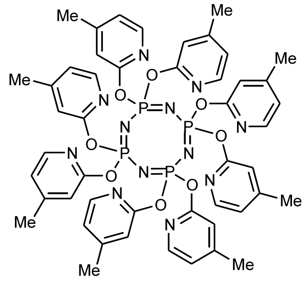
Tuneable crystal host properties in (pyridyloxy)cyclotetraphosphazenes

The introduction of a 4-methyl substituent into the pyridyloxy rings of octakis(2-pyridyloxy)cyclotetraphosphazene causes a change in the crystal structure of the cyclotetraphosphazene to a clathrate-type structure with tunnels extending through the lattice which are occupied by either dichloromethane or water guest molecules.



Guang Zhu, Joseph M. Tanski, Gerard Parkin

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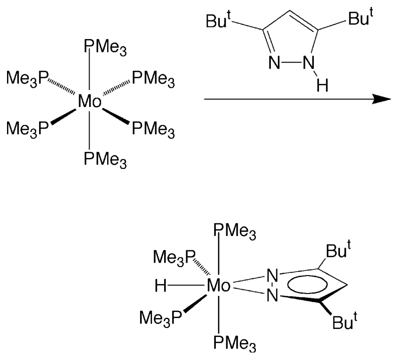
Synthesis and structure of $[\mathrm{pz}^{\mathrm{Bu}^t_2}]\mathrm{Mo}(\mathrm{PMe}_3)_4\mathrm{H}$, a d^4 molybdenum complex that exhibits η^2-coordination of the 3,5-di-*t*-butylpyrazolyl ligand

$\mathrm{Mo}(\mathrm{PMe}_3)_6$ reacts with $[\mathrm{pz}^{\mathrm{Bu}^t_2}]\mathrm{H}$ at 80 °C to give $[\eta^2\text{-}\mathrm{pz}^{\mathrm{Bu}^t_2}]\mathrm{Mo}(\mathrm{PMe}_3)_4\mathrm{H}$, the first structurally characterized d^4 η^2-pyrazolyl complex of molybdenum. The hydride ligand of $[\eta^2\text{-}\mathrm{pz}^{\mathrm{Bu}^t_2}]\mathrm{Mo}(\mathrm{PMe}_3)_4\mathrm{H}$ is displaced from the mean Mo–N–N–P_{cis}–P_{cis} plane, such that the distorted seven-coordinate geometry may be viewed as being based on a distorted dodecahedron with a vacant coordination site. DFT (B3LYP) calculations suggest that the origin of the displacement of the hydride ligand is due to steric interactions with the pair of '*cis*' PMe_3 ligands.



Patrick Gamez, Paul de Hoog, Martin Lutz, Willem L. Driessen, Anthony L. Spek, Jan Reedijk

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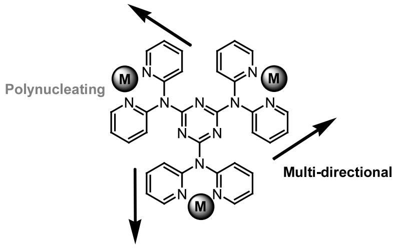
The new multi-directional polydentate ligand 2,4,6-(di-pyridin-2-yl-amino)-[1,3,5]triazine (dpyatriz) can discriminate between Zn(II) and Co(II) nitrate

Zinc(II) nitrate and cobalt(II) nitrate react with the rigid multidentate tri-directional dpyatriz ligand to form the polynuclear complexes $[\mathrm{Zn}_4(\mathrm{dpyatriz})_2(\mathrm{NO}_3)_8]$ (**2**) and $[\mathrm{Co}_2(\mathrm{dpyatriz})_2(\mathrm{NO}_3)_2(\mathrm{MeOH})_2](\mathrm{NO}_3)_2\cdot(\mathrm{MeOH})_2$ (**3**), respectively. Their crystal structures, as well as their UV and IR spectra, have been obtained. The crystal structure of the free ligand dpyatriz, **1** is also reported.



Michael A. Paver, Jonathan S. Joy, Simon J. Coles, Michael B. Hursthouse, J.E. Davies

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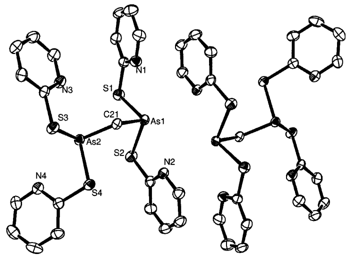
Organo-functionalised arsine and stibine organometallics; syntheses and structural characterisations of $1,3\text{-}[(\mathrm{PhC{\equiv}C})_2\mathrm{Sb}]_2(\mathrm{CH}_2)_3$, $\mathrm{As}(\mathrm{C{\equiv}CPh})_3$, $\mathrm{R}_2\mathrm{AsCH}_2\mathrm{AsR}_2$ [R = $\mathrm{Me}_3\mathrm{SiC{\equiv}C}$-, $(\mathrm{Me}_3\mathrm{Si})_2\mathrm{N}$- and 2-SPy] with π-stacking in the latter

A series of dinuclear organo-functionalised stibine and arsine ligands incorporating a range of hard, soft and π-donor moieties have been synthesised from the reactions of $\mathrm{Cl}_2\mathrm{Sb}(\mathrm{CH}_2)_3\mathrm{SbCl}_2$ and $\mathrm{Cl}_2\mathrm{AsCH}_2\mathrm{AsCl}_2$ with a range of organolithium reagents. The X-ray structures of $1,3\text{-}[(\mathrm{PhC{\equiv}C})_2\mathrm{Sb}]_2(\mathrm{CH}_2)_3$ (**1**), $\mathrm{As}(\mathrm{C{\equiv}CPh})_3$ (**2**), $\mathrm{R}_2\mathrm{AsCH}_2\mathrm{AsR}_2$ [R = $\mathrm{Me}_3\mathrm{SiC{\equiv}C}$, **3**; $(\mathrm{Me}_3\mathrm{Si})_2\mathrm{N}$, **4**; and 2-SPy **5**] have been determined. Compound **5** associates into pseudo dimers as a result of intermolecular π–π stacking between the pyridyl groups on one end of two separate diarsine molecules. Whereas the bridging unit remains intact during the syntheses of **1** and **3**–**5**, the formation of the mononuclear trisacetylide species **2**, involves the unexplained cleavage of the bridging methylene unit.



Quan-Ming Wang, Guo-Cong Guo, Thomas C.W. Mak

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Anion-controlled assembly of layer-type structures in double and triple salts of silver cyanide

Layer-type networks are constructed from octahedral F@Ag_6 units linked by μ_4-CN groups, or chain-like $[Ag_2CN]_\infty$ and $[Ag_3CN]_\infty$ motifs, with all co-existing anions displaying unusual coordination modes in the silver-rich environment.