Polymetallic Cobalt and Manganese Cages with Phosphinate and Phosphonate Ligands**

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Paramagnetic metal cage complexes have become a focus for a great deal of research since the discovery that certain cages could retain magnetic orientation in the absence of a magnetic field.[1] These "single-molecule magnets" therefore act as molecular magnetic storage devices, and accompanying physical phenomena, such as quantum-tunneling of the magnetization,[2] make them objects of both technological and fundamental scientific interest. Ligands used in synthesizing such cage complexes are however comparatively restricted, with the majority of examples involving carboxylates and alkoxides.[1, 3]

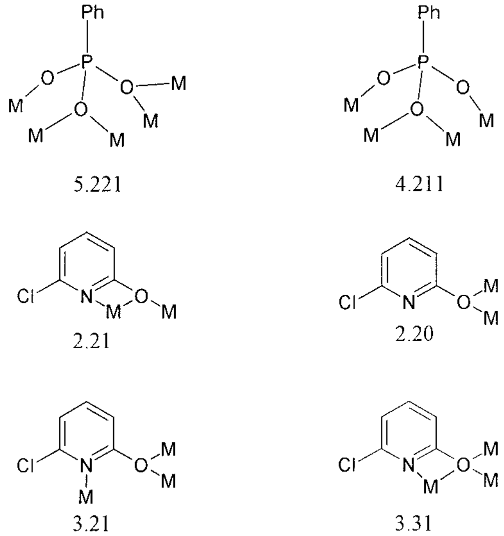
Cage complexes featuring phosphonate ligands are rare. Several cages involving vanadium have been reported, chiefly by Zubieta and co-workers,[4] some cages featuring aluminum have appeared recently,[5] and a fascinating dodecanuclear copper(II) cage was reported in 2000 by Chandrasekhar and Kingsley.[6] Perhaps most exciting are the redox-active $\{Mn_4\}$ cages described by the Dismukes group.[7] Other than the $\{Cu_{12}\}$ example complexes of the later 3d metals with phosphonate ligands tend to be restricted to layered structures.[8] This observation is intriguing, for it suggests that if phosphonate ligands could be induced to form cage complexes, the propensity to support two-dimensional (2D) structures might lead to preferential formation of disclike cages. The structural anisotropy might in turn lead to anisotropy in magnetic behavior, which could be of interest in the formation of new single-molecule magnets.[1] Here we report studies of the reactions of these ligands with middle and late 3d metals, which demonstrate that phosphonates can be incorporated in such cages, but only in the presence of coligands.

The chief difficulty in the use of phosphonates for cage formation is the insolubility of the products of reactions between 3d metal salts and the ligands. For example, reaction of cobalt hydroxide with phenylphosphonate leads to intractable powders that do not dissolve in any common solvent. However, if a second ligand is added to the mixture, and the phosphonate concentration kept low, intensely colored solutions can be produced. Thus cobalt hydroxide and $PhPO_3H_2$ were added to 6-chloro-2-hydroxypyridine (Hchp) in molar ratios of 1:1/3:2, and the mixture heated to above the melting point of Hchp. The purple paste that results could be dissolved in a range of solvents. Crystals of **1** form in moderate yield from EtOAc, while crystals of **2** form in poor yield from MeCN/Et_2O. In both cases X-ray analysis[9] reveal formation of $\{Co_{13}\}$ cages. The crystallization of two very similar cages from different solvents suggests that the cages are formed during the initial reaction, rather than forming during crystallization.

$[Co_{13}(OH)_3(chp)_{19}(O_3PPh)_2(H_2O)_2(EtOAc)_2]$ **1**

$[Co_{13}(OH)_3(chp)_{19}(O_3PPh)_2(H_2O)_2(Hchp)_2]$ **2**

The structures are highly irregular and essentially identical, differing in the replacement of the two terminal EtOAc ligands in **1** by Hchp ligands in **2**. The following description and figure use the atom numbering for **1**. At the core of both cages are two phosphonate ligands, which each bind to five cobalt centers; adopting a [5.221] mode (as described using Harris notation,[10] see Scheme 1). Four cobalt centers (Co1, Co2, Co4, and Co11) are bound to both of these ligands, with a further two Co atoms (Co3 and Co5) bound to a single $PhPO_3^{2-}$ ligand (Figure 1a). Each of these six cobalt centers is six-coordinate, and shares two O atoms with neighboring cobalt centers of the core (Figure 1b). This creates a helical array of cobalt centers, beginning with Co5 and moving in an anticlockwise direction to Co3. The remaining seven cobalt sites are arranged around three sides of this central core (Figure 1b). Three of these sites share two O atom bridges with Co sites of the core (Co6, Co8, and Co12), while two sites share a single oxygen with a Co atom of the core (Co7 and Co13). Co9 shares three O atoms with two different central cobalt centers (Co1 and Co5), while the final site (Co10) shares two bridging oxygen atoms with two different cobalt centers (Co2 and Co11).



Scheme 1. The bonding modes displayed by phosphonate and pyridonate ligands, with the Harris notation for each mode.

The cage also contains three μ_3-hydroxide ligands: O1 is bound exclusively to Co atoms of the core (Co3, Co4, and

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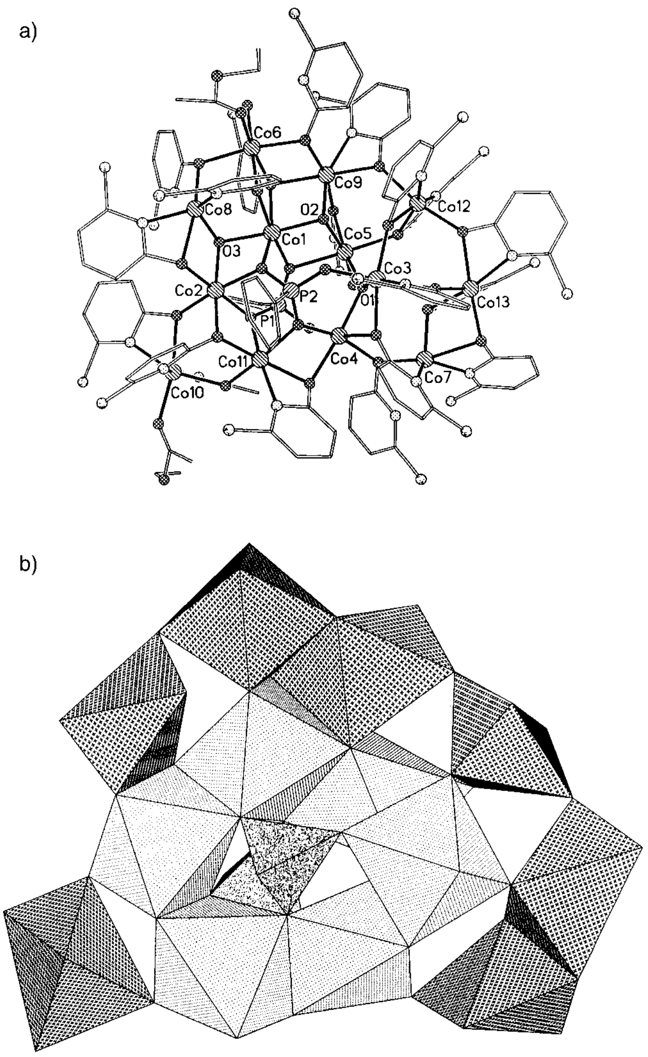

Figure 1. a) The structure of **1** in the crystal. Bond length ranges [Å]: Co-O(O_3PPh) 1.988 – 2.259, Co-O(chp) 1.994 – 2.348, Co-O(hydroxide) 1.998 – 2.109, Co-O(H_2O) 2.049 – 2.094, Co-O(EtOAc) 2.120 – 2.175, Co-N(chp) 2.050 – 2.241 (av esd 0.013). b) A polyhedral representation of the Co and P sites in **1** and **2**, viewed from the same position as Figure 1 a. Shading: P sites, random heavy dots; core Co sites, regular dots; external Co sites, regular crosses.

Co5), while O2 and O3 each bind to two cobalt centers from the core and one of the exterior cobalt sites. The nineteen chp ligands in the cage adopt four bonding modes. Using Harris notation[10] these can be described as a [2.21] mode, adopted by eleven pyridonates, a [2.20] mode, adopted by three ligands, a [3.21] mode, adopted by two ligands, and the [3.31] mode, adopted by one pyridonate (see Scheme 1). In the homoleptic complex $[Co_9(chp)_{18}]$, which is prepared from a similar reaction in the absence of the phosphonate, all pyridonates adopt the [2.21] mode.[11] Two water and two ethylacetate molecules are found bound as terminal ligands. The cobalt sites can all be considered six-coordinate, however in some cases the sixth bond is markedly longer. Five cobalt centers (Co1, Co2, Co4, Co5, and Co6) are each bound to six O donors, three (Co3, Co9, and Co11) are bound to five O and one N donors, three (Co8, Co12, and Co13) to four O and two N atoms, and two (Co7 and Co10) to three O and three N donors.

High-nuclearity Co^{II} cages remain comparatively rare. Two nonanuclear cages are known, with pyridonate[11] and di-2-pyridylketone[12] as ligands. A series of deca- and dodecanuclear cages based on trigonal prisms have been reported featuring pyridonates and carboxylates.[13] Another tridecanuclear cage has been described,[14] and one larger cage which contains twenty-four metal centers.[15] There are also many larger clusters known with cobalt in lower oxidation states.[16]

A second method for introducing a phosphonate or phosphinate ligand without causing an immediate precipitate is to react the ligand with a preformed cage. Reaction of the mixed-valence cage $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$ (py = pyridine)[17] with an equimolar quantity of phenylphosphinic acid in MeCN gives crystals of **3**. Structural analysis[9] shows that the triangular oxo-centered array of manganese centers found in the precursor cage is retained, but two such triangles have been linked through two phosphinate and two phosphonate ligands (Figure 2). The formation of the phosphonate in **3** is presumably through aerial oxidation in presence of the manganese centers.

$[Mn_6O_2(O_3PPh)_2(O_2PHPh)_2(O_2CPh)_8(py)_2]$ **3**

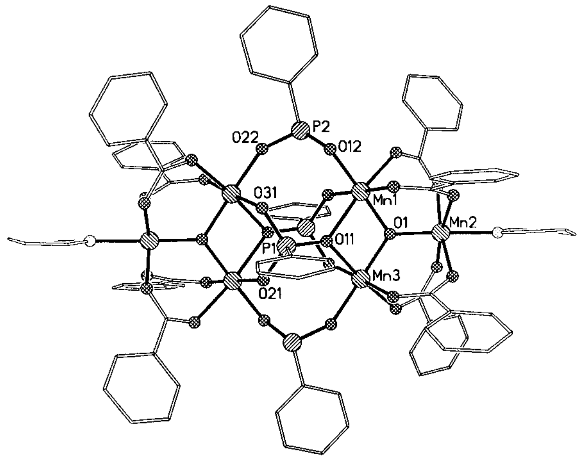

Figure 2. The structure of **3** in the crystal. Bond length ranges [Å]: Mn-O(equatorial sites) 1.844 – 2.042, Mn-O(Jahn – Teller elongated sites) 2.105 – 2.257 (av esd 0.008). Bond angle ranges [°]: *cis* at Mn 78.6 – 99.1, *trans* at Mn 169.5 – 178.7 (av. esd 0.3).

Complex **3** is centrosymmetric. The unique phosphonate ligand bridges four manganese centers, using a [4.211] binding mode (see Scheme 1).[10] Therefore one edge of the manganese triangle in one cage is bridged by the phosphonate in a 1,3-manner akin to a carboxylate, while a single μ_2-oxygen from the symmetry-equivalent phosphonate bridges the same edge. The two phosphinate ligands form a bridge between the two triangles in a 1,3-fashion. The remainder of the triangles are unchanged from those in the precursor cages, with four bridging benzoate groups and a terminal pyridine completing the coordination spheres of the manganese centers, which are all six-coordinate. Charge balance requires that the metals are present as Mn^{III}, and the Jahn – Teller elongation typical of this oxidation state is observed for all three crystallographically independent sites. Complex **3** can also be made from the homovalent triangle $[Mn_3O(O_2CPh)_6(py)_3](ClO_4)$.

The formation of **3** suggests many further reactions, which may prove exciting. It appears that phosphonate ligands can displace carboxylate ligands from one cage and simultaneously act as a bridge to a related cage. This implies a method for synthesizing larger metal arrays from reaction of metal carboxylate cages with phosphonates. Hexanuclear manganese cages are far from rare.[3] A series of such cages exist in which the metal polyhedron is based on an edge-sharing bitetrahedron,[18] and several $\{Mn_6\}$ cages have very high magnetic spin ground states, for example, a radical-bridged Mn^{II} wheel[19] and Mn^{III} octahedron featuring dibenzoylmethane ligands.[20]

Magnetic studies of **1** and **3** in both cases show a decline in $\chi_m T$ as the temperature is lowered (χ_m = molar magnetic susceptibility). For **1** this decline, from a room temperature value of about 42.2 $emu\,K\,mol^{-1}$ to a value of 10.1 $emu\,K\,mol^{-1}$ at 1.8 K, is presumably due to a combination of antiferromagnetic exchange between Co^{II} centers and the usual crystal field effects of Co^{II}. For **3** the decline, from a room temperature value of 21.5 $emu\,K\,mol^{-1}$ to zero at 1.8 K, is due to antiferromagnetic exchange. Isolated oxo-centered triangles display spin frustration, and tend to have non-diamagnetic ground states.[17, 21] Therefore the low-temperature value suggests there is significant exchange between the Mn^{III} triangles, presumably mediated by the phosphinate and phosphonate ligands.

Experimental Section

1: Freshly prepared cobalt hydroxide (5.4 mmol) was mixed with Hchp (11 mmol) and $PhPO_3H_2$ (1.8 mmol), and the mixture heated to 130 °C for 10 min. The resulting purple paste was extracted repeatedly with aliquots of EtOAc (5 mL), and the solutions allowed to stand at room temperature. Yield: 34%. Elemental analysis calcd (%) for $C_{119}H_{98}Cl_{19}Co_{13}N_{19}O_{36}P_2$: C 36.89, H 2.53, N 6.87; found: C 36.89, H 2.35, N 6.77.

2: This was prepared by an analogous procedure to **1** but crystallized by extracting the sample with aliquots of MeCN (5 mL) and allowing diethyl ether to diffuse into the solutions. Yield: <5%. No elemental analysis obtained.

3: $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$[17] (0.23 mmol) was dissolved in MeCN (10 mL) and HO_2PHPh (0.21 mmol) in MeCN (5 mL) added. The solution was filtered and allowed to evaporate slowly at room temperature. Yield: 26%. Elemental analysis calcd (%) for $C_{90}H_{72}Mn_6N_2O_{28}P_4$: C 51.89, H 3.48, N 1.34; found: C 50.42, H 3.52, N 1.05.

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[9] Crystal data for **1**: $C_{119}H_{98}Cl_{19}Co_{13}N_{19}O_{36}P_2$, $M_r = 3872$, triclinic, $P\bar{1}$, $a = 16.880(5)$, $b = 17.978(5)$, $c = 29.874(10)$ Å, $\alpha = 104.47(2)$, $\beta = 102.391(15)$, $\gamma = 94.077(18)°$, $V = 8499(4)$ Å^3, $Z = 2$, $T = 220.0(2)$ K, crystal size $0.39 \times 0.35 \times 0.19$ mm, $\mu(Mo_{K\alpha}) = 1.619$ mm^{-1}. Crystal data for **2**: $C_{139.5}H_{135}Cl_{21.5}Co_{13}N_{23.5}O_{37.5}P_2$, $M_r = 4331$, triclinic, $P\bar{1}$, $a = 16.964(7)$, $b = 21.564(9)$, $c = 25.142(10)$ Å, $\alpha = 98.556(7)$, $\beta = 98.280(7)$, $\gamma = 101.171(7)°$, $V = 8780(6)$ Å^3, $Z = 2$, $T = 150.0(2)$ K, crystal size $0.15 \times 0.13 \times 0.08$ mm, $\mu(Mo_{K\alpha}) = 1.615$ mm^{-1}. Crystal data for **3**: $C_{95}H_{79.5}Mn_6N_{4.5}O_{28}P_4$, $M_r = 2186$, triclinic, $P\bar{1}$, $a = 12.440(3)$, $b = 13.640(3)$, $c = 17.010(4)$ Å, $\alpha = 96.511(4)$, $\beta = 109.479(3)$, $\gamma = 112.445(4)°$, $V = 2417.2(9)$ Å^3, $Z = 1$ (the molecule lies on an inversion center), $T = 150.0(2)$ K, crystal size $0.20 \times 0.05 \times 0.02$ mm, $\mu(Mo_{K\alpha}) = 0.906$ mm^{-1}. Data for **1** were collected with a Stoe Stadi-4 diffractometer; data for **2** and **3** were collected on a Bruker Smart APEX CCD area detector. Both diffractometers were equipped with an Oxford Cryosystems low-temperature device. Absorption corrections were applied to all data by face-indexing for **1** (min./max. transmission: 0.624/0.829), by using ψ scan data for **2** (min./max. transmission: 0.658/0.928), and by using Sadabs (area-detector absorption correction; Siemens Industrial Automation Inc., Madison, WI, **1996**) for **3** (min./max. transmission: 0.806/0.928). The structures were solved by direct methods using SHELXS-97 for **1** and **2** (G. M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis, University of Göttingen, **1998**), and SIR92 for **3** (A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343), and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F^2 (G. M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis, University of Göttingen, **1998**). In **2** there is one chp ligand disordered over two orientations, with a common oxygen position, while in **3** the crystallographically unique $PhPHO_2$ ligand is disordered over two orientations with common O sites. In **1** and **2** there were diffuse regions of solvent of crystallization, which was treated by the method of van der Sluis and Speck (P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194–201). A half-occupancy molecule of Hchp was also found in the lattice of **2**. Hydrogen atoms were included in calculated positions, riding on parent carbon atoms, with $U(H) = 1.2\,U_{eq}(C)$ for aromatic H atoms and $U(H) = 1.5\,U_{eq}(C)$ for methyl hydrogen atoms. All full-weight non-hydrogen atoms were refined with anisotropic displacement parameters to give: for **1**, for 995 parameters, $wR2 = 0.1959$ for 15739 unique data ($2\theta \leq 40°$), $R1 = 0.0854$ for 6002 data with $F_o > 4\sigma(F)$, max./min. residual electron density 0.724/−0.540 e Å^3; for **2**, for 1955 parameters, $wR2 = 0.2456$ for 30480 unique data ($2\theta \leq 50°$), $R1 = 0.0868$ for 13202 data with $F_o > 4\sigma(F)$, max./min. residual electron density 1.327/−1.233 e Å^3; for **3**, for 622 parameters, $wR2 = 0.1597$ for 4510 unique data ($2\theta \leq 40°$), $R1 = 0.0673$ for 2297 data with $F_o > 4\sigma(F)$, max./min. residual electron density 0.401/−0.419 e Å^3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158429, CCDC-158430, and CCDC-158431. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] Harris notation describes the binding mode as $[X.Y_1Y_2Y_3\ldots Y_n]$, where X is the overall number of metals bound by the whole ligand, and each value of Y refers to the number of metal atoms attached to

the different donor atoms. Therefore for chp, there will be two values for Y, while for PhPO$_3^{2-}$ there will be three values of Y. The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules, hence O before N. See: R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker, R. E. P. Winpenny, *Dalton Trans.* **2000**, 2349–2356.

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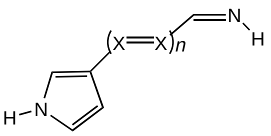
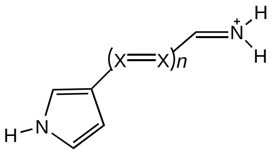
Remote Communication between Charge Centers and Hydrogen-Bonding Sites: Possibility for a Signal Transducer?**

Ito Chao* and Tsong-Song Hwang

Hydrogen bonding and charge interactions are both essential for molecular recognition and the self-assembly of biological macromolecules. They are also employed heavily in the design of new systems for fundamental, biological, and materials research. The influence of a charge-bearing functional group on pK_a values[1] and chemical reactivity[2] has been well documented in the form of Hammett-type substituent constants in physical organic studies. Changes in the hydrogen-bonding behavior of ligands upon complexation with cationic transition metal centers have been indicated by theoretical calculations.[3] Such calculations also indicated that anions could induce a large cooperative effect in the hydrogen-bonding network of peptides.[4] Enhancement was observed experimentally in urea · carboxylate binding when the carbonyl group of the urea molecule was coordinated to a Lewis acid.[5] The optical property of [Ru(bpy)$_3$]$^{2+}$ (bpy = bipyridine) in a phosphodiester sensor was changed when the hydrogen-bonding sites were bound.[6] Although both hydrogen-bonding and charge-bearing sites are important in molecular recognition, interestingly, it is not common to find examples in supramolecular chemistry in which hydrogen-bonding sites are designed to be controlled by a covalently bound charge-bearing substituent. Charge-assisted C–H$\cdots$X hydrogen bonds have been recognized in recent years[7] and metallocene complexes have been used to achieve redox-switched binding.[8] Nevertheless, the binding sites are basically adjacent to the charged centers, and we felt that charge centers can have a more far-reaching influence on a binding site.





1a: X = CH, *n* = 1
1b: X = CH, *n* = 2
1c: X = CH, *n* = 3
1d: X = CH, *n* = 4

3a: X = N, *n* = 1
3b: X = N, *n* = 2
3c: X = N, *n* = 3
3d: X = N, *n* = 4

2a: X = CH, *n* = 1
2b: X = CH, *n* = 2
2c: X = CH, *n* = 3
2d: X = CH, *n* = 4

4a: X = N, *n* = 1
4b: X = N, *n* = 2
4c: X = N, *n* = 3
4d: X = N, *n* = 4

If a charged group and a binding site can communicate with each other, one can use a three-component system (a charged group, a linker, and a binding site) as a signal transducer. The charge-bearing group can be viewed as a reaction site, whose charge state can be altered by reactions such as protonation, metalation, oxidation, reduction, or chemical transformation of a functional group. On the basis of this concept we designed test compounds **1a**–**d** and **2a**–**d**, and calculated the energies of formation of a hydrogen bond (binding energies) to find out how efficiently the reaction and binding centers can communicate with each other. In these compounds the reaction center is an imine group and the binding center is pyrrole; compounds **1a**–**d** are neutral imines and **2a**–**d** are cationic iminium compounds. Ammonia was chosen as the hydrogen-bonding partner of the N–H group of pyrrole for the sake of geometric simplicity, since it only has one lone pair of electrons. The ammonia binding energy of **2a** (-13.17 kcal mol^{-1}) at the HF/6-31G* level is double that of cationic **1a** (-6.84 kcal mol^{-1}) (Table 1).[9] While the binding energies of neutral systems (**1a**–**d**) remain fairly constant as the linker gets longer, the binding energies of cationic systems

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