A novel pentamanganese(II) cluster produced by a controlled self assembly process; an exact match between the coordination algorithm of the metals and the ligand binding site arrangement

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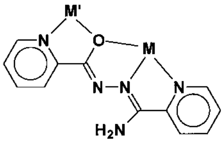
The tetradentate ligand phaap combines a bridging alkoxide oxygen and diazine and pyridine nitrogen donors, with five critically positioned binding sites, and on reaction with $Mn(ClO_4)_2 \cdot 6H_2O$ undergoes a controlled self assembly to produce a unique trigonal bipyramidal oxygen bridged metal cluster with an exact match between the coordination requirements of the five six-coordinate metals and the donor arrangements of the six coordinated ligands.

The continued investigation of low molecular weight models for the oxygen evolving manganese complex of photosystem (II) has produced a range of homotetranuclear complexes, which have been bridged by oxygen centres and involved a variety of geometric arrangements, *e.g.* dimer of dimers, butterfly, cubane and adamantane type structures and mixed valence aggregates.[1–4] These have primarily been synthesized using strategies that utilize pre-organized macrocyclic hosts[1] or by employing self assembly reactions involving 'simple' carboxylates,[5] and substituted pyridonates.[6] The former method is a more rational approach because of the reduced tendency to form large aggregates, whereas the latter approaches often generate high nuclearity clusters that are difficult to predict in advance. There has also been a parallel increase in the number of higher nuclearity polymanganese aggregates, some of which possess manganese ions of variable oxidation state, and display single molecule magnetic behaviour.[7] However homopentanuclear Mn^{II} clusters[8] are poorly represented and their chemistry virtually unknown, while mixed oxidation state Mn_5 systems are rare ($Mn^{III}{}_4Mn^{II}$,[9] $Mn^{II}{}_4Mn^{III}$[10]). This situation can perhaps be attributed to the apparent lack of a general strategy for the synthesis of high nuclearity clusters, although several groups are attempting to overcome the problem by using *e.g.* small nuclearity clusters as 'building blocks'.[11]

We have discovered that it is possible to combine the attributes of a bridging donor (alkoxide), and terminal donors in one 'planar' tetradentate ligand phaap which is capable of acting in a polynucleating, bridging capacity to aggregate several transition metal centres into an alkoxo-bridged cluster in an apparently controlled way. A number of square tetranuclear, homometallic (Ni^{II}, Co^{II}, Cu^{II}), and heterometallic ($Co^{II}{}_2Fe^{III}{}_2$, $Fe^{III}Cu^{II}{}_3$) complexes of phaap have been produced,[12] but with Mn^{II} the preferred arrangement is a pentanuclear cluster.



phaap

Reaction of phaap with $Mn(ClO_4)_2 \cdot 6H_2O$ in aqueous methanol produced an orange product (90% yield),‡ which gave orange crystals of $[Mn_5(phaap - H)_6](ClO_4)_4 \cdot 3.5MeOH \cdot H_2O$ **1** from ethanol suitable for structural analysis.§ A similar pentanuclear nitrate cluster complex $\{[Mn_5(phaap - H)_6](NO_3)_4 \cdot 5H_2O\}$¶ is produced by reaction of phaap with manganese(II) acetate in methanol followed by addition of $NaNO_3$.[12] The structure of the cation in **1** is unique (Fig. 1), with three pairs of almost parallel tetradentate ligands arranged around a pentanuclear, trigonal bipyramidal manganese(II) core, with each ligand filling five metal coordination sites and providing an alkoxide type bridge between adjacent pairs of pseudo-octahedral manganese atoms. The NH_2 ends of the ligands terminate at the equatorial manganese centers, and the O ends terminate at the apical centers, with each tetradentate (N_3O) ligand bridging each adjacent pair of metal centers along the six non-equatorial edges of the trigonal bipyramid. This arrangement provides an exact match between the coordination environment provided by the ligands and the coordination requirements of the five pseudo-octahedral metal centers. Within the Mn_5 core (Fig. 2) each apical metal atom is linked to an equatorial metal atom by an oxygen bridge, and each equatorial metal atom is linked to the apical pair of manganese atoms by two oxygen bridges. The equatorial manganese atoms are quite distorted, with *cis* and *trans* ligand angles as low as 70 and 140° respectively. The apical manganese centres have more normal pseudo-octahedral angles. Mn–N and Mn–O distances fall in the ranges 2.14–2.41 and 2.14–2.22 Å, respectively.

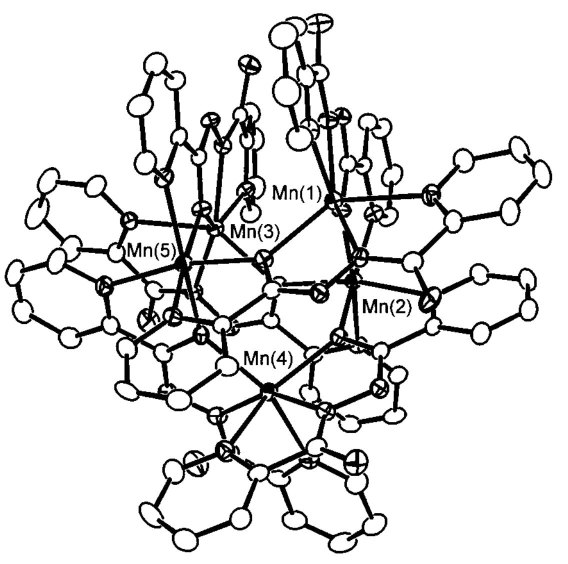


Fig. 1 Structural representation of the cation $[Mn_5(phaap - H)_6]^{4+}$ (40% probability thermal ellipsoids). Mn(1)–Mn(2) 3.9474(14), Mn(1)–Mn(5) 3.9630(12), Mn(3)–Mn(5) 3.9208(14), Mn(4)–Mn(5) 3.9059(13), Mn(2)–Mn(3) 3.9116(12), Mn(2)–Mn(4) 3.9190(13), Mn–N 2.144–2.403, Mn–O 2.140–2.218 Å.

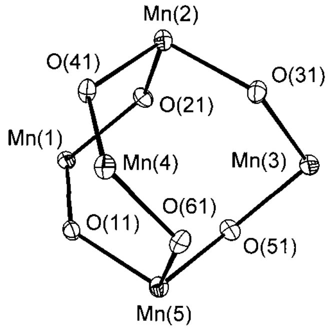


Fig. 2 Structure of the trigonal-bipyramidal core in $[Mn_5(phaap - H)_6]^{4+}$.

Adjacent Mn···Mn separations fall in the range 3.90–3.97 Å, with Mn–O–Mn angles in the range 128–131°. Within each ligand N–N distances average 1.399 Å, indicating single bond character, while average C–O and $C–N_{diazine}$ distances of 1.311 and 1.297 Å, respectively, indicate some charge delocalization within each N–C–O framework.

Variable temperature magnetic susceptibility measurements were carried out on a powdered sample of **1** in the temperature range 5–300 K.‖ Magnetic moments (per mole) drop smoothly from 13.4 μ_B at 296 K to 5.8 μ_B at 5 K, indicating the presence of antiferromagnetic coupling within the pentanuclear manganese(II) core, and the likelihood of an $S = 5/2$ ground state. This is consistent with the presence of oxygen bridges between the manganese(II) centres. An evaluation of the exchange coupling will be described elsewhere.

Electrochemical studies carried out in acetonitrile (1.0 mM, 0.1 M NEt_4ClO_4; Pt working electrode, Pt counter electrode, SSCE reference electrode) revealed three sequential, reversible, one electron waves (cyclic voltammetry; $\Delta E_p = \approx 90$ mV for each wave, and remains essentially constant from 100–1000 mV s^{-1}) in the range 0.6–1.0 V (Fig. 3), with equal current heights (coulometry at 1.1 V required 3.0 equivalents of charge for full oxidation to a brown colored solution, and with the potential set at 0.5 V after oxidation 3.0 equivalents of charge were required for full reduction to the original yellow orange colored solution) corresponding to the formation of a Mn^{II}_2-Mn^{III}_3 species. The Mn^{III} sites are assumed to be those in the equatorial plane. An irreversible wave at $E_{1/2} = 1.5$ V, similar to an irreversible wave observed in an acetonitrile solution of the zinc perchlorate complex, is associated with ligand oxidation. No EPR signal (X band) was observed for the $Mn^{II}_2Mn^{III}_3$ solution at ambient temperature, but in the UV–VIS spectrum an intense band appears at 937 nm ($\varepsilon = 720$ dm^3 mol^{-1} cm^{-1}), which is absent in the spectrum of **1**. On prolonged standing the spectrum reverts to that of the Mn^{II}_5 species.

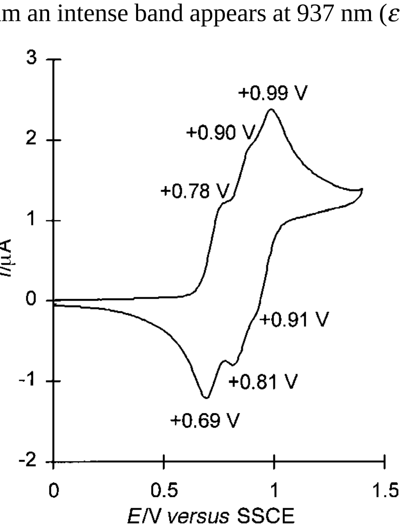


Fig. 3 Cyclic voltammetry for $[Mn_5(phaap - H)_6](ClO_4)_4$ in acetonitrile (1.0 mM, 0.1 M NEt_4ClO_4; Pt working electrode, Pt counter electrode, SSCE reference electrode; BAS CV27 Voltammograph; 100 mV s^{-1}).

The aggregation of five six-coordinate manganese(II) centres (thirty coordination positions) into an alkoxo-bridged, trigonal bipyramidal cluster by the six phaap ligands (thirty donor atoms) can be regarded as directed synthesis followed by self assembly, where the coordination site arrangement presented by the ligands matches exactly the coordination algorithm of the five metals. The fact that this geometrical arrangement seems to be unique for Mn^{II} may arise from the coordination flexibility of this metal ion due to its high spin d^5 electron configuration and zero crystal field stabilization energy.

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Notes and references

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‡ Ligand phaap (0.241 g, 1.00 mmol) was added to a hot solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.362 g, 1.00 mmol) in methanol–water (4 : 1) and the mixture stirred for 30 min, resulting in the formation of an orange precipitate. Found (vacuum dried recrystallized sample): C, 40.81; H, 2.93; N, 19.83. Calc. for $Mn_5(C_{12}H_{10}N_5O)_6(ClO_4)_4$ **1**: C, 40.91; H, 2.86; N, 19.88. IR (Nujol mull, cm^{-1}): ν(NH) 3441, 3336 ; ν(CN) 1649; $\nu(ClO)_4$ 1087, 620. UV–VIS. (Nujol mull): 541 nm (sh), 426 (sh): (MeCN) 579 nm ($\varepsilon = 63$ dm^3 mol^{-1} cm^{-1}). $\mu_{RT} = 5.8\ \mu_B$.

§ *Crystal data* for $C_{75.5}H_{76}Cl_4N_{30}Mn_5O_{26.5}$ **1**; $M = 2248.17$, triclinic, space group $P\bar{1}$, $a = 13.3249(7)$, $b = 18.8617(9)$, $c = 20.9513(10)$ Å, $\alpha = 85.3696(9)$, $\beta = 74.1679(10)$, $\gamma = 74.3330(9)°$, $V = 4877.6(4)$ Å^3, $\lambda = 0.71073$ Å, $Z = 2$, $D_c = 1.531$ g cm^{-3}, $T = 193(2)$ K, orange plate (0.10 × 0.20 × 0.40 mm), $\mu = 0.828$ mm^{-1}. Data were collected using a Siemens Smart three-circle diffractometer, equipped with a CCD area detector using graphite-monochromatized Mo-Kα X-radiation, and with an LT-II low temperature device. Diffracted data were corrected for absorption using the SADABS program. (G. M. Sheldrick, SADABS. Empirical Absorption Correction Program. University of Göttingen: Göttingen, Germany, 1996). SHELXTL (G. M. Sheldrick, SHELXTL 5.04/VMS, An integrated system for solving, refining and displaying crystal structures from diffraction data. Siemens Analytical X-ray Instruments Inc., Madison, WI) was used for the structure solution and the refinement based on F^2. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at idealized positions with isotropic U values set 1.2 × U (atom connected), and not refined. H atoms on one badly disordered methanol were not included. For 1260 parameters $R1 = 0.0637$, $wR2 = 0.1473$, for 11531 unique reflections with $I > 2.0\sigma(I)$ (12481 independent reflections), for 2θ in the range 2.02–46.0° (GOF = 1.085). CCDC 182/1142. See http://www.rsc.org/suppdata/cc/1999/347/ for crystallographic files in .cif format.

¶ The analogous nitrate complex has comparable pentanuclear core dimensions [$a = 17.968(7)$, $b = 20.444(8)$, $c = 13.429(8)$ Å, $\alpha = 108.67(4)$, $\beta = 102.71(4)$, $\gamma = 84.60(3)°$, $V = 4557(4)$ Å^3, $Z = 2$, space group $P\bar{1}$, $R = 0.076$, $R_w = 0.091$ (Rigaku AFC6S); Mn···Mn 3.91–4.01 Å, Mn–O–Mn 128–131°].

‖ SQUID magnetometer (Quantum Design MPMS5S) with a field of 2000 Oe. Diamagnetic corrections for the sample holder and with sample were applied.

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