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# A novel magnetically coupled nonamanganese(II) 3 × 3 portcullis-like grid involving just oxygen bridges, generated by strict self assembly of the metal cation and a single heptadentate ligand

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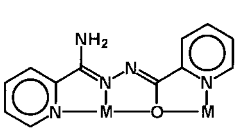
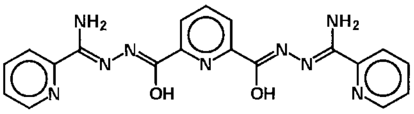
**The heptadentate ligand 2POAP combines two bridging alkoxide oxygen donors with diazine and pyridine terminal nitrogen donors in a linear array with the binding sites positioned critically to accommodate three metal centres, but on reaction with $Mn(ClO_4)_2·6H_2O$ a strict self assembly process occurs, producing a unique homoleptic nonamanganese 'square' grid complex, involving six ligands.**

Self assembly strategies for the formation of clusters with predetermined topological architectures are limited, and succeed only when carefully programmed subunits are incorporated in the ligand(s). The use of a single ligand with a repeating array of coordination pockets arranged in a 'linear' fashion has the potential to create a grid-like arrangement of metal centers, and some success has been achieved with linear polytopic ligands of this sort based on pyridazine and pyrimidine as a bridging subunit. Essentially flat 2 × 2 homotetranuclear grids have been achieved with Cu(I)[1] and Co(II)[2] with pyridazine and pyrimidine based ligands respectively, and a flat 3 × 3 nonanuclear grid with Ag(I)[3] involving a pyridazine based ligand. The Co(II) centers were shown to be antiferromagnetically coupled within the cluster, despite long distances of separation between the metals (6.5 Å).[4] The *n*-topic nature of the ligand creates a grid-like cluster of $n^2$ metal centres.[3] The ordering of paramagnetic metal ions in these grid-like arrays presents the possibility of extended spin communication within a lattice of closely spaced metal ion centers, if appropriate bridge groups can be incorporated into the ligand backbone.

Previous studies on tetradentate ligands (*e.g.* POAP) built on a flexible diazine (N–N) backbone, with a strategically positioned alkoxide fragment, have been shown to organize Mn(II), Co(II), Ni(II) and Cu(II) centers into square homotetranuclear clusters with just alkoxide bridges between the metal centers.[5,6] These systems display dominant antiferromagnetic exchange, except in the copper case where ferromagnetic coupling prevails.[6] In addition a unique, spin coupled, homoleptic trigonal-bipyramidal alkoxo-bridged cluster has been produced with Mn(II).[7]


POAP


2POAP

This report describes the synthesis‡ and study of a heptadentate ligand that is a systematic extension of POAP, in which repeating $N_2O$ coordination pockets are built on a 2,6-disubstituted pyridine central fragment (2POAP). Reaction of 2POAP with $Mn(ClO_4)_2·6H_2O$ in MeCN–$H_2O$ produced red crystals (72% yield)‡ suitable for structural analysis.§ The structure of $[Mn_9(2POAP–2H)_6](ClO_4)_6·3.57MeCN·11H_2O$ **1** is unique (Fig. 1) with a 3 × 3 grid of nine pseudo-octahedral, alkoxo-bridged Mn(II) centres coordinated by two groups of three roughly parallel dianionic ligands arranged above and below the metal pseudo-plane. The Mn centres comprise three different types; *trans*-$MnN_2O_4$ (central), *cis*-$MnN_4O_2$ (corners) and *mer*-$MnN_3O_3$ (sides). The $Mn_9O_{12}$ core (Fig. 2) shows that within each $Mn_4O_4$ subunit a puckered boat-like bridging arrangement exists involving an alternation of oxygens above and below the $Mn_4$ pseudo-plane. This then translates symmetrically throughout the fused arrangement that comprises the whole grid.

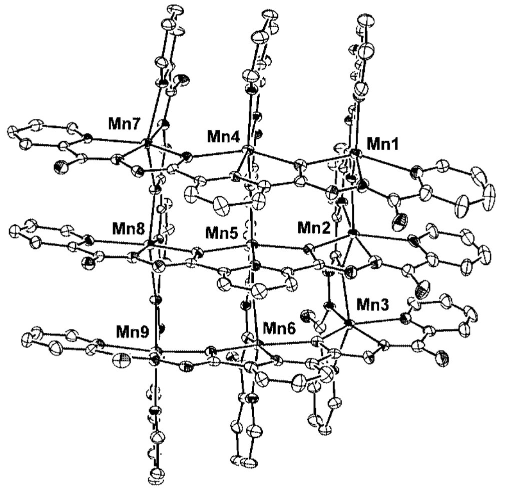


**Fig. 1** Structural representation of the cation $[Mn_9(2POAP - 2H)_6]^{6+}$ (**1**) (40% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°) Mn(1)–Mn(2) 3.953(3), Mn(1)–Mn(4) 3.956(4), Mn(2)–Mn(5) 3.918(4), Mn(4)–Mn(5) 3.928(3), Mn(2)–Mn(3) 3.909(3), Mn(3)–Mn(6) 3.956(4); Mn–O–Mn 126.6–130.0.

Variable temperature magnetic susceptibility measurements were carried out on a powdered sample of **1** in the temperature range 2–300 K.¶ Magnetic moments (per mol) drop smoothly from 16.9 $\mu_B$ at 300 K to 6.9 $\mu_B$ at 5 K, and then there is a very slight rise below this temperature. The room temperature value is consistent with the presence of nine high spin Mn(II) centers, and the drop to 6.9 $\mu_B$ at 5 K is associated with the presence of intramolecular antiferromagnetic exchange with the equivalent of one residual Mn(II) center in the spin coupled ($S$ = 5/2) ground state. This situation is an exact parallel to that occurring in the pentamanganese(II) cluster of POAP.[7] The slight rise in $\mu_B$ at temperatures $<5$ K may be due to a very weak

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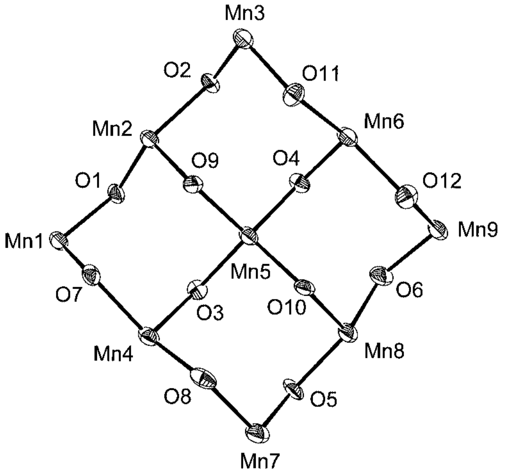

**Fig. 2** Structural representation of the nonanuclear core in $[Mn_9(2POAP - 2H)_6]^{6+}$.

ferromagnetic component. An evaluation of the complex exchange coupling situation will be attempted and described elsewhere.

Electrochemical studies in acetonitrile revealed five sequential redox waves (cyclic voltammetry; $E^{1/2}$/(V)($\Delta E_p$mV) 0.61(220), 0.92(100), 1.13(140), 1.33(130), 1.53(110) at 100 mV s$^{-1}$ (Fig. 3)). The $Zn(ClO_4)_2$ complex of 2POAP exhibits no significant waves in the range 0–1.6 V in acetonitrile. Coulometry (acetonitrile at 0.8 V) indicates that the first wave corresponds to a four-electron oxidation process, while the following four waves correspond to a further four-electron oxidation process in total (potential set at 1.65 V). Appropriate reduction sequences showed that eight electrons were required for complete reduction. The first wave reasonably corresponds to the oxidation of four equivalent Mn(II) centers to Mn(III), and is tentatively assigned to Mn(1), Mn(3), Mn(7) and Mn(9), which are equivalent and well separated. The sequence of four following waves is assigned to four other Mn(II) centers, which appear to be in communication, such that the oxidation potentials to Mn(III) become progressively more positive. These are assigned to Mn(2), Mn(6), Mn(4) and Mn(8), which are linked though Mn(5), and clearly all antiferromagnetically coupled to it. The visible spectrum of an oxidized acetonitrile solution of **1** shows the appearance of an intense band at 985 nm during the first four-electron oxidation process, followed by a further intensity increase after the full eight electron oxidation is complete. This band is reasonably assigned to an intervalence process.

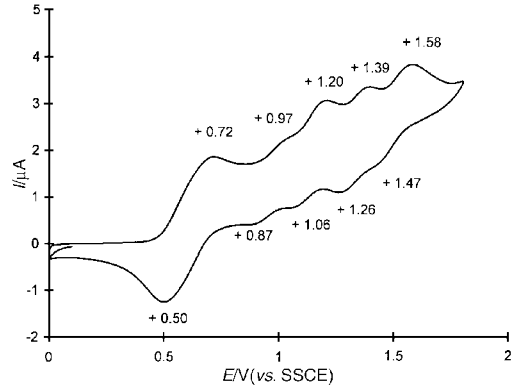

**Fig. 3** Cyclic voltammetry for $[Mn_9(2POAP - 2H)_6](ClO_4)_6 \cdot 18H_2O$ **1** in acetonitrile (0.5 mM, 0.1 M $NEt_4ClO_4$; Pt working electrode, Pt counter electrode, SSCE reference electrode; BAS CV27 voltammograph; 100 mV s$^{-1}$).

The aggregation of nine octahedral manganese(II) centers (fifty four coordination positions) into an alkoxo-bridged, portcullis-like 3 × 3 grid by six heptadentate 2POAP ligands (fifty four donor positions) is a unique example of a self assembly process in which the coordination algorithm of the nine metal assembly is exactly matched by the aligned arrangement of the two sets of ‘parallel’ ligands arranged above and below the metal grid pseudo-plane. This strategy has general application, and $Cu(II)_9$ analogues have been prepared.[5] A simple extension of this type of ligand with additional five-membered chelate ring compartments can be envisaged to produce 4 × 4 and 5 × 5 grids, and even higher homologues. Efforts are currently underway to achieve this goal.

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## Notes and references

‡ 2POAP was synthesized in 85% yield by the reaction of 2,6-pyridinedihydrazide with the methyl ester of iminopicolinic acid. 2POAP (0.403 g, 1.00 mmol) was added to a hot solution of $[Mn(H_2O)_6](ClO_4)_2$ (1.45 g, 4.00 mmol) in water (5 mL). MeCN (15 mL) was then added and the mixture left at room temperature. Red crystals (72% yield) formed after several days. Found (vacuum dried sample): C, 35.77; H, 2.63; N, 19.61. Calc. for $Mn_9(C_{19}H_{15}N_9O_2)_6\ (ClO_4)_6 \cdot 18H_2O$ **1**: C, 35.81; H, 3.29; N, 19.78%. IR (Nujol mull, cm$^{-1}$): $\nu$NH/$H_2O$ 3450, 3339, 3247 ; $\nu$CO/CN 1689, 1654; $\nu ClO_4$ 1095. UV–VIS. (Nujol mull): 546 nm (sh); (MeCN) 1027 nm ($\varepsilon$ 19.6 dm$^3$ mol$^{-1}$ cm$^{-1}$). $\mu_{RT} = 16.9\ \mu_B$ (mol$^{-1}$).

§ *Crystal data* for $[Mn_9(2POAP - 2H)_6](ClO_4)_6 \cdot 3.57MeCN \cdot 11H_2O$: $C_{121.14}H_{122.71}N_{57.57}O_{47}Cl_6Mn_9$ **1**; $M = 3844.3$, monoclinic, space group $C2/c$, $a = 26.0641(16)$, $b = 26.0910(16)$, $c = 53.291(3)$ Å, $\beta = 102.473(1)°$, $U = 35385(4)$ Å$^3$, $Z = 8$, $D_c = 1.443$ g cm$^{-3}$, $T = 150(2)$ K, $\mu$(Mo-K$\alpha$) = 0.800 mm$^{-1}$. 2075 parameters were refined with 17267 unique reflections ($I > 2.0\sigma(I)$) to give $R1 = 0.1419$, $wR2 = 0.3936$ (30409 independent reflections, $R_{int} = 0.0668$) (Bruker Smart three-circle diffractometer with a CCD area detector set at 6 cm, graphite-monochromatized Mo-K$\alpha$ X-radiation). Only the non-hydrogen atoms of the cation and the chlorine atoms of the anions were refined anisotropically. Hydrogen atoms were fixed at idealized positions (U 1.2 × U (riding atom)), except for the amino groups, and the eleven identified waters of crystallization, where they were not included. The structure also contains three fully occupied acetonitrile molecules of crystallization and one partially occupied molecule refined to an occupancy of 0.57. The perchlorate anions are very disordered and the oxygen atoms were modeled isotropically, each with its own free variable, giving a total of 6.9 perchlorates in the final cycle of least-squares. Attempts to use a SUMP command to constrain the total perchlorate occupancy to six resulted in unstable refinements. The cation is however clearly defined, despite difficulties with the structural refinement and identification of all lattice fragments. A preliminary structure on $[Mn_9(2POAPZ - 2H)_6](NO_3)_6 \cdot xH_2O$ shows that it has the same structure (2POAPZ is the terminal pyrazine equivalent of 2POAP).[5]

CCDC 182/1521. See http://www.rsc.org/suppdata/cc/a9/a909180g/ for crystallographic files in .cif format.

¶ SQUID magnetometer (Quantum Design MPMS5S) with a field of 1000 Oe. Diamagnetic corrections for the sample holder and the sample were applied.

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