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A 1-D coordination polymer based on a Mn₄₀ octagonal super-structure**

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Supporting information:

†Electronic Supplementary Information (ESI) available: Crystallographic data (CIF format) for (1)_n, and various structural and magnetism figures. See <http://dx.doi.org/10.1039/C2CC36412C>

Graphical abstract:



Abstract

A 1-D coordination polymer, constructed using a combination of diols and phenolic oximes, contains a novel [Mn₉] sub-unit, a nanosized [Mn₄₀] octagonal super-structure and a [Mn₂₁] repeating unit.

Introduction

High nuclearity metal clusters continue to attract significant interest mainly due to their intriguing molecular structures and fascinating chemical and physical properties.¹ One important challenge for coordination chemists is the synthesis of multidimensional and multifunctional coordination polymers based on high nuclearity metal clusters, since such compounds could combine interesting structural architectures and topologies with the novel physical properties appearing in their building-blocks.² Although several discrete (0-D), large polynuclear complexes consisting of 3d and/or 4f metal ions with nuclearities up to 168³ have been reported⁴ there are only a few that have been recognised in 1-, 2- and 3-D coordination networks. Examples of the latter include [Er₃₆]⁵ and [M₂₄] (M = Co,^{6a} Ni^{6a}, Cu^{6b}) wheels, [Ln₂₆] spheres (Ln = Dy, Gd),⁷ [Mn₁₉] tetrahedra,⁸ and various other types of polyhedra (e.g. [Mn₆₂],⁹ [Mn₂₂],¹⁰ [Mn₂₁]¹¹ clusters), some of which^{6a,8,10} also display very interesting magnetic behaviour.

We have been interested in the development of synthetic methodology towards the construction of new high nuclearity metal clusters appearing in 0-, 1-, 2- and 3-D materials.^{4b-e} One of the reaction systems being explored for this purpose involves the combined use of diols and phenolic oximes, and initial results have been encouraging with the formation of a [Mn₃₂] “double-decker” wheel.^{4c} Herein we extend this strategy by reporting the synthesis, structure and magnetic behaviour of an unusual high nuclearity cluster appearing in the 1-D coordination polymer $\{(\text{Et}_4\text{N})[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_9(\mu_3\text{-O})_6(\mu_3\text{-OH})_2(\text{sao})_{12}\text{Br}_3(\text{O}_2\text{CMe})_{12}(\text{H}_2\text{O})_{10}(\text{CH}_3\text{CN})]\text{Br}_2\}_n$ (**1**)_n (sao²⁻ = the dianion of salicylaldoxime). The 1-D chain is based on a nanosized octagonal [Mn₄₀] super-structure consisting of four [Mn₉] sub-units connected through single Mn ions and is one of the largest structures that has appeared in any polymeric species.⁹

Reaction of MnBr₂·4H₂O with saoH₂ and 1,3-butanediol (H₂bd) in the presence of tetraethylammonium bromide (Et₄NBr) in a 1:1:8:1 ratio in MeCN leads to the formation of complex **1** in ~30% yield‡. The diol does not appear in the final product, but its presence in the reaction mixture is essential, since reactions in its absence do not result in (**1**)_n. The structure of (**1**)_n‡ reveals that it is a mixed-valent one-dimensional chain, which is best described as a ribbon of [Mn₄₀] octagonal units (Fig. 1). The repeating unit of (**1**)_n is the cation $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_9(\mu_3\text{-O})_6(\mu_3\text{-OH})_2(\text{sao})_{12}\text{Br}_3(\text{O}_2\text{CMe})_{12}(\text{H}_2\text{O})_{10}(\text{CH}_3\text{CN})]^+$ (Fig. 2a) with two Br⁻ ions and one Et₄N⁺ ion

compensating the positive cluster charge. The cluster cation of $(\mathbf{1})_n$ consists of two $[\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_3(\mu_3\text{-O})_3(\mu_3\text{-OH})(\mu_3\text{-Br})(\mu_3\text{-sao})_6(\text{O}_2\text{CMe})_6]^{2-}$ sub-units (Fig. 2b), which, although not crystallographically equivalent, display very similar structures and metric parameters. These are each linked to a neighbouring $[\text{Mn}_9]$ unit through “single” Mn^{2+} ions (Mn10, Mn14, Mn18 and symmetry equivalents; Figure 1 shows Mn14 and Mn18 only), the result being the formation of a rather beautiful $[\text{Mn}_{40}]$ octagonal super-structure, with the vertices of the latter alternately occupied by $[\text{Mn}_9]$ sub-units and single Mn^{2+} ions.

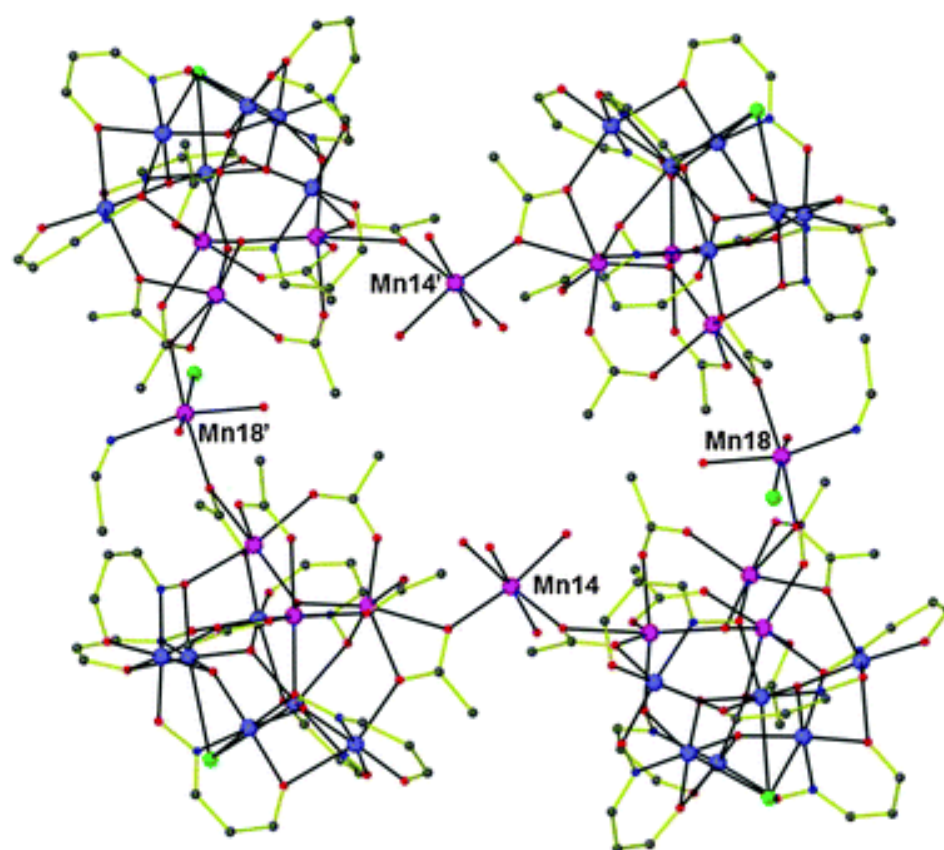


Figure 1. Representation of the $[\text{Mn}_{40}]$ octagonal super-structure. Colour scheme, Mn^{III} : blue; Mn^{II} : pink; O: red; Br: green; N: dark blue; C: grey. Many C and all H atoms have been omitted for clarity. Symmetry code: (') $2-x, -y, 2-z$.

The metallic skeleton of the $[\text{Mn}_9]$ sub-unit describes a distorted partial supertetrahedron (or two inverted triangles) in which the “upper” vertex (as drawn in Fig 2c) is missing. It comprises a basal $[\text{Mn}^{\text{III}}_6]$ unit (or a super-triangle) and a capping triangle of Mn^{2+} ions. The $[\text{Mn}^{\text{III}}_6]$ base is constructed from three corner-sharing $[\text{Mn}^{\text{III}}_3(\mu_3\text{-O})]^{7+}$ triangles and deviates significantly from planarity, with a mean deviation from the best fit plane of ~ 0.41 Å.

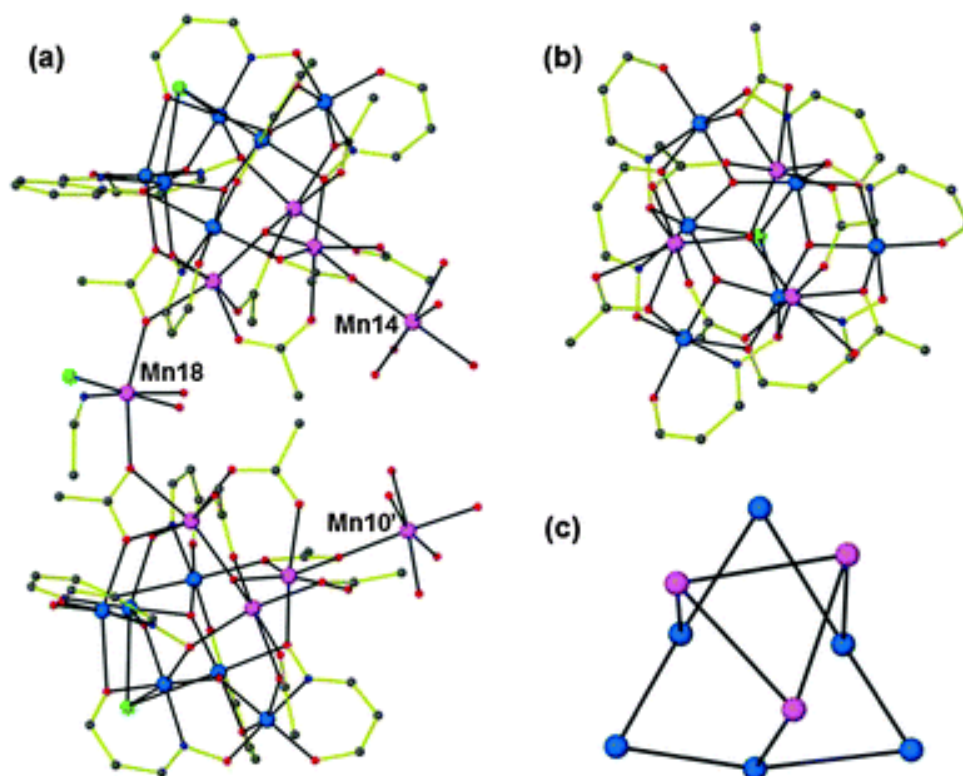


Figure 2. Representations of the structure of (a) the cluster cation of $(\mathbf{1})_n$; (b) the $[\text{Mn}_9]$ sub-unit; and (c) its metallic core with the black solid lines emphasising the distorted partial supertetrahedron. Colour scheme as in Fig. 1. Many C and all H atoms have been omitted for clarity. Symmetry code: (') $1-x, -y, 2-z$.

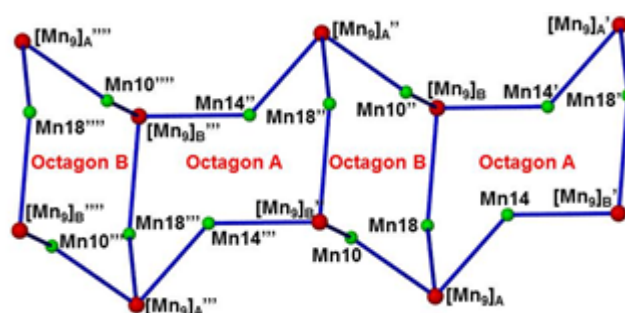


Figure 3. A simplified representation of a part of the zig-zag chain of $(\mathbf{1})_n$ emphasising the $[\text{Mn}_{40}]$ super-structure and the two types of $[\text{Mn}_{40}]$ octagons. Symmetry codes: (') $2-x, -y, 2-z$; (') $1-x, -y, 2-z$; (') $x-1, y, z$; (') $-x, -y, 2-z$.

The Mn ions of the “upper” $[\text{Mn}^{\text{II}}_3]$ triangle are bridged through a $\mu_3\text{-OH}^-$ which resides $\sim 0.5 \text{ \AA}$ below the $[\text{Mn}_3]$ plane, towards the $[\text{Mn}_6]$ base. The sole Br⁻ ion per $[\text{Mn}_9]$ unit caps the lower face of the

[Mn₆] basal plane, μ_3 -bonding to the Mn ions on the edges of the super-triangle. The sao^{2-} ligands are of two types: three are $\eta^1:\eta^1:\eta^2:\mu_3$ -bridging between the Mn³⁺ ions in the [Mn₆] basal plane, and three are $\eta^2:\eta^1:\eta^1:\mu_3$ -bridging between the Mn³⁺ ions in the [Mn₆] basal plane and the Mn²⁺ ions in the triangular cap. The acetates are also of two types: three μ -bridge across the edges of the [Mn₃^{II}] triangle, and three coordinate in a $\eta^2:\eta^2:\mu_3$ -fashion, chelating to a Mn²⁺ ion and bridging to a Mn³⁺ ion in the [Mn₉] sub-unit, and further bridging to the “single” Mn²⁺ ion (Mn10, Mn14, Mn18 and symmetry equivalent). The latter ion links neighbouring [Mn₉] units to form the [Mn₂₁] repeating unit of the polymer, while Mn10 and Mn14 are responsible for the formation of the octagonal [Mn₄₀] super-structure and its assembly into a 1-D chain. Each octagon contains four [Mn₉] sub-units which are separated by alternating Mn14 and Mn18 (octagon A) and Mn10 and Mn18 (octagon B) ions (Fig. 3 and S1) and thus the chain of (1)_n consists of two types of octagons, albeit with similar metric parameters. A better appreciation of the size of the Mn₄₀ octagonal units is provided by the simplified representation of Figure 4 which shows that the various dimensions of the two types of octagons are in the range ~10 – 20 Å. A close examination of the packing of complex (1)_n reveals the formation of zig-zag chains of [Mn₄₀] octagons running parallel in the crystal (Fig. S2), but with no significant interchain H-bonds. The oxidation states of the Mn ions and the protonation levels of the O-atoms of the ligands were determined by BVS calculations, charge balance considerations and inspection of metric parameters.¹² The Mn ions are all in distorted octahedral geometries with the twelve Mn³⁺ ions displaying the expected Jahn–Teller (JT) axial elongation, although the JT axes are not co-parallel.

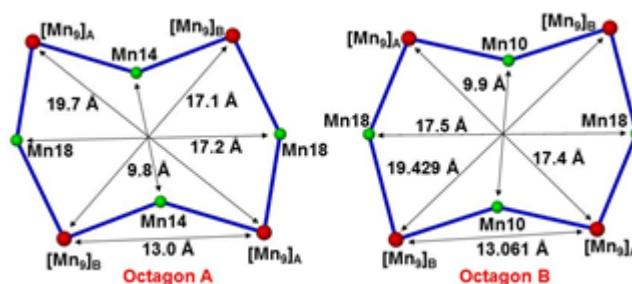


Figure 4. A simplified ball and stick representation of the dimensions of the two types of octagons in (1)_n.

Compound **1** combines several attractive structural features. The [Mn₉] sub-unit is structurally novel, despite exhibiting some similarity to an oxime-based [Mn₉] cluster reported recently.¹³ Indeed it differs in the relative orientations of the [Mn₆]/[Mn₃] sub-units, the type and connectivity of the bridging ligands, and the oxidation state distribution (all Mn³⁺ in ref 13). In addition, the [Mn₂₁] repeating unit is one of the largest observed in any coordination polymer, and the [Mn₄₀] octagonal super-structure is unprecedented in structural type, representing an unusual example of a nanosized cluster appearing in a polymeric species. Furthermore, the [Mn₄₀] octagonal super-structure joins a

small family of large clusters consisting of repeating polynuclear M_x ($x > 6$) clusters, demonstrating that such compounds can appear not only in 0-D systems as reported recently,^{4b,e} but also in multidimensional coordination polymers.

Variable temperature direct current (dc) magnetic susceptibility (χ_m) measurements were performed on a powdered crystalline sample of dried complex $(1)_n \cdot \text{MeCN}$ in the 5 - 300 K temperature range in a 0.1 T magnetic field and are plotted as the $\chi_m T$ product versus temperature in Figure 5. The $\chi_m T$ value decreases slowly from $\sim 59 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K to $\sim 37 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 30 K, and then more rapidly to a value of $18.65 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 5 K. The room temperature $\chi_m T$ value is significantly smaller than the spin-only ($g = 2$) value of $75.375 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ expected for nine Mn^{2+} and twelve Mn^{3+} [non-interacting] ions. Magnetisation versus field data (Figures S3-4), collected at temperatures between 2 and 7 K and in applied fields of 0.5-7 T, show $M/N\mu_B$ increasing almost linearly with applied field. The dc data is therefore suggestive of dominant, but rather weak antiferromagnetic exchange between the constituent metal ions likely resulting in the formation of a continuum-like band of spin states even at the lowest temperatures measured. This is as would be expected [in the weak exchange limit] for such a large nuclearity cluster possessing several Mn^{2+} ions that are known to propagate very weak exchange interactions.

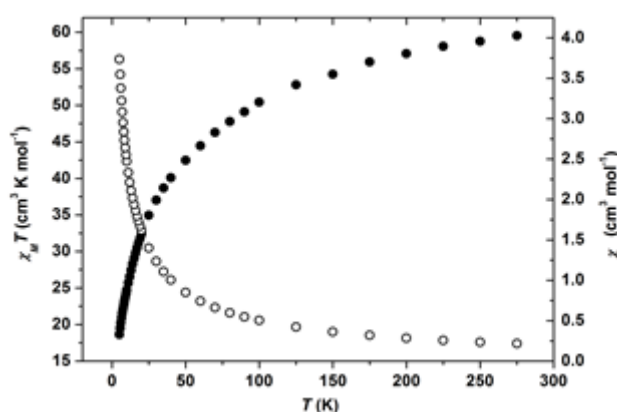


Figure 5. Plot of χ (○) and $\chi_m T$ (●) versus T in the 300-5 K temperature range for $(1)_n \cdot \text{MeCN}$. The data was collected in an applied field of 0.1 T.

In conclusion, a novel $[\text{Mn}_9]$ sub-unit, a $[\text{Mn}_{21}]$ repeating unit and an unprecedented nanosized octagonal $[\text{Mn}_{40}]$ super-structure have appeared in a 1-D chain that is best described as a ribbon of octagons. The $[\text{Mn}_{40}]$ octagonal super-structure represents a rare example of a large cluster consisting of covalently linked polynuclear M_x ($x > 6$) complexes, and is one of very few examples of such clusters appearing in coordination polymers. Its isolation, following on from the construction of a $[\text{Mn}_{32}]$ double-decker wheel, proves that the combined use of oximes and diols in Mn cluster chemistry can afford novel compounds with aesthetically pleasing structures.

Notes and references

‡ Vacuum-dried solid analysed (C, H, N) as (1)_n·MeCN. Calcd. (found): C 32.71 (32.89), H 3.29 (3.35), N 4.77 (4.82).

Crystal data for **1**: C₁₁₈H₁₁₆Br₅Mn₂₁N₁₄O₆₆, *M* = 4339.54, Triclinic, *a* = 18.5805(7) Å, *b* = 22.1360(7) Å, *c* = 27.3338(10) Å, *α* = 111.986(3)°, *β* = 91.140(3)°, *γ* = 109.790(3)°, *V* = 9669.5(6) Å³, *T* = 100(2) K, space group *P* $\bar{1}$, *Z* = 2, *ρ*_{calcd} = 1.490 g cm⁻³, 75111 reflections collected, 19082 reflections used (*R*_{int} = 0.0646), *R*₁ [*I* > 2*s*(*I*)] = 0.0669, *wR*₂ = 0.1970. The asymmetric unit also contains severely disordered water and acetonitrile molecules that could not be modeled properly. Thus, the SQUEEZE program was used to eliminate the contribution of the electron density in the disordered solvent region from the overall intensity data. CCDC 894406.

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