A 1-D coordination polymer based on a Mn$_{40}$ octagonal super-structure†

Maria Manoli, a Ross Inglis, b Manolis J. Manos, a Giannis S. Papaefstathiou, c Euan K. Brechin a,b and Anastasios J. Tasiopoulos a,**

A 1-D coordination polymer, constructed using a combination of diols and phenolic oximes, contains a novel [Mn$_{3}$] sub-unit, a nanosized [Mn$_{40}$] octagonal super-structure and a [Mn$_{21}$] repeating unit.

High nuclearity metal clusters continue to attract significant interest mainly due to their intriguing molecular structures and fascinating chemical and physical properties.† 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.‡ Although several discrete (0-D), large polynuclear complexes consisting of 3d and/or 4f metal ions with nuclearities up to 168 have been reported there are only a few that have been recognised in 1-, 2- and 3-D coordination networks. Examples of the latter include [Er$_{26}$$]^{3-}$ and [Mn$_{3}$] (M = Co$^{6+}$, Ni$^{6+}$, Cu$^{6+}$) wheels, [Ln$_{53}$] spheres (Ln = Dy, Gd), [Mn$_{31}$] tetrahedra, and various other types of polyhedra (e.g. [Mn$_{62}$], [Mn$_{12}$], [Mn$_{21}$] clusters), some of which 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. 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 [Mn$_{32}$] “double-decker” wheel. 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}]_2\text{Mn}^{III}_{12}\text{Mn}^{II}_{18}[(\text{H}_2\text{O})_3\text{Mn}^{III}_{12}\text{Mn}^{II}_{18}][\text{H}_2\text{O}]_10(\text{CH}_3\text{CN})\]_2\text{Mn}^{II}_{19}[(\text{H}_2\text{O})_3\text{Mn}^{III}\text{Mn}^{II}](\text{sao})_{12}\text{Br}_3(\text{O}_2\text{CMe})_{12}\}$ (Fig. 2a) with two Br$^{-}$ ions and one Et$_3\text{N}^{+}$ ion compensating the positive charge.

\[\text{Fig. 1} \quad \text{Representation of the [Mn}_{30}\] 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 octahedral geometry with the twelve \(\text{Mn}^{3+}\) ions in a polymeric species. Furthermore, the \([\text{Mn}_{40}]\) octagonal super-structure is unprecedented in structural type, representing an unusual example of a nanosized cluster appearing not only in 0-D systems as reported recently,\(^4\) but also in multidimensional coordination polymers. The \([\text{Mn}_{9}]\) sub-unit is structurally novel, despite exhibiting some similarity to an oxime-based \([\text{Mn}_{9}]\) cluster reported recently.\(^1^{3}\) Indeed it differs in the relative orientations of the \([\text{Mn}_{9}]\)\([\text{Mn}_{3}]\) sub-units, the type and connectivity of the bridging ligands, and the oxidation state distribution (all \(\text{Mn}^{3+}\) in ref. 13). In addition, the \([\text{Mn}_{21}]\) repeating unit is one of the largest observed in any coordination polymer, and the \([\text{Mn}_{40}]\) octagonal super-structure is unprecedented in structural type, representing an unusual example of a nanosized cluster appearing not only in 0-D systems as reported recently,\(^4\) but also in multidimensional coordination polymers.
Variable temperature direct current (dc) magnetic susceptibility ($\chi_m$) measurements were performed on a powdered crystalline sample of dried complex (1)$_n$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 Fig. 5. The $\chi_m T$ value decreases slowly from ~59 cm$^3$ mol$^{-1}$ K at 300 K to ~37 cm$^3$ mol$^{-1}$ K at 30 K, and then more rapidly to a value of 18.65 cm$^3$ mol$^{-1}$ K at 5 K. The room temperature $\chi_m T$ value is significantly smaller than the spin-only (g = 2) value of 75.375 cm$^3$ mol$^{-1}$ K expected for nine Mn$^{2+}$ and twelve Mn$^{3+}$ [non-interacting] ions. Magnetisation versus field data (Fig. S3 and S4, ESI), collected at temperatures between 2 and 7 K and in applied fields of 0.5–7 T, show MnN$_{10}$H$_8$ 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 nucleiarity cluster possessing several Mn$^{2+}$ ions that are known to propagate very weak exchange interactions.

In conclusion, a novel [Mn$_{9g}$] sub-unit, a [Mn$_{14}$] repeating unit and an unprecedented nanosized octagonal [Mn$_{40}$] superstructure have appeared in a 1-D chain that is best described as a ribbon of octagons. The [Mn$_{40}$] octagonal superstructure 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 [Mn$_{14}$] double-decker wheel, proves that the combined use of oximes and diols in Mn cluster chemistry can afford novel compounds with aesthetically pleasing structures.

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Notes and references


