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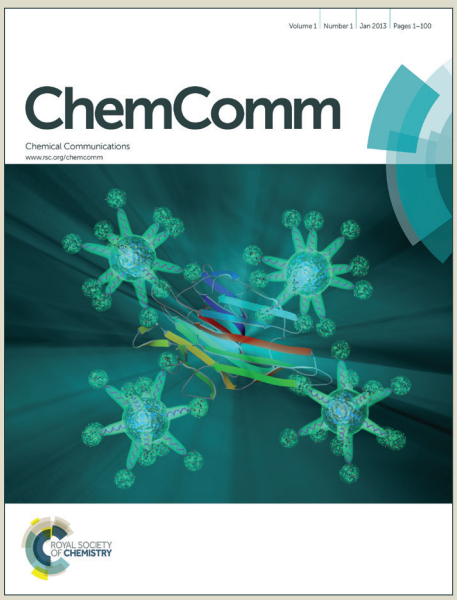

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"Converting" an hexametallic Mn^{III} wheel to a dodecametallic Mn^{III} wheel *via* ligand oximation

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Ligand oximation "converts" an hexametallic Mn^{III} wheel into a dodecametallic Mn^{III} wheel, while the magnetic exchange switches from ferro- to antiferromagnetic.

Understanding the fundamentally important relationship between molecular structure and magnetic behaviour requires the construction of large families of related molecules.[1] Ligand design is therefore a vital component for the construction of polymetallic molecules, and scientists interested in investigating the magnetic properties of cages containing multiple paramagnetic metal ions have employed synthetic strategies encompassing the whole spectrum from "predictable" to "serendipitous" self-assembly employing both rigid and flexible structural building blocks.[2] Indeed hundreds if not thousands of beautiful cluster compounds with fascinating physical properties have been reported for more than half a century.[3] Mining structural databases provides invaluable information about what synthetic strategies have been most successful, and perhaps more importantly informs us of the ligand bridging moieties that are most prominent for a particular metal in a particular oxidation state. For Mn^{III} a search of the CSD reveals that phenolic oximes[4] and diols[5] are two particularly successful examples. The former are somewhat more rigid and predictable in their behaviour, commonly μ–bridging, while the latter are more flexible (μ– to μ_5–bridging) and thus rather unpredictable, although each alkoxide moiety within the ligand is more often than not found to be μ–bridging. Herein we introduce two new ligand systems, H_3L^1 and H_4L^2 (Figure 1), for the synthesis of Mn^{III} wheels. The latter is analogous to the former but with the ketone moiety oximated. This simple change converts it from a tridentate to a tetradentate ligand and the result is a doubling in the size of the wheel.

Reaction of $MnCl_2{\cdot}4H_2O$ and H_3L^1 in a basic MeOH solution produces hexagonal black crystals of $[Mn^{III}_6Na(L^1)_6]Cl$ (**1**) after five days (see the ESI for full details). The crystals were in a cubic crystal system and structure solution was obtained in the *Ia-3d* space group†. The structure (Figure 2) describes a Na^+-centred $[Mn^{III}_6]$ wheel in which all the Mn^{III} ions and ligands are symmetry equivalent. The ligand is fully deprotonated and μ_3-bridging: the N-atom and phenolic O-atom are terminally bonded with one alkoxide arm (O3) bridging between neighbouring Mn^{III} ions (Mn-O3-Mn, 110.25°), the other (O4, Mn-O4-Mn, 101.29°) doing likewise, but also bridging to the central Na^+ ion. The ketone moiety remains non-bonded. The Mn^{III} ions are all six coordinate in distorted octahedral geometries, their Jahn-Teller axes being defined by the N1-Mn1-O4 vector. The distance between neighbouring Mn^{III} ions is 3.25 Å and the radius of the wheel (Mn…Mn) is ~6.5 Å. The central Na^+ is restrained by symmetry to be six coordinate and octahedral with Na-O4 = 2.314 Å. In the crystal the molecules pack in an aesthetically pleasing manner (Figure S1), with large accessible voids containing the Cl^- counter ions and heavily disordered solvent molecules. The closest cation…anion distances are of the order ~3.5 Å to the C atoms of the diol and ketone moieties, with the closest cluster…cluster interactions approximately 3.6 Å (C(Ph)…C(Ph); O(ketone)…C(diol)).

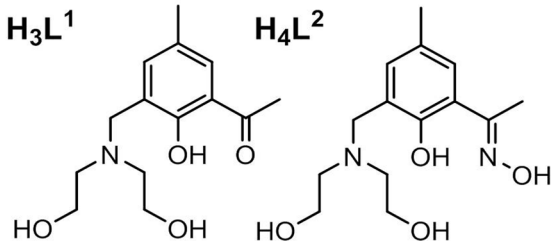

Figure 1. The structures of H_3L^1 (left) and H_4L^2 (right).

A similar reaction but employing H_4L^2 produces the dodecametallic complex $[Mn^{III}_{12}(OMe)_{20}(L^2)_4]$ (**2**) as brown plates in the monoclinic space group $P2_1/n$. The structure (Figure 3)

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contains a non-planar, saddle-shaped dodecametallic wheel. The Mn^{III} ions are all symmetry inequivalent, but there is repetition in the pattern of ligand bridging (Figure 3C): the first two Mn^{III} ions are bridged by two μ-methoxides, the next two Mn^{III} ions are bridged by one μ–methoxide and one μ–alkoxide of the diethanolamine moiety, and the third pair of Mn^{III} ions is bridged by two μ–methoxides and the –N-O- moiety of the phenolic oxime unit. The phenolic O-atom is terminally bonded (~1.89 Å), as is the remaining O-atom (~1.92 Å) of the diol moiety; the fully deprotonated L^2 ligand is thus μ_4–bridging. The Mn-O(OMe)-Mn bridging angles are rather varied, ranging from 91.95-104.99°; while the Mn-O(diol)-Mn angles all fall in the 103.78-105.39° range. The Mn-O-N-Mn torsion angles are all rather small, 6.77-16.78°. The Mn^{III} ions are all six coordinate and in distorted octahedral geometries, with the positions of the Jahn-Teller axes depicted in Figure 3D. The wheel is approximately 10 Å in diameter. The closest inter-cluster contacts are of the order of 3.4 Å between the methyl group of the phenyl rings to the phenoxide O-atoms and the $–CH_2$ groups of the diol moiety (Figure S2).

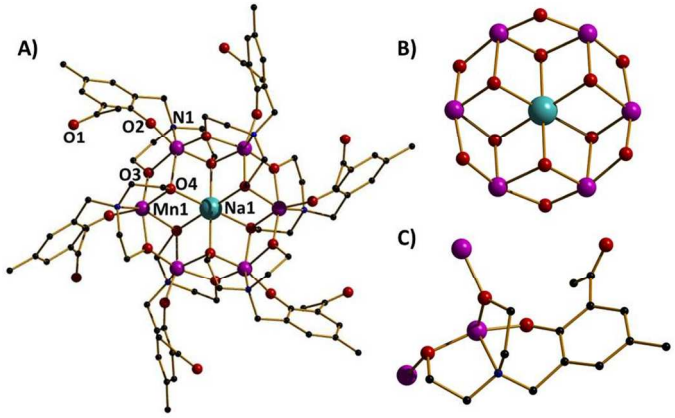

Figure 2. (A) The structure of the cation of **1**, viewed perpendicular to the $[Mn^{III}_6]$ plane. (B) The magnetic core. (C) The bridging mode of the ligand. Colour code: Mn = purple, Na = light blue, O = red, N = dark blue, C = black. H atoms and Cl^- anions omitted for clarity.

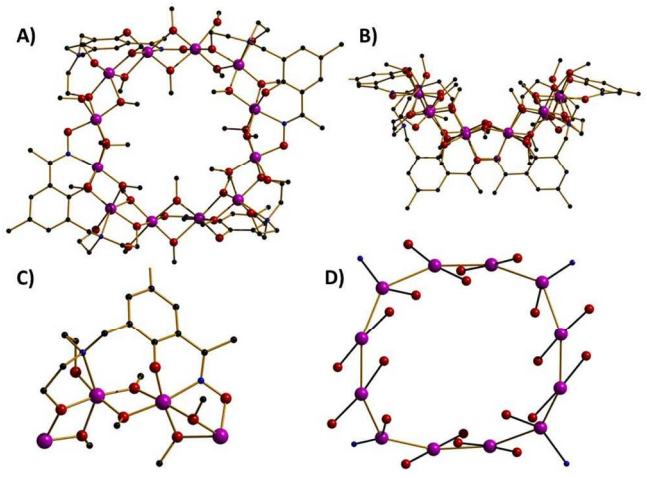

Figure 3. The structure of complex **2**, viewed (A) perpendicular and (B) parallel to the $[Mn^{III}_{12}]$ "plane". H atoms and Cl^- anions omitted for clarity. (C) The "repeat" unit of the wheel highlighting the ligand bridging modes. (D) Metallic skeleton highlighting the Jahn-Teller axes. Colour code: Mn = purple, O = red, N = blue, C = black. H-atoms omitted for clarity.

A search of the CSD reveals there to be eleven examples of $[Mn^{III}_6]$ wheels, of which five are centred wheels containing an alkali metal cation; three of these contain Na, two Ce and one Li.[6] $[Mn_{12}]$ wheels are far more unusual, indeed there are only three reported in the literature and only one of those, the complex $[Mn_{12}(tpeshz)_{12}(dmf)_{12}]$ (H_3tpeshz = *N-trans*-2-pentenoylsalicylhydrazide), contains Mn exclusively in the III+ oxidation state.[7]

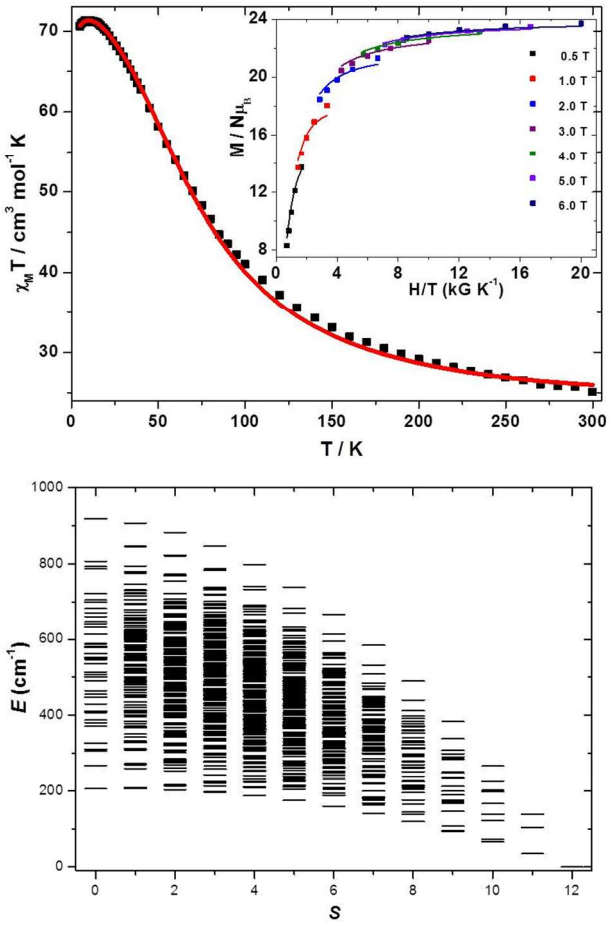

Figure 4. (top) Plot of the $\chi_M T$ product versus T for **1**. The inset shows a plot of reduced magnetisation. Solid lines are a fit of the experimental data. See text for details. (bottom) Plot of energy versus total spin state, derived from the isotropic fit of the susceptibility.

Direct current magnetic susceptibility studies were performed on polycrystalline samples of **1** and **2** in the 5–300 K range in an applied field of 0.1 T. The results are plotted as the $\chi_M T$ product versus T in Figure 4 and Figure S3. For **1** the $\chi_M T$ value of ~26 cm^3 K mol^{-1} at 300 K is above the spin-only (g = 2.0) value of 18 cm^3 K mol^{-1} expected for six non-interacting high-spin Mn^{III} ($3d^4$) ions. The value increases constantly with decreasing temperature reaching a maximum value of ~71 cm^3 K mol^{-1} at 10 K, where it then plateaus. This behaviour is indicative of the presence of ferromagnetic exchange between neighbouring

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metal ions. The experimental data can be fitted to the isotropic spin-Hamiltonian (1), by use of the Levenberg–Marquardt algorithm[8]:

$$\hat{H}_{iso} = -2\sum_{i,j>i} J\hat{S}_i \cdot \hat{S}_j + \mu_B Hg \sum_i \hat{S}_i \qquad (1)$$

where *i*, *j* are indices running through the constituent single ions, *J* is the isotropic exchange parameter, $\hat{S}$ is a spin operator, μ_B is the Bohr magneton, *g* = 2.0 is the *g*-factor of Mn^{III} and *H* is the applied magnetic field. We have used a "wheel" model, including just one exchange interaction between nearest neighbours. This affords *J* = +8.64 cm^{-1} with the resulting *S* = 12 ground state being separated by ~35 cm^{-1} from the first (*S* = 11) excited state (Figure 4, bottom). A ferromagnetic interaction for this molecule is expected based on a recently published magnetostructural correlation (MSC) for alkoxide-bridged Mn^{III} dimers in which ferromagnetic exchange is predicted when neighbouring Jahn-Teller axes are arranged perpendicular to each other.[9] The magnitude of the exchange observed in **1** is also consistent with this MSC. Magnetisation data (Figure 4, top, inset) collected in the 2-7 K and 0.5 – 6.0 T temperature and field ranges can be fitted by assuming only the ground spin-state is thermally populated under these experimental conditions. We therefore used anisotropic spin-Hamiltonian (2) that takes into account spin-variables relevant to the *S* = 12 ground spin-state only,

$$\hat{H}_{aniso} = D_{S=12}\left[\hat{S}_z^2 - (S+1)S/3\right] + \mu_B Hg \sum_i \hat{S}_i \qquad (2)$$

where *D* is the uniaxial anisotropy parameter of the *S* =12 ground spin-state. Spin-Hamiltonian (2) was fitted to the experimental data by use of the simplex algorithm,[8] to give the best-fit parameter $D_{(S=12)}$ = -0.086 cm^{-1}.

For complex **2**, the $\chi_M T$ value of ~35 cm^3 K mol^{-1} at 300 K is slightly below the spin-only value of 36 cm^3 K mol^{-1} expected for twelve non-interacting high-spin Mn^{III} ions (Figure S3). The value decreases continually with decreasing temperature reaching a minimum value of ~12.5 cm^3 K mol^{-1} at 5 K. This behaviour is indicative of the presence of antiferromagnetic exchange between neighbouring metal ions, and the presence of a small or diamagnetic spin ground state. This is corroborated by the magnetisation data (Figure S4) which rises in a near linear fashion with field and does not reach saturation. The sheer size of the cage precludes any quantitative analysis of the data. Neither complex shows any frequency-dependence in ac susceptibility above 2 K, ruling out slow relaxation of the magnetisation, at these temperatures.

At this stage it is difficult to determine the fundamental reasons why the magnetic exchange is ferromagnetic in **1**, but antiferromagnetic in **2**. From a structural perspective, the most obvious difference is the introduction of the bridging oxime -N-O- moiety in **2**. However, given the structural complexity of compound **2**, unravelling the answer will require both the construction of new family members and detailed theoretical analysis.

Conclusions

Combining phenolic oxime and diethanolamine fragments into the same organic framework affords the novel pro-ligands H_3L^1 and H_4L^2 and their initial use in Mn^{III} chemistry has led to the isolation of unusual hexa- and dodecametallic wheels; oximation of the ligand doubling the nuclearity of the wheel. The former complex displays dominant ferromagnetic exchange interactions and an *S* = 12 ground state, the latter antiferromagnetic exchange and a small or diamagnetic ground state. Given that this is the first investigation into the coordination chemistry of these two organic molecules, it is likely that many more polymetallic cages can be isolated. More generally, the concept of incorporating previously successful but independent ligands into one framework is likely widely applicable.

Notes and references

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†*Crystal data for **1**: $C_{84}H_{108}ClMn_6N_6NaO_{24}$, M = 1973.84, cubic, space group Ia–3d, a = 36.229(15) Å, α = 90°, V = 47552(59) $Å^3$, Z = 16, μ = 0.639 mm^{-1}, D_c = 1.103 Mg / m^3, 57326 reflections collected, 3502 unique (R_{int} = 0.2067), final R_1 = 0.1311, wR_2 = 0.3372, GoF = 1.226, data/restraints/parameters = 3502/0/194. CCDC 977703.*
*Crystal data for **2**: $C_{80}H_{148}Mn_{12}N_8O_{40}$, M = 2521.34, monoclinic, space group $P2_1/n$, a = 18.454(6), b = 37.410(11), c = 20.409(7) Å, α = 90, β = 114.966(4), γ = 90°, V = 12773(7) $Å^3$, Z = 4, μ = 1.212 mm^{-1}, D_c = 1.311 Mg / m^3, 127080 reflections collected, 22227 unique (R_{int} = 0.1745), final R_1 = 0.0685, wR_2 = 0.1637, GoF = 1.009, data/restraints/parameters = 22227/13/1305. CCDC 977704.*

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