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A [Mn-32] Double-Decker Wheel

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Synopsis:
A mixed - valent [Mn$_{32}$] cluster with a very rare "double - decker" wheel topology (see its metal-oxygen core: Mn^{III}, blue; Mn^{II}, pink; O, red) is reported. It is by far the highest nuclearity example of its type and it displays SMM behaviour with the largest effective barrier to magnetisation relaxation (U$_{eff}$ ~ 44.5 K) for any molecular wheel.

Graphical abstract:
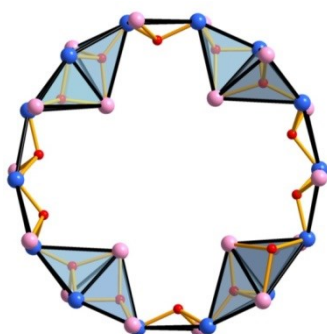
Keywords:
magnetic properties; manganese; molecular wheels; N,O ligands; single-molecule magnets

Main text

Polynuclear clusters of paramagnetic 3d metal ions continue to attract significant interest because of their intriguing geometrical characteristics (large size, high symmetry, aesthetically pleasing shapes and architectures), and fascinating physical properties. Such complexes often combine large and sometimes abnormally large spin ground states with easy-axis-type magnetic anisotropy resulting in a significant barrier to magnetisation relaxation.[1-3] Thus, at sufficiently low temperatures they function as single domain magnetic particles displaying magnetisation hysteresis and quantum tunneling of the magnetisation (QTM).[3,4] Such Single-Molecule Magnets (SMMs) represent a molecular approach to nanoscale magnetic materials with potential applications in information storage and molecular spintronics.[5] SMMs with nuclearities up to 84 and structural topologies as diverse as (amongst others) dimers, triangles, cubanes, tetrahedra, icosahedra and wheels are now known.[1-3,6] The latter of these have always attracted intense interest, partly because of their inherent structural beauty, but also because they represent model systems for the study of one-dimensional magnetism, spin frustration and quantum effects, and are promising candidates for use as qubits in quantum computation.[7] Homo- and heterometallic molecular wheels are commonly encountered in 3d cluster chemistry,[8-15] and in general they fall in to two distinct structural types. By far the most common are "single-stranded wheels" which simply describe linked monometallic units.[8,9] "Multiple-stranded wheels" are less common and encompass either (i) wheels built from repeating metal clusters,[10] or (ii) multiple-layer wheels, i.e. complexes that consist of two or more linked parallel wheels. Those of structural type (ii) are extremely rare, being restricted to [V12],[11] [Mn10],[12] [Mn16],[13] and [Cu12][14] "double–deckers",[15] with none displaying SMM behaviour. Herein we report a beautiful new mixed-valent [Mn32] "double-decker" wheel which is the highest nuclearity cluster possessing this topology and show that it has a large spin ground state and displays SMM behaviour with largest effective barrier to magnetisation relaxation ($U_{eff} \sim 44.5$ K) for any molecular wheel.

The reaction of $MnBr_2 \cdot 4H_2O$, NaO_2CMe, 2-phenyl-1,2-propanediol (Ph-pdH$_2$) and 2-hydroxyacetophenone oxime (Me-saoH$_2$) in a 1:1:1:1 molar ratio in MeCN leads to the isolation of [Mn$_{32}$(μ_4-O)$_8$(μ_3-OH)$_6$(Me-sao)$_{14}$(O$_2$CMe)$_{18}$Br$_8$(H$_2$O)$_{10}$](OH)$_2$ (**1**) in 30 % yield after $\sim$ 1 week. The diol does not appear in the final product, but its presence in the reaction mixture is essential since reactions in its absence lead to the formation of a known [Mn$_7$] cluster.[16] The structure of the cation of **1**[17] reveals it to be a centrosymmetric, mixed-valent [Mn$^{II}_{18}$Mn$^{III}_{14}$] "double-decker" wheel (Fig. 1a), consisting of two linked, parallel [Mn$^{II}_7$Mn$^{III}_7$] crown-shaped wheels (Fig. 1b-c), which house a [Mn$^{II}_4$] rectangle in their inner cavity. Each [Mn$_{14}$] unit consists of seven Mn^{III} and seven Mn^{II} ions arranged alternately in a single-stranded wheel (Fig. 1c). All of the Mn ions are six-coordinate with the Mn^{III} ions displaying the expected Jahn-Teller elongations; all of which are (approximately) perpendicular to the planes of the [Mn$_{14}$] wheels. The four Mn^{II} ions in the inner [Mn$_4$] rectangle are 5-coordinate. The Mn ions of each [Mn$_{14}$] crown are held together through a combination of μ_2-O$_{phenol}$ atoms from seven fully deprotonated Me-sao^{2-} ligands, three μ_3-OH$^-$ and four μ_4-O^{2-} ions, and seven

η^2:η^1:μ_3-acetates. The two [Mn$_{14}$] units are linked together to form the [Mn$_{28}$] "double-decker" wheel via the oximic μ_2-O atoms of all fourteen Me-sao^{2-} ligands, all six μ_3-OH$^-$ and all eight μ_4-O^{2-} atoms. The latter also connect the [Mn$_{28}$] "double-decker" to the central [Mn$^{II}_4$] rectangle. The four Mn ions of the rectangle are linked to each other through four η^1:η^1:μ-acetate ligands bridging in both anti–anti and syn–anti fashions. The remaining coordination sites [on the Mn^{II} ions] around the periphery of the wheel are completed by a disordered combination of terminally bonded H$_2$O and Br$^-$ ligands. The oxidation states of the Mn ions and the protonation level of the Me-sao^{2-}, MeCO$_2^-$, O^{2-}, OH$^-$ and H$_2$O ligands were determined by BVS calculations,[18] charge balance considerations and inspection of metric parameters.
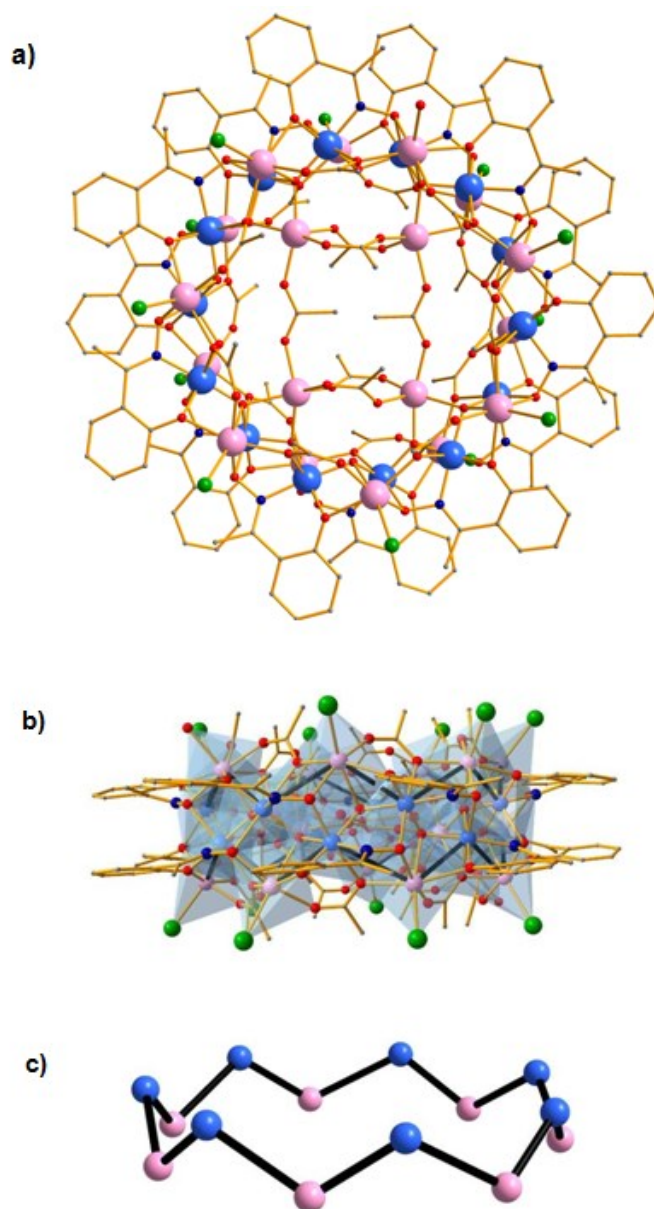

Figure 1. Representations (atoms are not to scale) of the molecular structure of the cation of **1**, viewed perpendicular **a**) and parallel **b**) to the "planes" of the [Mn$^{II}_7$Mn$^{III}_7$] wheels, with the metal ion polyhedra

included in the latter to emphasise the "double-decker" topology. **c**) The metallic skeleton of one of the two [$Mn^{II}_7Mn^{III}_7$] wheels highlighting the crown-shaped topology and the alternate Mn^{II}-Mn^{III} ordering of the metal ions. Colour scheme: Mn^{III}, blue; Mn^{II}, pink; O, red; disordered Br / O_{water}, green; N, dark blue; C, grey. H-atoms have been omitted for clarity.
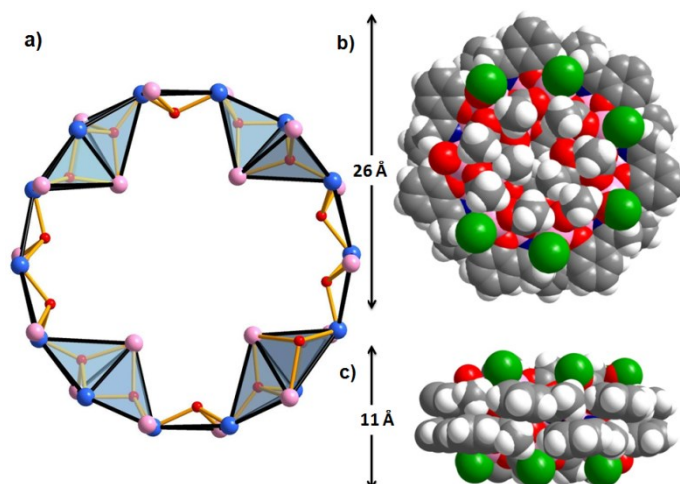

Figure 2. **a**) The metal-oxygen core of the cation of **1,** highlighting the constituent {M_4O} tetrahedral and {M_3O} triangular building blocks. Space filling diagram of the cation of **1** viewed perpendicular **b**) and parallel **c**) to the circular faces of the double-decker wheel. Colour scheme as Figure 1; H, white.

The metal-oxygen core of the cluster consists of four pairs of edge-sharing {M_4O} tetrahedra situated at the "corners of the wheel" (as drawn in Fig. 2a) linked to each other alternately by one and two [vertex-sharing] {Mn_3O} triangles. The "magnetic core" of the complex is then completed by the presence of the phenolic oximes bridging over the rectangular upper double-rim of the wheel and the acetates bridging across the circular faces of the wheel. Interestingly the Mn(III)-N-O-Mn(III) torsion angles are all very large, ranging between 40 and 48°. Previous reports have suggested that Mn(III)-N-O-Mn(III) angles above approximately 31° are likely to result in ferromagnetic pairwise exchange.[16b] The metal-oxygen core in Fig. 2a reveals a ficticious "Maltese Cross" like cavity; the space-filling diagram of Fig. 2b confirming the complete lack of free internal space. The [Mn_{32}]$^{2+}$ cation is an enormous molecule, measuring approximately 26 Å across its circular face (Fig. 2b) and approximately 11 Å across the rectangular rim (Fig. 2c). A close examination of the packing of the molecules in the crystal reveals that there are no significant inter-molecular interactions between neighbouring [Mn_{32}] cations; the shortest Mn⋯Mn distance between neighboring units is ~8.67 Å, with nearest neighbours oriented perpendicular to one another, *i.e.* packing rim-to-face (Figure S1 in the Supporting Information).

Direct current magnetic susceptibility (χ_m) measurements were performed on a powdered crystalline sample of **1** in the 5 - 300 K temperature range in a 0.1 T magnetic field and are plotted as χ_mT vs T in Fig. S2. The χ_mT value decreases slowly from ~89.4 cm^3 mol^{-1} K at 300 K to ~74.3 cm^3 mol^{-1} K at 15 K and then more rapidly to 60.7 cm^3 mol^{-1} K at 5 K. The room temperature χ_mT value is significantly smaller than the spin-only ($g = 2$) value of 120.75 cm^3 mol^{-1} K expected for eighteen Mn^{2+} and fourteen Mn^{3+} non–interacting ions. The 15 K value is indicative of $S = 11$ or 12, with the abrupt low temperature decrease assigned to zero–field splitting (ZFS), Zeeman effects from the applied field, and/or weak inter-molecular interactions. The magnetisation data (Figure S3) clearly show $M/N\beta$ increasing almost linearly with H and could not be fitted. The dc data is thus suggestive of the presence of competing ferro- and antiferromagnetic exchange interactions and population of numerous S states even at the lowest temperatures measured, as would be expected for such a large cluster possessing relatively weak exchange interactions.

Alternating current (ac) magnetic susceptibility measurements were performed in the 1.8 – 10 K temperature range in zero applied dc field and a 3.5 G ac field oscillating at 50 – 1000 Hz. Frequency-dependent out-of-phase (χ_M'') signals (Figure 3) are seen below approximately 4 K. The presence of fully visible χ_M'' signals is highly unusual for a) mixed valent Mn$^{II/III}$ clusters, b) high nuclearity clusters and c) molecular wheels, and is indicative of a significant barrier to magnetisation relaxation. The obtained ac data were fitted to the Arrhenius equation (Figure S4), affording U_{eff} = 44.5 K and τ_0 = 3.5 x10^{-12} s, where τ_0 is the pre-exponential factor. The small value of τ_0 (though common to all high nuclearlity SMMs) is assigned to the low-lying excited states and the weak inter-molecular interactions.[10b,d, 19]
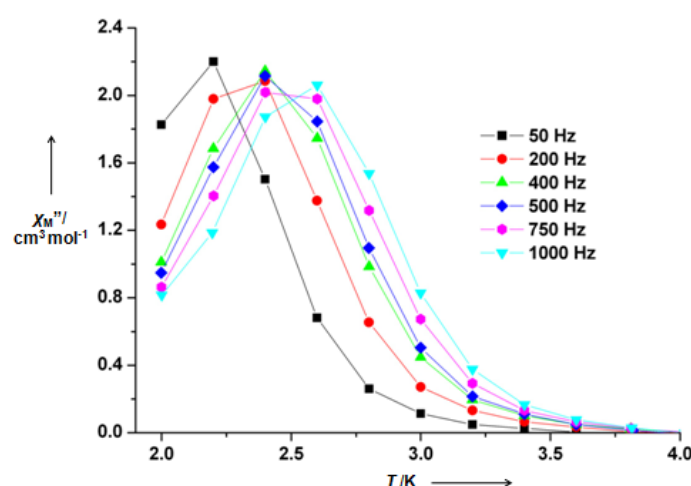

Figure 3. Plot of χ_M'' versus T for a microcrystalline sample of **1** at the indicated frequencies.

To confirm whether **1** is indeed a SMM, magnetisation versus dc field scans were carried out on a single crystal of **1**·3MeCN using a micro-SQUID apparatus.[20] The obtained magnetisation versus applied dc field responses are plotted in Figure 4, showing the temperature dependence at 0.002 T/s and the scan rate dependence at 0.04 K. Hysteresis loops were observed below ~1.6 K whose coercivities increase with decreasing temperature and increasing field sweep rate, as expected for the superparamagnetic–like properties of a SMM. The data thus confirm complex **1** to be a new addition to the family of SMMs, with a blocking temperature (T_B) of ~1.6 K. The hysteresis loops do not show steps characteristic of QTM, a phenomenon common to all high nuclearity SMMs.[2, 10a,b,d, 19, 21]

The above results thus establish [Mn$_{32}$] as a new giant SMM, one of the largest reported to date.[10a, 19c, 21] The U_{eff} = 44.5 K is one of the highest yet observed for a Mn$^{II/III}$ mixed–valent complex,[10d] and the highest observed for any molecular wheel. In addition, it is by far the highest barrier observed in the small family of giant SMMs (complexes with nuclearity ≥ 30) whose previous "record" barrier was 18 K. [10a]
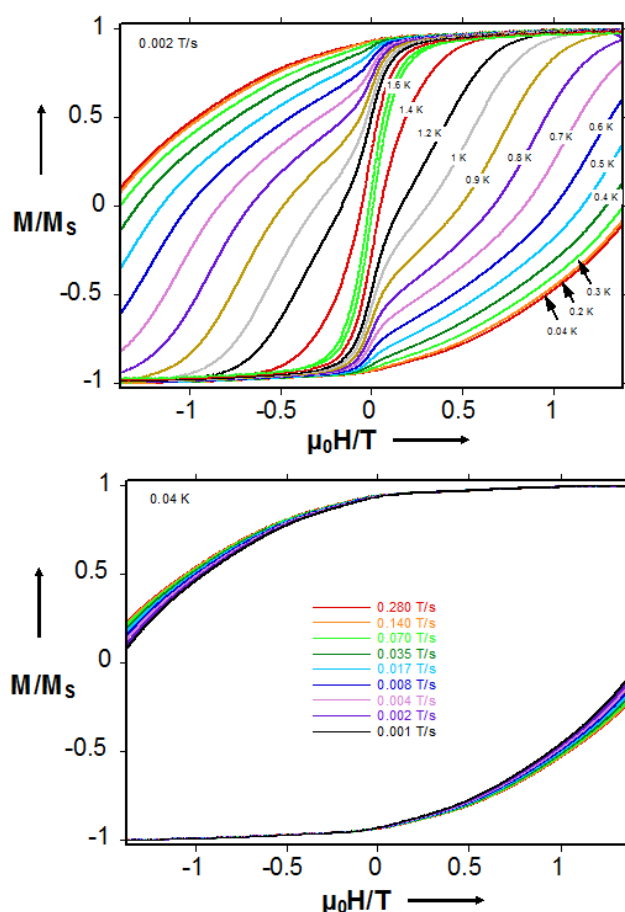

Figure 4. Magnetisation (*M*) vs applied magnetic field (μ_0H) hysteresis loops for a single crystal of **1**·3MeCN at the indicated temperatures and a fixed field sweep rate of 0.002 T/s (top) and at the indicated field sweep rates at 0.04 K. *M* is normalised to its saturation value, M_S.

In conclusion, complex **1** is a very rare example of a "double-decker" wheel. It is by far the highest nuclearity example of its type, the largest metal-oxime cluster ever reported and one of the largest known Mn clusters and SMMs. It is the only "double-decker" wheel to display SMM behaviour and it possesses a barrier to magnetization reversal significantly larger than any other previously reported molecular wheel or any SMM with nuclearity equal to or greater than 30. The current study also shows that topologies other than the common triangle-based $[Mn_3]_n$ (n = 1,2) clusters can be made using derivatised salicylaldoxime ligands and that they continue to produce molecules with fascinating structures and magnetic properties.

Experimental Section

1: Ph-pdH$_2$ (0.106 g, 0.697 mmol), NaO$_2$CMe (0.057 g, 0.697 mmol) and Me-saoH$_2$ (0.105 g, 0.697 mmol) were added to a solution of MnBr$_2$·4H$_2$O (0.200 g, 0.697 mmol) in MeCN. The resulting green-brown solution was stirred magnetically for ~15 minutes, filtered off and layered with Et$_2$O. Crystals of **1**·3MeCN were formed in 7 days in ~30% yield. Elemental analysis calcd (found) for Mn$_{32}$Br$_8$C$_{148}$N$_{14}$O$_{120}$H$_{240}$: C 27.21 (26.92), H 3.70 (3.45), N 3.00 (3.20), Metal analysis was performed *via* ICP-OES: calcd (found) Mn 26.91 (27.10).

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[15] a) There is a family of Cu complexes consisting of weakly interacting (the shortest inter-wheel distances are ~ 2.40 Å whereas the average inra-wheel bond lengths are ~ 1.95 Å) parallel wheels (two or three) and thus could be better described as possessing a "wheel(s) in a wheel" topology[15b]; b) G. Mezei, P. Baran, R. G. Raptis, *Angew. Chem. Int. Ed.* **2004**, *43*, 574-577.

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[17] Crystallographic data for **1**·3CH3CN·solvent: $C_{154}H_{189}Br_8Mn_{32}N_{17}O_{90}$, M_r= *6115.58,* monoclinic, space group P2$_1$/c, *a*= 23.5964(8), *b*= 23.4510(6), c= 26.0859(9) Å, β=116.648(4)^o, V= 12901.6(7)Å^3, T= 100(2)K, Z= 2, Oxford Diffraction Supernova A CCD diffractometer, Mo Ka radiation (λ = 0.71073), ρ_{calcd}= 1.574gcm^{-3} 22483 reflections collected, 22483 unique (R_{int}= 0.0), Final *GooF*= 1.009, *R*1= 0.0714, w*R*2= 0.1819, for 11275 reflections with *I*>2σ(I). The asymmetric unit consists of half of the Mn$_{32}$ wheel, one hydroxide anion, one and a half acetonitrile and severely disordered solvent molecules that could not be modeled properly. Thus, the program SQUEEZE was used to calculate the disordered solvent area and

remove its contribution from the overall intensity data. Two of the acetate ligands connecting the Mn12 and Mn5 ions are disordered with O_{water} groups (O25/O25A, O26/O26A, O29/O29A, O30/O30A) with 0.50 occupancy, i.e. half of the time the Mn ions are linked to an $O_{carboxylate}$ and the other half to an O_{water} atom. In addition, all Br^- ions are disordered with O_{water} ligands a situation that is rather common for metal clusters that contain similar type of ligation. CCDC-809809 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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