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Single-Molecule Magnets

A $[Mn_{32}]$ Double-Decker Wheel**

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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 magnetization relaxation.[1–3] Thus, at sufficiently low temperatures they function as single-domain magnetic particles displaying magnetization hysteresis and quantum tunneling of the magnetization (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 into 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 1) wheels built from repeating metal clusters,[10] or 2) multiple-layer wheels, that is, complexes that consist of two or more linked parallel wheels. Those of structural type (2) are extremely rare, being restricted to $[V_{12}]$,[11] $[Mn_{10}]$,[12] $[Mn_{16}]$,[13] and $[Cu_{12}]$[14] double-deckers,[15] none of which display SMM behavior. Herein we report a beautiful new mixed-valent $[Mn_{32}]$ 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 behavior with the largest effective barrier to magnetization relaxation ($U_{eff} \approx 44.5$ 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 $[Mn_{32}(\mu_4\text{-}O)_8(\mu_3\text{-}OH)_6(\text{Me-sao})_{14}(O_2CMe)_{18}Br_8(H_2O)_{10}](OH)_2$ (**1**) in 30% yield after approximately 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 (Figure 1a), consisting of two linked, parallel $[Mn^{II}_7Mn^{III}_7]$ crown-shaped wheels (Figure 1b,c) that 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 (Figure 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 five-coordinate. The Mn ions of each $[Mn_{14}]$ crown are held together through a combination of $\mu_2\text{-}O_{phenol}$ atoms from seven fully deprotonated Me-sao^{2-} ligands, three μ_3-OH^- and four μ_4-O^{2-} ions, and seven $\eta^2{:}\eta^1{:}\mu_3$-acetates. The two $[Mn_{14}]$ units are linked together to form the $[Mn_{28}]$ double-decker wheel through the oximic μ_2-O atoms of all fourteen Me-sao^{2-} ligands, all six μ_3-OH^- units, 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 $\eta^1{:}\eta^1{:}\mu$-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 occupied by a disordered combination of terminally bonded H_2O 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_2O ligands were determined by bond-valence sum (BVS) calculations,[18] charge-balance considerations, and inspection of metric parameters.

The metal–oxygen core of the cluster consists of four pairs of edge-sharing $\{M_4O\}$ tetrahedra situated at the "corners" of

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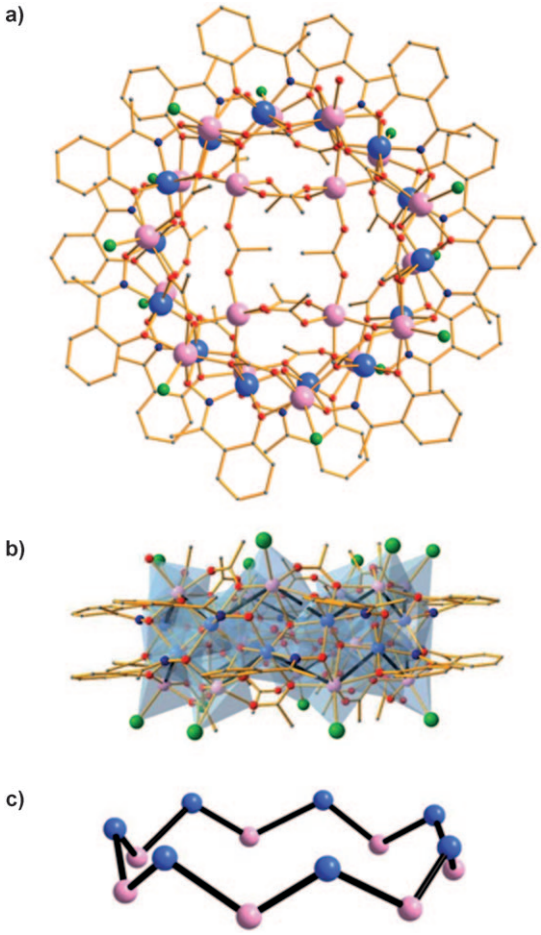

Figure 1. Representations (atoms are not to scale) of the molecular structure of the cation of **1**, viewed a) perpendicular and b) parallel to the "planes" of the $[Mn^{II}_7Mn^{III}_7]$ wheels, with the metal ion polyhedra included in the latter to emphasize the double-decker topology. c) The metallic 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. Mn^{III} blue, Mn^{II} pink, O red, disordered Br/O_{water} green, N dark blue, C gray. Hydrogen atoms have been omitted for clarity.

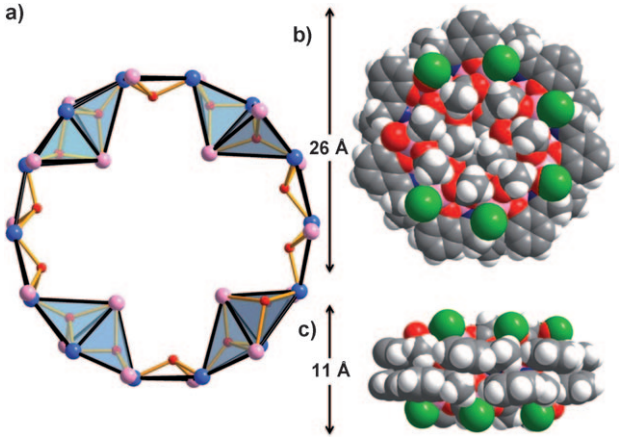

Figure 2. a) The metal–oxygen core of the cation of **1**, highlighting the constituent $\{M_4O\}$ tetrahedral and $\{M_3O\}$ triangular building blocks. b,c) Space-filling diagram of the cation of **1** viewed perpendicular (b) and parallel (c) to the circular faces of the double-decker wheel. Color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

the wheel (as drawn in Figure 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 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 Figure 2a reveals a ficticious "Maltese Cross"-like cavity; the space-filling diagram in Figure 2b confirms the complete lack of free internal space. The $[Mn_{32}]^{2+}$ cation is an enormous molecule, measuring approximately 26 Å across its circular face (Figure 2b) and approximately 11 Å across the rectangular rim (Figure 2c). A close examination of the packing of the molecules in the crystal reveals that there are no significant intermolecular interactions between neighboring $[Mn_{32}]$ cations; the shortest Mn···Mn distance between neighboring units is approximately 8.67 Å, with nearest neighbors oriented perpendicular to one another, that is, packing rim-to-face (Figure S1 in the Supporting Information).

Direct-current (dc) 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 $\chi_m T$ versus T in Figure S2 in the Supporting Information. The $\chi_m T$ value decreases slowly from approximately 89.4 $cm^3 mol^{-1} K$ at 300 K to about 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 $\chi_m T$ 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 weak intermolecular interactions. The magnetization data (plotted as reduced magnetization ($M/N\beta$) versus field (H) in Figure S3 in the Supporting Information), clearly show $M/N\beta$ increasing almost linearly with field strength 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 magnetization relaxation. The obtained ac data were fitted to the Arrhenius equation (Figure S4 in the Supporting Information), affording $U_{eff} = 44.5$ K and $\tau_0 = 3.5 \times 10^{-12}$ s, where τ_0 is the pre-exponential factor. The small value of τ_0 (though

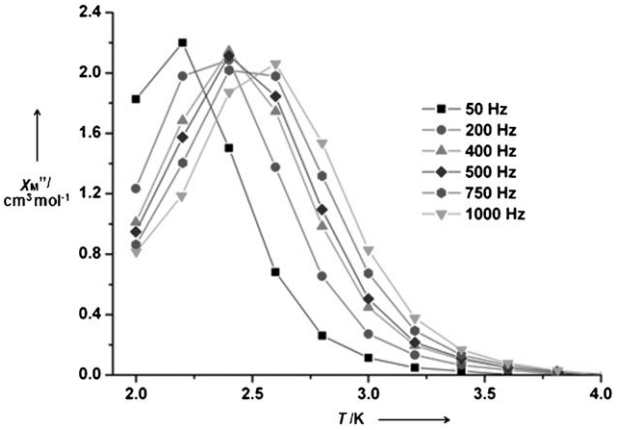

Figure 3. Plot of χ_M'' versus T for a microcrystalline sample of **1** at the indicated frequencies.

common to all high-nuclearity SMMs) is assigned to the low-lying excited states and the weak intermolecular interactions.[10b,d,19]

To confirm whether **1** is indeed a SMM, magnetization versus dc field scans were carried out on a single crystal of **1**·3 MeCN using a micro-SQUID apparatus.[20] The obtained magnetization versus applied dc field responses are plotted in Figure 4, showing the temperature dependence at 0.002 T s^{-1} and the scan-rate dependence at 0.04 K. Hysteresis loops were observed below approximately 1.6 K, the coercivities of which 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 approximately 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} value of 44.5 K is one of the highest observed to date for a $Mn^{II/III}$ mixed-valent complex[10d] and is the highest observed for any molecular wheel. Furthermore, 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]

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 behavior, and it possesses a barrier to magnetization reversal significantly larger than any other 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 derivatized salicylaldoxime ligands, and that they continue to produce molecules with fascinating structures and magnetic properties.

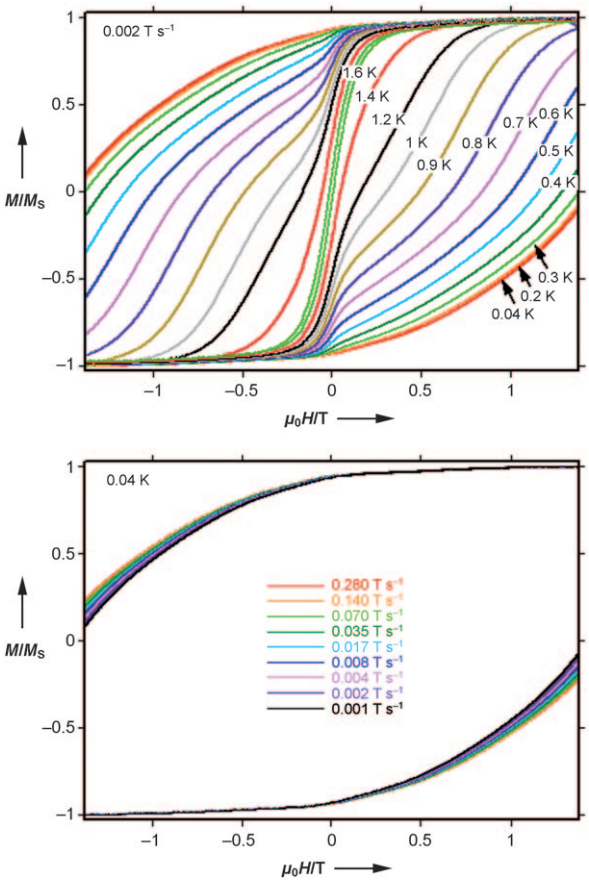

Figure 4. Magnetization (M) versus applied magnetic field ($\mu_0 H$) hysteresis loops for a single crystal of **1**·3 MeCN at the indicated temperatures and a fixed field sweep rate of 0.002 T s^{-1} (top) and at the indicated field sweep rates at 0.04 K. M is normalized to its saturation value, M_s at 1.4 T.

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$_2$·4 H$_2$O (0.200 g, 0.697 mmol) in MeCN. The resulting green-brown solution was stirred magnetically for approximately 15 min, filtered off, and layered with Et$_2$O. Crystals of **1**·3 MeCN formed in 7 days in approximately 30% yield. Elemental analysis calcd for $Mn_{32}Br_8C_{148}N_{14}O_{120}H_{240}$: C 27.21, H 3.70, N 3.00; found: C 26.92, H 3.45, N 3.20. Metal analysis was performed by inductively coupled plasma optical emission spectrometry (ICP-OES): calcd Mn 26.91; found: Mn 27.10.

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[17] Crystallographic data for **1**·3 CH_3CN·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, $\beta = 116.648(4)°$, $V = 12901.6(7)$ Å^3, $T = 100(2)$ K, $Z = 2$, Oxford Diffraction Supernova A CCD diffractometer, Mo K_α radiation ($\lambda = 0.71073$), $\rho_{calcd} = 1.574$ gcm^{-3}, 22483 reflections collected, 57487 unique ($R_{int} = 0.0548$), final GooF = 1.009, $R1 = 0.0714$, $wR2 = 0.1819$, for 11275 reflections with $I > 2\sigma(I)$. The asymmetric unit consists of half of the Mn_{32} wheel, one hydroxide anion, one and a half acetonitrile molecules, 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, that is, half of the time the Mn ions are linked to an $O_{carboxylate}$ and the other half to an O_{water} atom. Moreover, all Br^- ions are disordered with O_{water} ligands, a situation that is rather common for metal clusters that contain a 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 Centre via www.ccdc.cam.ac.uk/data_request/cif.

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