A High Nuclearity, Mixed-Valence Manganese(III,IV) Complex: $[Mn_{21}O_{24}(OMe)_8(O_2CCH_2tBu)_{16}(H_2O)_{10}]$**

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High-nuclearity manganese carboxylate clusters have been attracting intense interest during the last several years from scientists in various disciplines. This is because of a combination of factors, not least their aesthetic qualities and their unusual magnetic properties.[1, 2] The latter arise from their large, and often abnormally large, ground-state spin values, which, in combination with significant easy-axis-type magnetoanisotropy, leads to Mn clusters exhibiting the new magnetic phenomenon of single-molecule magnetism.[2] This property is the ability of discrete molecules to exhibit the superparamagnet-like property of slow magnetization relaxation and thus to behave as magnets below their blocking temperature by exhibiting magnetization versus field hysteresis.[3, 4] The first single-molecule magnet (SMM) was $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ (**1**), which possesses an $S=10$ ground state,[3, 5] and a number of other Mn_x SMMs have since been discovered.[1, 2, 6–9]

As part of a continuing effort to prepare new clusters with large S values that might be SMMs, we have been exploring new reactions of **1**, or its derivatives, such as $[Mn_{12}O_{12}(O_2CCH_2tBu)_{16}(H_2O)_4]$ (**2**), which can readily be prepared from **1** by a ligand-substitution procedure.[10] A solution of **2** in CH_2Cl_2 was treated with an equal volume of MeOH, and the solution concentrated by slow evaporation over several days. After a brown solid was removed by filtration, black crystals of $[Mn_{21}O_{24}(OMe)_8(O_2CCH_2tBu)_{16}(H_2O)_{10}]$ (**3**) formed over few days. The yield is very low (~3%) but the reaction has been reproduced several times. The structure of **3** (Figure 1, top)[11] consists of an Mn core that is approximately planar and is ligated on the periphery by 16 μ-O_2CCH_2tBu groups and 10 H_2O molecules. The complex is trapped valence, the Mn^{III} ions being the outer Mn6–Mn11 atoms and their symmetry-related partners; the complex has crystallographic C_i symmetry. The Mn^{III} ions were identified by their metric parameters and Jahn–Teller distortions. As expected, the Jahn–Teller elongated Mn^{III}–O bonds (2.135(9)–2.323(8) Å) are significantly longer than the other Mn^{III}–O bonds (1.858(7)–1.981(8) Å). The Mn^{IV}–O bonds are in a narrower range (1.838(7)–1.956(8) Å). The 21 Mn ions are not all in the same plane: the nine Mn^{IV} ions (Mn1–Mn5) and two Mn^{III} ions (Mn8) are co-planar, but the two Mn_5 crescents (Mn7, Mn6, Mn11, Mn10, Mn9) at top and bottom are slightly above and below this plane (Figure 1, bottom). The central oxide-bridged Mn_9 unit is reminiscent of the planar CdI_2-type sheet structure, as indeed is known for Mn^{IV} in the mineral lithiophorite (Al, Li) $MnO_2(OH)_2$.[12, 13] Thus, a useful description of the $[Mn_{21}O_{24}(OMe)_8]$ core is as a CdI_2-like $[Mn^{IV}_9O_{20}]$ sheet held within a non-planar $[Mn^{III}_{12}O_{12}]$ ring. This description relates the Mn_{21} structure to that of **1** and **2**, which can be described as a $[Mn^{IV}_4O_4]$ cube held with a non-planar $[Mn^{III}_8O_8]$ ring (Figure 2).[5, 14, 15] Complex **3** also has similarity to $[Mn_{19}O_{12}(OC_2H_2OMe)_{14}(HOC_2H_2OMe)_{10}]$, which also has an approximately planar Mn_{19} topology but all the metal ions are Mn^{II} centers.[16] Similarly, complex **3** is also related to the $[Fe_{17}O_4(OH)_{16}(heidi)_8(H_2O)_{12}]^{3+}$ and $[Fe_{19}O_6(OH)_{14}(heidi)_{10}(H_2O)_{12}]^+$ ($heidiH_3 = N(CH_2CO_2H)_2(CH_2OH)(CH_2CH_2OH)$) clusters with planar Fe_x cores.[17, 18]

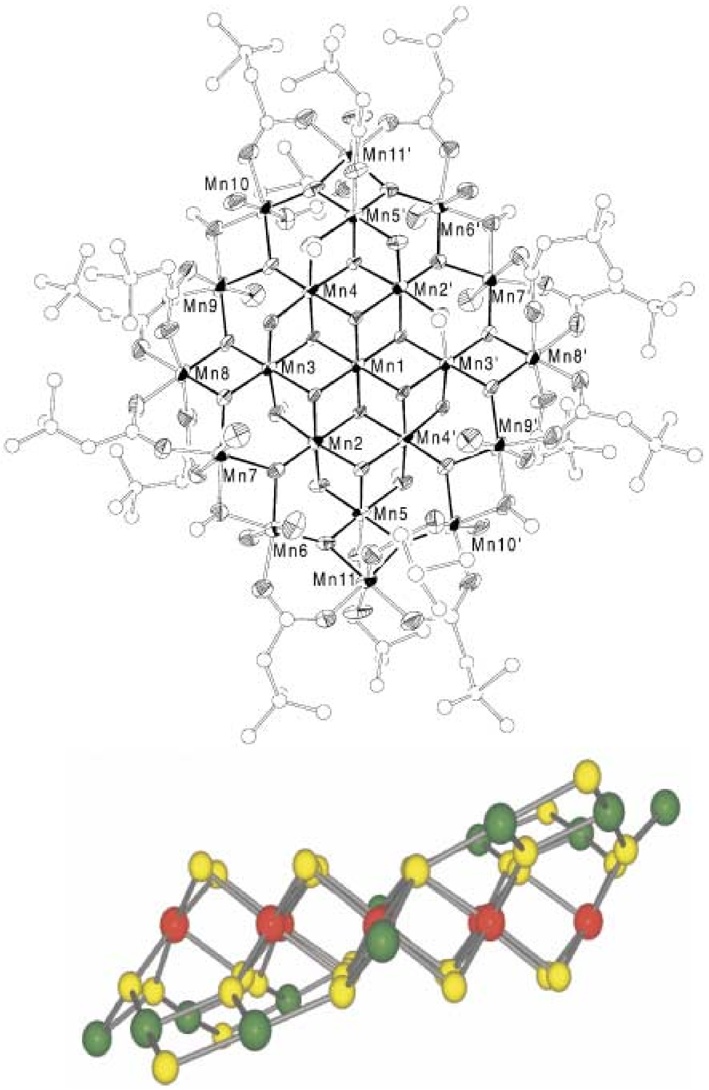

Figure 1. Top: ORTEP plot of the molecular structure of complex **3** (the thermal ellipsoids are set at 50% probability). Bottom: side view showing Mn^{4+} (red), Mn^{3+} (green), and O (yellow) atoms to emphasize the planar central Mn_{11} unit.

The magnetic properties of **3** were investigated by solid-state magnetic susceptibility (χ_M) measurements in the 1.8 to 300 K range and DC fields up to 7 Tesla. The $\chi_M T$ value

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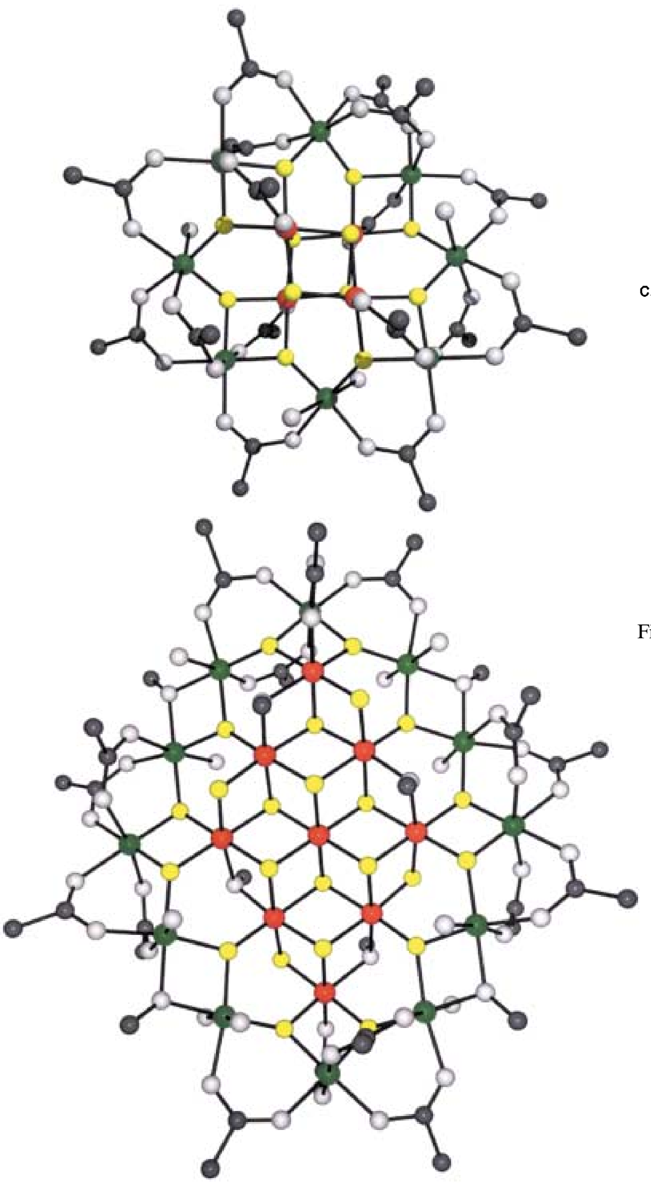

Figure 2. Comparison of the structures of Mn_{12} (top) and Mn_{21} (bottom) compounds. Color scheme: Mn^{4+} (red), Mn^{3+} (green), O^{2-} (yellow), other types of O atom (off-white), C (black).

steadily decreases from 42.1 $cm^3 K mol^{-1}$ at 300 K to 19.0 $cm^3 K mol^{-1}$ at 25.0 K, and then decreases more rapidly to 4.47 $cm^3 K mol^{-1}$ at 2.00 K (Figure 3). The data strongly suggest predominantly antiferromagntic exchange interactions within **3**. To determine the ground state, magnetization versus field and temperature data were collected in the 1–7 T and 1.9–10 K ranges and fitted by a matrix-diagonalization method to a model that assumes only the ground state is populated and includes axial zero-field splitting ($\hat{S}_z^2 D$).[8] The best fit gave $S = 13/2$, $g = 1.79$, and $D = -0.53\ cm^{-1}$. Comparable fits were obtained with $S = 15/2$, $g = 1.55$, $D = -0.40\ cm^{-1}$, and $S = 11/2$, $g = 2.10$, $D = -0.75\ cm^{-1}$, but were rejected owing to their unreasonable g value. The obtained $S = 13/2$ value is reasonable given that the $Mn^{IV} \cdots Mn^{IV}$ and $Mn^{IV} \cdots Mn^{III}$ interactions within the sheetlike structure are expected to be antiferromagnetic, but that spin frustration[19] within the triangular M_3 units will prevent maximum spin compensation to give a $S = ½$ ground state. In $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ complexes, the acute angles within the central $[Mn^{IV}_4O_4]$ cubane lead to ferromagnetic $Mn^{IV} \cdots Mn^{IV}$ interactions and a correspondingly higher ($S = 10$) ground state, even though the nuclearity of Mn_{12} clusters is almost half that of **3**.

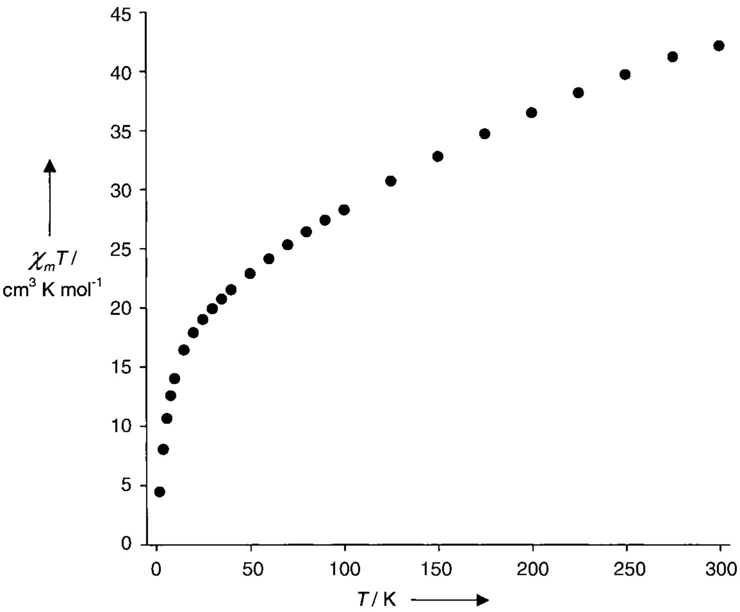

Figure 3. Plot of $\chi_M T$ versus T for complex **3**.

The relatively large S and D values suggested **3** might display the slow magnetization relaxation of a single-molecule magnet, and preliminary AC magnetic susceptibility studies were therefore performed in a 3.5 G field oscillating at frequencies up to 1500 Hz. No significant out-of-phase (χ''_M) signal was observed at temperatures > 1.8 K (the limit of our instrument), which suggests that further studies at lower temperatures are required.

In summary, the methanolysis of **2** in $MeOH/CH_2Cl_2$ has led to an interesting new structural type in higher-oxidation-state Mn cluster chemistry, a disk-like Mn_{21} mixed-valent complex. Mn chemistry continues to surprise and astound with the remarkable variety and aesthetic beauty of its molecular offspring.

Experimental Section

A brown solution of $\mathbf{2} \cdot CH_2Cl_2 \cdot MeCN$ (0.50 g, 0.18 mmol) in CH_2Cl_2 (50 mL) was treated with MeOH (50 mL). The solution was allowed to slowly concentrate by evaporation over 5 days, during which time a brown precipitate was obtained. The solid was removed by filtration and the filtrate maintained for two more days at room temperature to give well-formed black crystals of $\mathbf{3} \cdot 10\,H_2O$ in about 3 % yield. Despite the low yield, the reaction is reproducible, although the quality of the black crystals varies. Solid dried in vacuo analyzed as solvent-free, elemental analysis: (%) calcd for $C_{104}H_{220}Mn_{21}O_{74}$: C 32.80, H 5.82; found for dried sample: C 32.99, H 5.55; selected IR data (KBr pellet): $\tilde{\nu} = 1634$(s), 1559 (w), 1539 (w), 1477 (w), 1456 (w), 1436 (w), 1410 (m), 1384 (s), 1275 (w), 1232 (w), 1121 (m), 1033 (m), 667 (m), 596 (br, s), 503 cm^{-1} (w). The brown powder has an IR spectrum similar to that of the crystals, but could not be purified to our satisfaction. Thus, only the black crystals were employed for characterization and study.

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[11] Crystal structure data for **3** $\cdot 10\,H_2O$: $C_{104}H_{240}Mn_{21}O_{84}$, $M_r = 3988.70$, triclinic, space group $P\bar{1}$, $a = 12.4031(5)$, $b = 19.0808(7)$, $c = 19.6760(7)$ Å, $\alpha = 108.149(1)$, $\beta = 90.450(1)$, $\gamma = 106.773(1)^\circ$, $V = 4212.11$ Å^3, $T = 111$ K, $Z = 1$, 64219 reflections collected, 19399 unique ($R_{av} = 0.099$), $R(F) = 0.0503$ and $R_W(F) = 0.0506$ using 5975 reflections with $I > 2.33\sigma(I)$. CCDC-177268 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Starched Carbon Nanotubes[**]

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Dedicated to Professor David N. Reinhoudt on the occasion of his 60th birthday

Since their discovery[1] in 1993, single-walled carbon nanotubes (SWNTs) have found numerous applications[2] in chemistry and physics on account of their anisotropic shapes (diameters of around 1 nm and lengths of micrometers), remarkable strengths and elasticities, and unique physical properties, for example, high thermal and electrical conductivities. By contrast, and despite their clear potential, SWNTs have not yet been fully integrated into biological systems,[3] mainly because of the considerable difficulty in rendering them soluble in aqueous solutions.

Initially, the challenge of achieving soluble SWNTs in organic solvents was addressed by their covalent modification—examples include both end-group[4] and side-wall[5] functionalization. Covalent modification, however, has the disadvantage that it impairs their physical properties. For these, and other reasons, we have been attracted by a supramolecular approach[6] to the solubilization problem—namely, the noncovalent functionalization of SWNTs by wrapping polymers around them in the knowledge that desired features can be grafted onto the polymers, prior to their being self-assembled around the SWNTs. Considerable progress[6, 7] has been made in the use of synthetic polymers to render SWNTs soluble in organic solvents. However, while some water-soluble polymers[8] and surfactants[9] can bring aqueous solubilities to SWNTs, they may not be as biocompatible as would be desirable.

It was for this reason, amongst others, that we decided to explore the possibility of solubilizing SWNTs in aqueous solutions of starch.[10] We knew from our knowledge of the supramolecular chemistry of fullerenes[11] that cyclodextrins (CDs) of the appropriate dimensions (γ-CD commonly and δ-CD occasionally), and in the correct stoichiometries, will dissolve fullerenes (C_{60} and C_{70}, for example) in water.[12] CDs are the macrocyclic analogues[13] of starch. The connection is clear. Here, we report 1) that common starch, provided it is activated toward complexation by wrapping itself helically around small molecules, will transport SWNTs competitively into aqueous solutions, 2) that the process is sufficiently reversible at high temperatures to permit the separation of SWNTs in their supramolecular starch-wrapped form by a series of physical manipulations from amorphous carbon, and 3) that the addition of glucosidases to these starched carbon nanotubes results in the precipitation of the SWNTs from aqueous solution.

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