resonance does not belong to a proton of Man-4′. Inspection of the structure of **1** shows that a likely candidate is the H-4 of the neighboring Man-3. The proximity of the Man-3 H-4 to the Man-4′ H-3 and H-5 atoms would confirm the existence of a 1-6 linkage in which the conformation with (ϕ,ψ,ω) = (-60°,180°,180°) must be present.

The present work illustrates the usefulness of 3D NMR techniques in structure elucidations of complicated oligosaccharides. The examples of Figure 2, parts A and B, show that unique asssignments of NOE's can be made, which would have required certain assumptions in 2D NMR. Furthermore the observation of NOE's between protons within the bulk region would be very difficult in 2D NMR.

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$[Mn_{10}O_{14}\{N(CH_2CH_2NH_2)_3\}_6]^{8+}$: A Mixed-Valence Polyoxomanganese Polycation Possessing Structural Similarities to Naturally Occurring Layered Manganese Oxides

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Early transition element polyoxoanions have received a great deal of attention for many years,[1,2] in part because of the analogy between these compounds and extended metal oxide materials. As a consequence, many discrete polyoxo anionic aggregates of V(V), Nb(V), Ta(V), Mo(VI), and W(VI) have been characterized. In contrast, there are relatively few well-defined polyoxo/hydroxo complexes of manganese and iron. This situation is presumably a consequence of the difficulty in controlling the hydrolytic or oxidative aggregation chemistry of these latter elements. High-nuclearity[3] carboxylate-bridged polyoxo Mn and Fe complexes, including those with 9,[4,5] 11,[6] and 12[7] metal atoms, have been reported recently. In addition, hydrolysis of Fe(tacn)Cl_3 yields an octanuclear complex.[8] Our interest in manganese oxo chemistry originates not only from the desire to understand and control the formation of soluble polyoxo aggregates as analogues of metal oxide surfaces but also because the oxygen-evolving complex of photosystem II most likely consists of a polynuclear manganese-oxo complex.[9] Herein we report the synthesis, isolation, and structure of a discrete polyoxomanganese cation, $[Mn_{10}O_{14}(tren)_6]^{8+}$ (**1**), which resembles in some respects the layered structures[10] of naturally occurring manganese oxide minerals chalcophanite ($ZnMn_3O_7{\cdot}3H_2O$),[11a,12] and lithiophorite ((Al,Li)$MnO_2(OH)_2$).[11b,12]

In a previous report,[13] we described the synthesis of a binuclear manganese complex obtained by controlled air oxidation of a solution containing $Mn(CF_3SO_3)_2$ and tren. In that case, air exposure was terminated after 2 h to yield a green complex, $[Mn_2O_2(tren)_2](CF_3SO_3)_3$ (**2**). It was noted that further air oxidation resulted in a brown solution. Characterization of a brown species from this latter solution constitutes the basis of this communication. The synthesis of **1** is initiated by dissolving 1.6 g of $Mn(CF_3SO_3)_2{\cdot}2MeCN$ and 0.64 g of tren in 10 mL of MeCN under N_2. After overnight exposure to the air, 5 mL of Et_2O was carefully layered on top of the MeCN solution. The crystals of **1**$(CF_3SO_3)_8{\cdot}6MeCN$ that deposit over 3 days lose solvent rapidly when removed from the mother liquor. However, they were suitable for X-ray diffraction experiments,[14] provided crystal mounting and data collection were carried out at low temperature in order to prevent loss of MeCN from the crystal lattice. The remaining crystals were collected and washed with Et_2O and dried in vacuo to yield 0.49 g of product[15] (47% yield) which analyzes as the desolvated cluster.

The centrosymmetric structure of **1** is shown from two perspectives in Figure 1.[16] On the basis of charge considerations, there are four Mn(III) and six Mn(IV) atoms in the cation. As is the case for other trapped valence manganese complexes **2**,[13] $[Mn_4O_3Cl_6(HIm)(CH_3COO)_3]^{2+}$ (**3**),[17] and the dodecanuclear carboxylate species $[Mn_{12}O_{12}(CH_3COO]_{16}(H_2O)_4]$ (**4**);[7] for example, Mn(III) atoms can be identified by the presence of axial bond distances which are elongated due to Jahn-Teller distortions. Thus, Mn(3) and Mn(5),[18] which have long Mn-N distances of 2.291 (2), 2.287 (2), and 2.283 (2) Å are assigned as Mn(III) ions. In contrast, the longest Mn-N distance for Mn(4) is 2.065 (3) Å and is assigned as Mn(IV) along with the remaining Mn atoms, Mn(1) and Mn(2). Three types of bridging oxo groups are present in the structure, including six doubly bridging atoms (O(5), O(6), O(7)) and two types of triply bridging oxo atoms. Of the eight μ_3-oxo bridges, four (O(3), O(4)) have a "t-shaped" geometry similar to that found in $[Fe_3O(TIEO)_2(O_2CPh)_2Cl_3]$.[5,19] The remaining four oxo groups (O(1), O(2)) are in sites of near trigonal microsymmetry and well out of the plane of the three manganese atoms to which they are attached. Compounds **3** and **4** have similar nonplanar μ_3-oxo bridges.

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(14) X-ray analysis: The compound $[Mn_{10}O_{14}(tren)_6](CF_3SO_3)_8{\cdot}6MeCN$ crystallizes in the triclinic system space group $P\bar{1}$, with a = 15.658 (7) Å, b = 15.681 (3) Å, c = 15.557 (3) Å, α = 115.80 (1)°, β = 92.26 (2)°, γ = 119.21 (2)°, V = 2842 Å^3, ρ(calcd) = 1.756 g cm^{-3}, and Z = 1. With the use of 8003 reflections collected at 163 K with Mo Kα (λ = 0.71073 Å) radiation out to 2θ = 45° on a single-crystal X-ray diffractometer, the structure was solved by a combination of Patterson and direct methods (SHELXS 86) and difference Fourier methods and refined to R (R_w) values of 3.6% (4.7%).

(15) Anal. Calcd for $C_{44}H_{108}F_{24}Mn_{10}N_{24}O_{38}S_8$: C, 18.58; H, 3.83; N, 11.82. Found: C, 18.17; H, 3.70; N, 11.58.

(16) Selected bond distances and angles (a full listing is provided as Supplementary Material): Mn(1)-O(1) 1.980 (2), Mn(1)-O(2) 1.874 (2), Mn(1)-O(3) 1.914 (2), Mn(1)-O(5) 1.804 (2), Mn(1)-O(1′) 1.898 (2), Mn(1)-N(21) 2.058 (2), Mn(3)-O(2) 1.918 (2), Mn(3)-O(5) 1.828 (2), Mn(3)-O(4′) 2.136 (2), Mn(3)-N(11) 2.291 (2), Mn(3)-N(31) 2.070 (3), Mn(3)-N(41) 2.083 (2), Mn(1)-O(1)-Mn(1′) 96.7 (1), Mn(1)-O(1)-Mn(2) 93.95 (8), Mn(2)-O(1)-Mn(1′) 96.89 (6), Mn(1)-O(3)-Mn(2) 99.4 (1), Mn(1)-O(3)-Mn(5) 165.4 (2), Mn(2)-O(3)-Mn(5) 92.51 (9), Mn(1)-O(5)-Mn(3) 98.0 (1), Mn(2)-O(6)-Mn(5) 96.6 (1).

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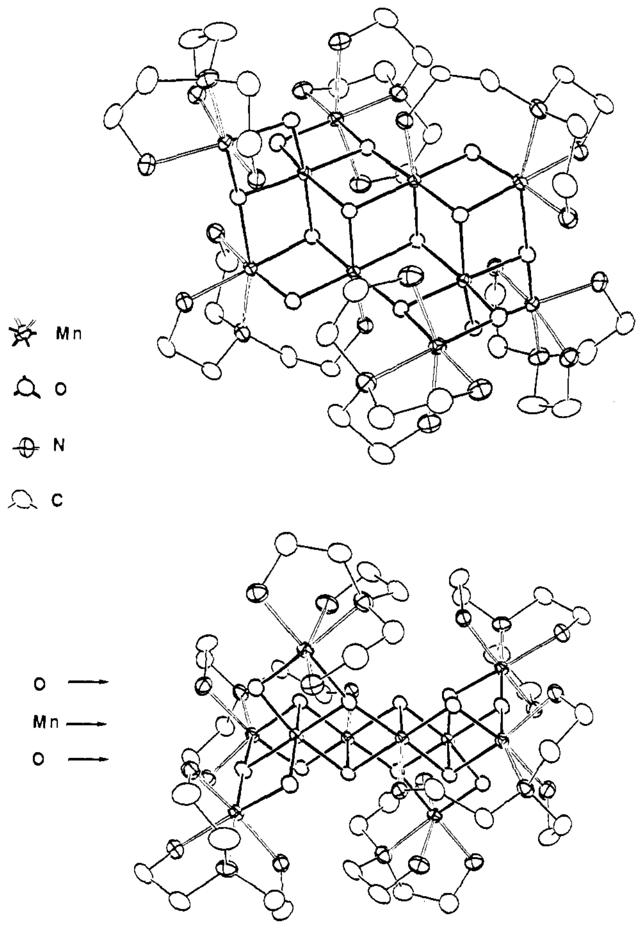

Figure 1. Two views of $[Mn_{10}O_{14}(tren)_6]^{8+}$ depicting 50% ellipsoids. Bottom view includes arrows pointing out layers of O and Mn.

The inner core of six Mn atoms (Mn(1), Mn(2), and Mn(3))[18] can be viewed as four partial cubane Mn_3O_4 units fused together along common faces. This structural motif is reminiscent of the layered CdI_2-like structure of chalcophanite and lithiophorite. An alternate description of layered structures of this sort is an extended lattice of edge-sharing MX_6 octahedra (Figure 2c). The inner Mn_6 core of **1** consists of two each of MnO_6, MnO_5N, and MnO_3N_3 edge-sharing pseudooctahedra (Figure 2b). The lengths of the shared edges are considerably shorter (2.55 (6) Å) than the others (2.79 (4) Å).[20] The rest of the cluster consists of four MnO_2N_4 pseudooctahedra. We suggest that it is partially the inability of the nitrogen atoms to serve as bridging linkages which restricts the growth of the cluster. Short Mn···Mn separations in compound **1** range from 2.713 (1) Å for Mn(2)···Mn(4) to 2.940 (1) Å for Mn(2)···Mn(3′). The distances between Mn(IV) ions within the inner Mn_6 core as defined above are 2.888 (1), 2.897 (1), and 2.895 (1) Å, which may be compared with a value of 2.85 Å for Mn···Mn contacts in $ZnMn_3O_7{\cdot}3H_2O$. Bond distances to oxo atoms range from 1.791 (2) Å for Mn(4)–O(4) to 2.136 (2) Å for Mn(3)–O(4′). The average Mn–O distance for the trigonal μ_3-oxo groups is 1.93 (4) Å, in good agreement with the corresponding average distance in chalcophanite (1.95 (2) Å). Four of the six tren ligands which cap the $\{Mn_{10}O_{14}\}^{8+}$ core are each bound to a single Mn atom, whereas the remaining two ligands each bridge two Mn atoms with one of their $-CH_2CH_2NH_2$ groups. Bridging tren ligands are also a feature of the structure of **2**.[13]

Preliminary room temperature magnetic measurements indicate a value of 3.2 μ_B per Mn atom as compared to a calculated average value of 4.3 μ_B per Mn for 10 independent Mn atoms (6 × Mn(IV) + 4 × Mn(III)), implying net antiferromagnetic interactions within the aggregate. A frozen acetonitrile solution of **1** is EPR-silent at 4 K. Despite the possibility for rich electrochemistry in a polynuclear complex of this type, cyclic voltammetry of **1** in acetonitrile reveals no reversible redox behavior in the range of 1.5 to −1.5 V (vs Ag/Ag^+).

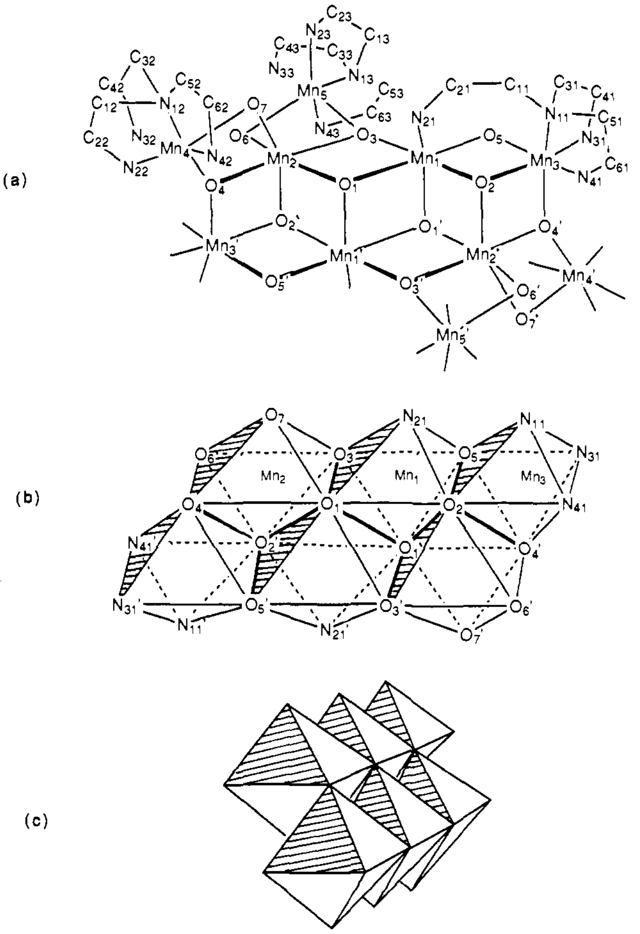

Figure 2. Atom labeling scheme for **1** showing (a) atom linkages, (b) $Mn_6O_{14}N_8$ core showing edge-sharing (in bold) octahedra, and (c) oblique view of (b) showing layered nature of edge-sharing octahedra.

In conclusion, the first example of a structurally defined high-nuclearity[3] non-carboxylate manganese-oxo complex has been discovered.[21] Distinct structural similarities between the novel discrete aggregate and layered oxide minerals are evident. It is conceivable that one has trapped by crystallization a species that would continue to grow in the presence of oxygen and/or water to form larger soluble complexes, which may then more closely approximate the properties of a manganese-oxo mineral surface. Indeed, we have obtained crystalline materials with solubility properties unlike those of compound **1** which are under further investigation. Furthermore, since manganese oxides are known to catalyze oxidation reactions,[22] the reactivity behavior of **1** is being examined.

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Supplementary Material Available: Atomic positional and thermal parameters and intramolecular distances and angles for $[Mn_{10}O_{14}(tren)_6](CF_3SO_3)_8{\cdot}6MeCN$ (8 pages). Ordering information is given on any current masthead page.

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(20) This excludes distances 3.04–3.34 Å to the μ_3-N,N(11), which is involved in a Jahn–Teller distorted interaction to Mn.

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