Synthesis and Crystal Structure of a $Mn^{II,III}$ Mixed-Valence Cluster with the Decametallate Core Geometry

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Polynuclear manganese complexes have received considerable attention because of their relavence to the polymetallic active sites of an increasing number of metalloproteins.[1] In addition, an intensive effort to design and understand new molecular magnet has been one of the most active research fields in inorganic chemistry.[2] Our interest in these area has been stimulated by a number of points, including the aesthetically pleasing structures of Mn clusters and their propensity to exhibit highly unusual magnetic properties. Mn clusters often display high spin(S) values in the ground state, a property resulting from the presence of at least some intramolecular exchange interactions that are ferromagnetic in nature.[3]

From a synthetic point of view, such high nuclearity spin clusters can be obtained by the aggregation of small nuclearity species with $[Mn_3O]^{6+,7+}$ or $[Mn_4O_2]^{8+}$ cores[4] or by proper use of suitable organic ligands such as carboxylates, polyamines, and polyols, *et al.*[5~7]

In relation to this study, we have taken up alkoxides as a organic ligand for assembling metal clusters, of which the oxo-groups serve in a multiple bridging capacity to anchor the polynuclear framework.[8] However, the oxoalkoxomanganese complexes remained relatively unexplored, and little information is available in general about Mn^{II}-containing species.[2b] Therefore, we report here the synthesis and structural characterization of an anionic mixed valence $Mn^{II,III}$ cluster with the decametallate core geometry, $(Et_4N)_2[Mn_{10}O_2X_8\{(OCH_2)_3CCH_2CH_3\}_6]$ (X = Cl (**1**) and Br (**2**)).

Experimental Section

Materials and Measurements. All reagents and solvents were used as received. Tris(hydroxymethyl)propane, $CH_3CH_2C(CH_2OH)_3$ was purchased from Aldrich Chemical Co. $(Et_4N)_2MnCl_4$ and $(Et_4N)_2MnBr_4$ were prepared as described in the literature, respectively.[9]

C, H, N elemental analyses were performed using a Carlo Erba 1106 automatic analyzer. The IR spectra were recorded as KBr disks using a Mattson Polaris FT-IR spectrophotometer in the range of 4,000-500 cm^{-1}. Magnetic moment at room temperature were measured by using a 7 Tesla SQUID magnetometer system of the Korea Basic Science Institute Daejun Branch and corrected for molecular diamagnetism from Pascal's constants.

Synthesis. All procedures were performed under aerobic conditions.

$(Et_4N)_2[Mn_{10}O_2Cl_8\{(OCH_2)_3CCH_2CH_3\}_6]$ (1). The reaction mixture of $(Et_4N)_2MnCl_4$ (0.457 g, 1 mmol) and tris(hydroxymethyl)propane (0.137 g, 1 mmol) in 20 mL of acetonitrile were refluxed for 24 hrs. After cooling the colorless solution to room temperature, triethylamine (0.304 g, 3 mmol) was added dropwise with stirring, and then refluxed for 24 hrs further. The resulting dark brown solution was filtered and the filtrate was layered with a double volume of diethyl ether in a test tube. Black crystals were formed in 2 weeks. The crystals were collected by filtration, washed with diethyl ether, and dried in *vacuo*. Yield: 4% (based on Mn). mp 260 °C (dec.). Anal. Calcd. for $C_{52}H_{106}N_2O_{20}Cl_8Mn_{10}$: C, 32.66; H, 5.59; N, 1.46. Found: C, 31.75; H, 5.82; N, 1.50. IR (KBr, cm^{-1}): 2976, 2915, 2859, 1624, 1464, 1397, 1198, 1038, 941, 576.

$(Et_4N)_2[Mn_{10}O_2Br_8\{(OCH_2)_3CCH_2CH_3\}_6]$ (2). The complex was prepared in a manner analogous to that for **1**, replacing the $(Et_4N)_2MnCl_4$ with $(Et_4N)_2MnBr_4$ in ethanol solution. Yield: 22% (based on Mn). mp 300 °C above. Anal. Calcd. for $C_{52}H_{106}N_2O_{20}Br_8Mn_{10}$: C, 27.54; H, 4.71; N, 1.24. Found : C, 28.67; H, 5.30; N, 1.50. IR (KBr, cm^{-1}): 2967, 2907, 2855, 1615, 1473, 1393, 1110, 1041, 942, 573.

Crystal Structure Determination of 1. X-ray quality crystals of **1** were obtained as described above. A crystal size $0.3 \times 0.3 \times 0.2$ mm was used for data collection on a STOE STAD14 four-circle-diffractometer with graphite-monochchromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Cell parameters and an orientation matrix for data collection were obtaind from least-squares refinement, using 25 reflections in $19.2^o < 2\theta < 20.9^o$. Intensities were collected ω scan tachnique and performed up to $2\theta = 54.88^o$. Three standard reflections monitored every 1 hr of X-ray exposure: no significant decay was observed. The intensity data were collected for Lorentz and polarization effects, and absorption correction was also applied. The structure was solved by direct method (SHELXS-97, Sheldrick, 1990) and refined by full-matrix least-squares methods (SHELXL-97, Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically. One of the carbon atoms in one of the alkoxide ligands appeared to be disordered and was

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Table 1. Crystal data and structure refinement for **1**

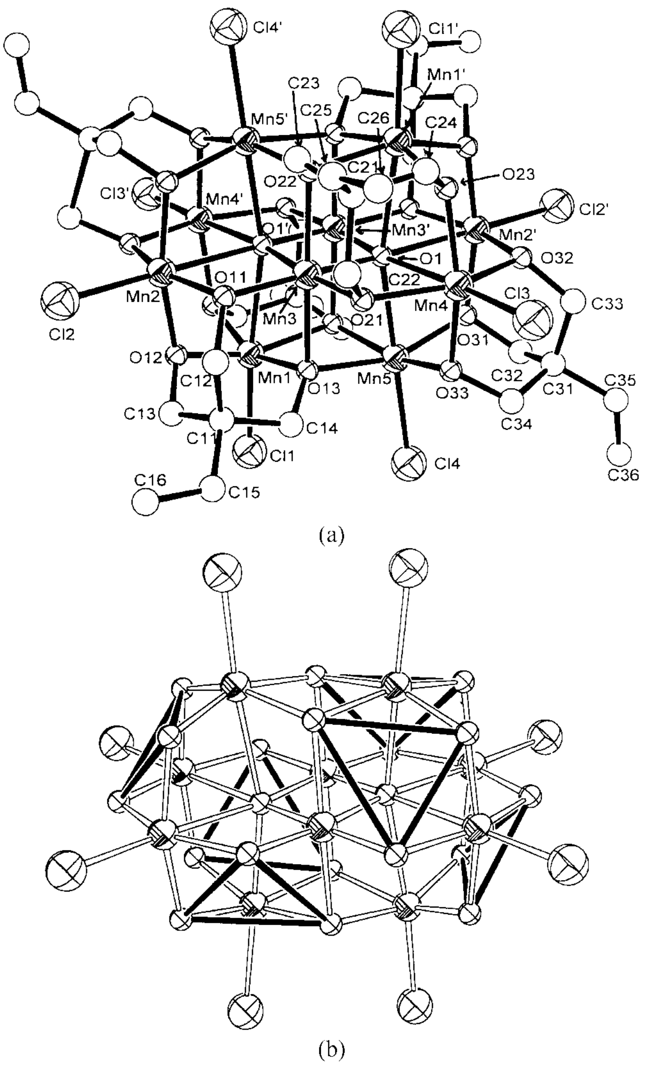
Empirical formula	$C_{52}H_{106}N_2O_{20}Cl_8Mn_{10}$
Fw	1912.39
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	
a(Å)	28.489(15)
b(Å)	11.7698(17)
c(Å)	27.434(4)
α(°)	90
β(°)	126.31(3)
γ(°)	90°
V(Å^3)	7412(4)
Z	4
D_{calc}(Mg/m^3)	1.714
F(000)	3912
μ (mm^{-1} with Mo-Kα)	1.995
Scan type	ω
Scan range	$1.63^\circ \leq 2\theta \leq 27.44^\circ$
No. of reflections measured	8465
No. of reflections observed ($I>2\sigma(I)$)	5037
No. of variable	425
R^a	0.0859
Rw^b	0.1652
Goodness-of-fit on F$^{2,\,c}$	1.083
Largest diff. peak and hole	1.907 and -1.984 e · Å^{-3}

^{a}R = $\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. ^{b}Rw = $[\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma|F_o|)^4]^{1/2}$, w = $1/[\sigma^2(F_o^2) + (0.0427P)^2 + 138.9777P$, where P = $(F_o^2+2F_c^2)/3$. ^{c}G.O.F. = $[\Sigma w(|F_o|^2-|F_c|^2)^2/(n-p)]^{1/2}$

refined as atoms C(26) and C(26') in a 0.43985 : 0.56015 ratio. The positions of hydrogen atoms were idealized (*d*(C-H) = 0.96 Å) and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter of 1.2 times that of attached atom. The data collection and structure solution parameters are listed in Table 1, together with standard discrepancy indicies *R* and *Rw*.

Result and Discussion

The reaction of $(Et_4N)_2MnCl_4$ with an equivalent amount of $CH_3CH_2C(CH_2OH)_3$ in acetonitrile with vigorous stirring in a flask open to air, followed by careful addition of diethyl ether yielded shiny black crystals of **1** in 4% yield. However, it was failed to get X-ray quality crystals of **2**. The IR spectra of the complexes exhibited two or three bands in the range of 2976-2855 cm^{-1} due to ν (C-H) and a strong band at *ca.* 1040 cm^{-1}, characteristic of ν (C-O) of the ligands.



(a)

(b)

Figure 1. (a) ORTEP diagram of $[Mn_{10}O_2Cl_8\{(OCH_2)_3CCH_2CH_3\}_6]^{2-}$ (**1**) showing the 50% probability thermal ellipsoids. Hydrogen atoms and counter ions are omitted for clarity. (b) Schematic representation of the $[Mn_{10}L_{28}]$ core, highlighting the triangular cavities available for occupancy by the oxygen donors of trisalkoxy ligands.

The structure of the molecular anion of **1**, shown in Figure 1(a), consists of the decametallate core $\{Mn_{10}(\mu_6\text{-}O)_2\}$ lying on an inversion center and containing distorted octahedral(μ_6) bridging O atoms [Mn-(μ_6-O) = 1.934(5)-2.604(6) Å]. Peripheral ligation is provided by six chelating alkoxy ligands with fourteen doubly bridging [Mn-(μ_2-O) = 1.924(6)-2.063(6) Å], and four triply bridging oxo groups O(13), O(13'), O(22), and O(22') [Mn-(μ_3-O) = 2.066(6)-2.237(6) Å] and eight terminal chloride ligands [Mn-Cl = 2.397(2)-2.471(7) Å]. This structure is essentially identical to those of the anions of $[V_{10}O_{16}\{(OCH_2)_3CCH_2CH_3\}_4]^{2-,10}$ previously reported with the gross metal-oxygen framework of $\{V_{10}O_{28}\}$ core, which twelve oxygen atoms was replaced by alkoxy donors from the four tris-alkoxy ligands. All Mn is six-coordinate and distorted octahedral. Each of the Mn ions exhibits a marketed axial elongation, resulting in an average Mn-O (2.505(5) Å) and Mn-Cl (2.420(4) Å) distance, which may be attributed to a John-Teller effect. The geometry of the tris-alkoxy ligand is such that it will preferentially adopt a bridging mode between three metal sites to give triangular $[M_3\{(OCH_2)_3CCH_2CH_3\}]$ structural motifs, which condense to form larger aggregates. As shown schematically in Figure 1(b), the decametallate core can accommodate up to six tris-alkoxy ligands, which cap the triangular faces of the tetrahedral cavities formed by the fusion

Table 2. Selected bond lengths (Å) for the structure of **1**

Mn(1)-O(1)'	2.604(5)	Mn(4)-O(1)	2.488(5)
Mn(1)-O(12)	2.007(6)	Mn(4)-O(21)	2.063(6)
Mn(1)-O(13)	2.076(5)	Mn(4)-O(23)	2.026(8)
Mn(1)-O(22)	2.066(6)	Mn(4)-O(32)	2.045(6)
Mn(1)-O(23)'	1.982(7)	Mn(4)-O(33)	2.036(7)
Mn(1)-Cl(1)	2.414(3)	Mn(4)-Cl(3)	2.399(3)
Mn(2)-O(1)'	2.423(5)	Mn(5)-O(1)	2.352(7)
Mn(2)-O(11)	1.971(6)	Mn(5)-O(13)	2.106(5)
Mn(2)-O(12)	1.959(6)	Mn(5)-O(22)'	2.099(6)
Mn(2)-O(31)'	1.958(6)	Mn(5)-O(31)	2.035(7)
Mn(2)-O(32)'	1.937(6)	Mn(5)-O(33)	2.015(8)
Mn(2)-Cl(2)	2.397(2)	Mn(5)-Cl(4)	2.471(7)
Mn(3)-O(1)	1.935(5)	Mn(2)-Mn(3)	3.1004(18)
Mn(3)-O(1)'	1.934(5)	Mn(3)-Mn(3)'	2.860(2)
Mn(3)-O(11)	1.941(5)	Mn(3)-Mn(4)	3.1703(18)
Mn(3)-O(13)	2.237(6)	Mn(3)-Mn(5)	3.205(3)
Mn(3)-O(21)	1.924(6)	Mn(3)-Mn(5)'	3.196(3)
Mn(3)-O(22)	2.222(7)		

'Subscripts are used for symmetry-equivalent atoms: −x+1/2, −y+1/2, −z+1.

of metal octahedra in the core.

Oxidation states for the manganese ions require a mixed-valence 8 Mn(III) and 2 Mn(II) description as expected from overall charge considerations for the cluster. The average Mn-O distance for the two Mn ions, which are coordinated exclusively to oxygen donors is 2.032(6) Å. This value is shorter than the distance for the remaining eight Mn ions in a ClO_5 environment, for which Mn-Oav = 2.112(6) Å. Valence sum calculations[11] based on the bond length data of Table 2 also indicate that the two central Mn sites of the hexamanganese girdle of **1** are Mn(III) sites, while the remaining eight sites exhibit intermediate geometries. The room temperature magnetism of 15.8 BM/Mn_{10} is nearly agreement with the expected value of 16.2 BM[12] for high spin Mn (2 × II, 8 × III). From these results, we assign a total of two Mn(II) and eight Mn(III) ions to the cluster, giving an overall charge of 28^+ for the metal ions. The ligands $[2O^{2-} + 8Cl^{1-} + 6\{(OCH_2^{1-})_3CCH_2CH_3\}]$ give a total charge of 30^-, resulting in a 2^- charge for **1**, which is balanced by the two Et_4N^+ cations.

The complexes are uncommon examples of a high nuclearity Mn-oxo cluster that dose not contain carboxylate ligands,[13] and a unique example of an anionic low-valent, high-nuclearity cluster. The relatively facile isolation of **1** reflects the role of the tris-alkoxy ligand types in stabilizing $[M_3\{(OCH_2)_3CR\}]$ structural fragments that condense into larger aggregates, which often display classical polyoxoanion structural cores[8,14]

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Supporting Information Available. Details of X-ray data collection parameters, atomic coordinates, anisotropic thermal parameters, hydrogen atom coordinates, and lists of bond lengths and angles are available from the correspondence author.

References

1. Wieghardt, K. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 725.
2. (a) Caneschi, A.; Gatteschi, D.; Sessoli, R. *J. Chem. Soc., Dalton Trans.* **1997**, 3963. (b) Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Caneschi, A.; Gatteschi, D. *Inorg. Chem.* **1998**, *37*, 3759.
3. (a) Ballou, R.; Barbara, B; Lionti, F.; Gattischi, D.; Sessoli, R. *Nature* **1996**, *383*, 145. (b) Aubin, S. M. J.; Sun, Z.; Guzei, I.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun*. **1997**, 2239.
4. Wang, S.; Tsai, H.-L.; Streib, W. E.; Christou, G.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1992**, 677. (b) Wang, S.; Huffman, J. C.; Folting, K.; Streib, W. E.; Lobkovsky, E. B.; Christou, G. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1672. (c) Tsai, H.-L.; Wang, S.; Folting, K.; Streib, W. E.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1995**, *117*, 2503. (d) Libby, E.; Folting, K.; Huffman, J. C.; Christou, G. *J. Am. Chem. Soc.* **1990**, *112*, 5354. (e) Libby, E.; Folting, K.; Huffman, C. J.; Christou, G. *Inorg. Chem.* **1993**, *32*, 2549. (f) Wemple, M. W.; Tsai, M. L.; Streib, W. E.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1031.
5. (a) Squire, R. C.; Aubin, S.; Folting, K.; Streib, W.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1995**, *34*, 6463. (b) Eppley, H.; Tsai, H.; de Dries, N.; Folting, K.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc*. **1995**, *117*, 301. (c) Low, D. W.; Eichhorn, D. E.; Dragonescu, A.; Armstrong, W. H. *Inorg. Chem.* **1991**, *30*. 87. (d) Blackman, A.; Huffman, J. C.; Lobkovsky, E.; Christou, G. *Polyhedron* **1992**, *11*, 251.
6. (a) Bhula, R.; Weatherburn, D. C. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 688. (b) Grillo, V.; Knapp, M.; Bollinger, J.; Hendrickson, D. N.; Christou, G. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1818. (c) Hagen, K. S.; Armstrong, W. H.; Olmstead, M. *J. Am. Chem. Soc.* **1989**, *111*, 774.
7. Cavalluzzo, M.; Chen, Q.; Zubieta, J. *J. Chem. Soc. Chem. Commun.* **1993**, 191. (b) Goldberg, D. P.; Caneschi, A.; Delfs, C. D.; Sessoli, R.; Lippard, S. J. *J. Am. Chem. Soc.* **1995,** *117*, 5789. (c) Xia, X.; Verelst, M.; Daran, J. C.; Tuchagues, J. P. *J. Chem. Soc., Chem. Commun.* **1995**, 2155.
8. (a) Khan, M. I.; Chen, Q.; Goshorn, D. P.; Hope, H.; Parkin, S.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 3341. (b) Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 1556. (c) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Park, C. W.; Rosenberg, F. S. *J. Am. Chem. Soc.* **1991**, *113*, 8190. (d) Chen, Q.; Zubieta, J. *Coord. Chem. Rev.* **1992**, *114*, 107 and references cited therein.
9. Gill, N. S.; Taylor, F. B. *Inorg. Synth.*; Tyree, S. Y., Ed.; McGraw-Hill Press: New York, U. S. A., 1967; Vol. 9, p 137.
10. Khan, M. I.; Chen, Q.; Goshorn, D. P.; Zubieta, J. *Inorg.*

Chem. **1993**, *32*, 672.

11. Brown, I. D. In *Structure and Bonding in Crystals*; O'Keefe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; vol. II, pp. 1-30. (b) Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Caneschi, A.; Gatteschi, D. *Inorg. Chem*. **1998**, *37*, 3759.
12. Cavaluzzo, M.; Chen, Q.; Zubieta, J. *J. Chem. Soc. Chem. Commun.* **1993**, 131.
13. Hagen, K. S.; Armstrong, W. H.; Olmstead, M. M. *J. Am. Chem. Soc*. **1989**, *111*, 774.
14. Hegetschweiler, K.; Schmalle, H.; Streit, H. M.; Schneider, W. *Inorg. Chem*. **1990**, *29*, 3625.