Incomplete and complete manganese cubes

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Reactions of $MnCl_2{\cdot}4H_2O$ with 2-(5-bromo salicylideneamino)-1-propanol (H_2(5-Br-sap)) under aerobic conditions and with 2-salicylideneamino-1-propanol (H_2(sap)) under strict anaerobiosis yielded tri and tetranuclear manganese complexes of $[Mn^{III}{}_3(\mu_3\text{-}O)(5\text{-}Br\text{-}sap)_3(H_2O)_3]Cl{\cdot}5.5H_2O$ (**1**) and $[Mn^{II}{}_4(sap)_4(MeOH)_4]{\cdot}2H_2O$ (**2**), respectively; the magnetic susceptibility measurements revealed intramolecular antiferromagnetic interactions being operative in both compounds, of which exchange coupling constant for **2** was estimated to be $-1.6\,cm^{-1}$ ($H = -2J\Sigma S_i{\cdot}S_j$).

Cluster chemistry comprised of manganese ions is of great interest, both for the bioinorganic aspects such as the active centre for photosynthetic water oxidation,[1] and for their potential solid state properties of superparamagnetism and quantum spin tunneling.[2] Carboxylato-, oxo-, and alkoxo-bridges display diverse coordination chemistry of manganese clusters. By using such ligands, four manganese ions are assembled in butterfly, planar, and cubic core shapes, some of which showed spin frustration.[3] Derivatives of dodecanuclear $Mn^{III,IV}$ clusters have been proven to be single molecule magnets.[4] Manganese cluster chemistry has potential applications to chemically modified magnetic materials. We have been preparing alkoxo-bridged high-spin cubes of Cu^{II}, Ni^{II}, and Fe^{II} ions with spin ground states of $S = 2$, 4, and 8, respectively.[5] During the course of the study, we found that the alkoxide in Schiff bases has also potential to assemble manganese ions and that chemical modification of ligands and different reaction conditions allow to give cluster molecules with different nuclearity and oxidation number. We report here syntheses, structures, and magnetic properties of manganese complexes with incomplete and complete cubic structures.

The reaction of $MnCl_2{\cdot}4H_2O$ with H_2(5-Br-sap) in MeOH under the air yields a trinuclear Mn^{III} complex of $[Mn^{III}{}_3(\mu_3\text{-}O)(5\text{-}Br\text{-}sap)_3(H_2O)_3]Cl{\cdot}5.5H_2O$ (**1**).[6] Complex **1** crystallizes in monoclinic space group $C2/c$ and the unit cell contains four chloride ions and 5.5 solvate water molecules per molecule.[7] The cation of **1** (Figure 1) is composed of a Mn_3 triangular unit which is bridged by μ_3-oxide ion (O(7)) and μ_2-alkoxides (O(2), O(4), and O(6)) from tridentate chelating $(5\text{-}Br\text{-}sap)^{2-}$ groups. The cation of **1** forms an incomplete cube with one apex lacked from the cube. Each manganese ion has six coordination atoms of N_1O_5 atoms provided by $(5\text{-}Br\text{-}sap)^{2-}$ group, oxide ion and water molecule. Three manganese ions are assigned to the Mn^{III} ions on the bases of the bond valence sum calculation and the presence of Jahn-Teller elongation along the O(6)-Mn1-O(8), O(2)-Mn(2)-O(9), and O(4)-Mn(3)-O(10) axes. Bond lengths of the Mn^{III} ions with the equatorial coordination atoms are 1.872(3)–2.008(4) Å, while the Jahn Teller elongation (2.189(3)–2.335(3) Å) are observed in the axial bonds. The three Mn^{III} ions make a quasi-equilateral triangle with sides 3.012(1)–3.023(1), and 3.024(1) Å long, and the bridging angles about Mn-O(7)-Mn are in the range of 102.0(1)–102.9(1)°.

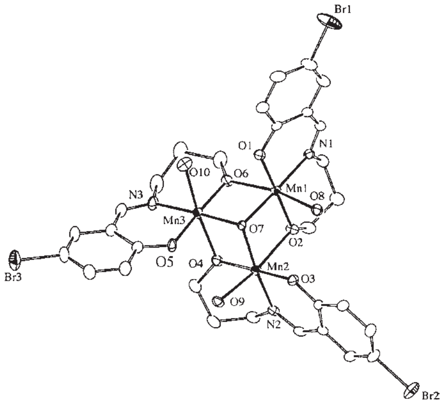

Figure 1. ORTEP drawing of **1**. Selected bond lengths (Å) of the core structure: Mn(1)–O(2) 1.872(3), Mn(1)–O(1) 1.896(3), Mn(1)–O(7) 1.934(3), Mn(1)–N(1) 2.004(4), Mn(1)–O(6) 2.199(3), Mn(1)–O(8) 2.317(3), Mn(2)–O(4) 1.874(3), Mn(2)–O(3) 1.914(3), Mn(2)–O(7) 1.944(3), Mn(2)–N(2) 2.000(4) Mn(2)–O(2) 2.193(3), Mn(2)–O(9) 2.276(3), Mn(3)–O(6) 1.875(3), Mn(3)–O(5) 1.899(3), Mn(3)–O(7) 1.931(3), Mn(3)–N(3), 2.008(4), Mn(3)–O(4), 2.189(3), Mn(3)–O(10) 2.335(3).

The reaction of $MnCl_2{\cdot}4H_2O$ with H_2(sap) in MeOH under N_2 atmosphere gives a tetranuclear Mn^{II} complex of $[Mn^{II}{}_3(sap)_4(MeOH)_4]{\cdot}2H_2O$ (**2**) (H_2(sap) = 2-salicylideneamino-1-propanol).[6] Complex **2** crystallizes in tetragonal space group $I4_1/a$ and the asymmetric unit contains quarter of cluster molecules in addition to solvent.[7] A complex molecule has S_4 symmetry and consists of a μ_3-alkoxo bridged tetranuclear core, giving an approximately cubic array of alternating manganese and oxygen atoms (Figure 2). Coordination geometry about each manganese(II) ion is a pseudo octahedron with one nitrogen and five oxygen atoms from tridentate sap^{2-} group and methanol molecule. Coordination bond lengths are 2.103(2)–2.272(2) Å for Mn-O and 2.209(2) Å for Mn-N, and the bridging bond angles of Mn-O(2)-Mn are in the range of 96.06(6)–102.01(6)°. The Mn^{II} assignment for **2** is evident from the coordination geometry and is also confirmed by the fact of the longer coordination bond lengths than those for **1**.

Magnetic susceptibility measurements were performed on **1** and **2** in the range of 1.8–300 K. The χ_mT value for **1** is $5.43\,emu\,mol^{-1}\,K$ at 300 K, which is lower than the value expected for the uncorrelated three Mn^{III} ions ($9.0\,emu\,mol^{-1}\,K$ for $g = 2.0$). The χ_mT values show monotonous decrease as the temperature is lowered, reaching $1.0\,emu\,mol^{-1}\,K$ at 6 K, followed by sudden decrease. The magnetic behavior for **1** is indicative of the occurrence of strong antiferromagnetic interac-

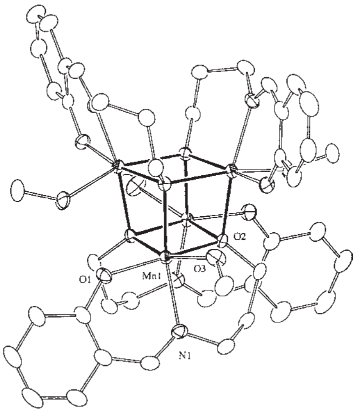

Figure 2. ORTEP drawing of **2**. Selected bond lengths (Å) of the core structure: Mn(1)–O(1) 2.103(2), Mn(1)–O(2) 2.151(2), Mn(1)–O(2)^1 2.182(2), Mn(1)–N(1) 2.209(2), Mn(1)–O(2)^2 2.233(2), Mn(1)–O(3) 2.272(2). Symmetry operation: #1 $y - 1/4, -x + 1/4, -z + 9/4$, and #2 $-x, -y + 1/2$, z.

tions operated in the triangular core. The three Mn^{III} ions are bridged by the oxide ion and the complex molecule has a pseudo C_3 axis. The amplitude of three exchange coupling constants, representing magnetic interactions between three Mn^{III} ions, are considered to be comparable to each other, and the spin ground state for **1** cannot be simply described. In addition, a Mn^{III} ion displays a Jahn-Teller distortion leading to a relatively large zero-field splitting, and this makes the analysis of the magnetic data more complicated. Further analysis of the magnetic data for **1** has not been done yet. The variable temperature magnetic susceptibility data for **2** also show the sign of antiferromagnetic interactions (Figure 3). The $\chi_m T$ value of 17.57 emu mol^{-1} K at 300 K gradually decreases as the temperature is lowered, reaching to 0.29 emu mol^{-1} K at 2.0 K. The spin-only value for a unit composed of noninteracting Mn$^{II}{}_4$ ions is 17.5 emu mol^{-1} K ($g = 2.0$). The temperature dependence of the $\chi_m T$ data was fitted in order to determine the magnitude of the antiferromagnetic coupling constant. Supposing the identical exchange coupling constants for intracube's magnetic pathways, the Kambe's vector coupling method[8] gives the eigenvalue expression as $E(S_T) = -JS_T\ (S_T + 1)\ (S_T = S_1 + S_2 + S_3 + S_4$ and $H = -2J\Sigma S_i{\cdot}S_j)$. The least squares calculation yielded the best fit parameters of g and J values being 2.141(1) and $-1.6(1)$ cm^{-1}, respectively. In summary, we prepared two types of manganese clusters by changing reaction conditions. Complex **1** is very soluble in polar solvents, therefore, **1** can be used as the starting material to prepare larger cluster molecules.

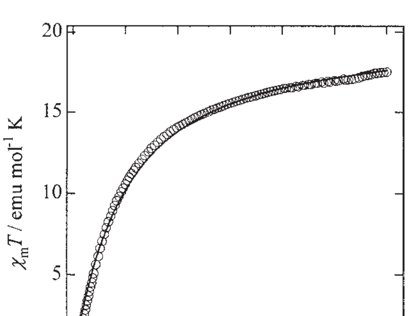

Figure 3. Plot of $\chi_m T$ vs T for **2**. The solid line crresponds to the fit of the data as described in the text.

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6 Schiff base ligands were prepared by condensation reactions of aminopropanol with the corresponding salicylaldehyde. The complexes were analysed satisfactory as solvent-free.

7 Crystal data: **1**: $C_{30}H_{47}Br_3Cl_1Mn_3N_3O_{15.5.}$ (including solvate molecules), $M = 1137.70$, monoclinic space group $C2/c$, $a = 28.907(7)$, $b = 13.925(4)$, $c = 21.898(6)$ Å, $\beta = 94.791(7)°$, $U = 8784(4)$ Å^3, $Z = 4$, $T = -70$ °C. A total of 28045 were collected ($3° < 2\theta < 50°$) of which 8702 unique reflections ($R(\mathrm{int}) = 0.051$) were measured. Residual R and wR were 0.0388 and 0.0898, respectively, from the refinement on F^2 with $I > 2\sigma(I)$. **2**: $C_{44}H_{68}Mn_4N_4O_{14.}$ (including solvate molecules), $M = 1096.23$, tetragonal space group $I4_1/a$, $a = 16.8773(6)$, $c = 17.6920(16)$ Å, $U = 5039.4(5)$ Å^3, $Z = 4$, $T = -70$ °C. A total of 14461 were collected ($3° < 2\theta < 50°$) of which 2492 unique reflections ($R(\mathrm{int}) = 0.029$) were measured. Residual R and wR were 0.0339 and 0.1052, respectively, from the refinement on F^2 with $I > 2\sigma(I)$. In the structure analyses, non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-187109 and 187110. Copies of the 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, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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