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Nanoscale Cages of Manganese and Nickel with "Rock Salt" Cores

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It is becoming clear that nanoscale cages of metals in a low oxidation state resemble either fragments of bulk metal, e.g., when ligated by carbonyls,[1] or fragments of relevant minerals, e.g., when chalcogenide bridges are present.[2] When the metal centers present are in moderate oxidation states, no simple correlation has been found; some examples exist where the structure can be considered to be a segment of a common mineral,[3] but in other cases elaborate and "unnatural" metal oxide cores are found.[4] These nanoscale structures may serve as models for intermediates in sol−gel syntheses, which offer control of structure in glasses, ceramics, and other materials; others demonstrate fascinating magnetic properties.[3,4] Furthermore, structural analysis of such cages can give important insight into the early stages of nucleation, which is of relevance to all scientists working in areas such as nanoparticulates. Here we report two new nanoscale oxide cages which can be synthesized using simple 1,3-bridging ligands, and which contain fragments of the rock salt structure.

Reaction of nickel hydroxide (4 mmol, made from nickel chloride and NaOH) with 2 equiv of 6-methyl-2-pyridone (Hmhp) under N_2 at 160 °C produces a green paste which, after drying *in vacuo*, can be redissolved in MeCN (20 mL). After standing for 1 day green crystals[5] formed in 74% yield. X-ray analysis[6] reveals a compound best written as $[Ni_6(OH)_6\{Ni(mhp)_3\}_5(Hmhp)(Cl)(H_2O)_2]$ (**1**) (Figure 1). The structure contains a face-sharing $Ni_6(OH)_6$ double cubane which is closely related to the NiO structure.

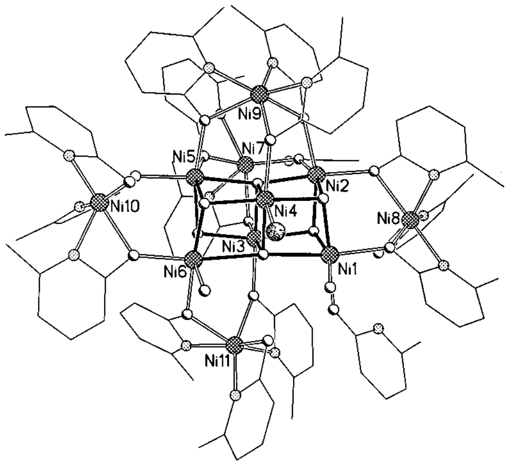

Figure 1. Structure of **1** in the crystal. Bond length ranges: (a) Ni atoms in cubane core, Ni−O(OH) 1.995−2.358, Ni−O(mhp) 2.020−2.088, Ni−O(H_2O) 2.071−2.074, Ni−Cl 2.418; (b) Ni atoms in complex ligands, Ni−O(mhp) 2.082−2.207, Ni−N(mhp) 2.048−2.079 Å (av esd 0.006 Å). [Unlabeled atoms: O, open circles; N, regular dot pattern; Cl heavy random dot pattern].

The double cubane is bound to five $\{Ni(mhp)_3\}$ "complex ligands". Within all of these $\{Ni(mhp)_3\}$ fragments the mhp ligands chelate to the Ni atom with a *fac*-geometry. This produces a potentially tridentate oxygen donor complex ligand. Two of these units [those featuring Ni(9) and Ni(7)] use all three O-atoms to bind to Ni-sites of the double cubane, while the remaining three units use two O-atoms to bind to Ni-atoms, and the final oxygen to form a hydrogen bond to a hydroxide of the central core. Four terminal ligands—an Hmhp, two H_2O, and a chloride (carried forward from the preparation of nickel hydroxide)—complete the coordination spheres of the Ni-centers of the double cubane.

A larger cage is formed from the reaction of manganese(II) chloride tetrahydrate (5.2 mmol), with sodium pivalate (10.4 mmol) and Na(mhp) (10.4 mmol) in MeOH, which gives a brown precipitate which can be extracted with hot MeOH. This pale solution was allowed to stand at room temperature, yielding crystals after 14 days (yield *ca.* 3%). The extremely small, weakly diffracting crystals[5] required synchrotron radiation for diffraction studies, and X-ray analysis[6] reveals an octadecanuclear cage $[Mn_{18}O_{14}(MeO)_{14}(O_2CCMe_3)_8(MeOH)_6]$ (**2**) (Figure 2). A more rational synthesis of **2** involves stirring a solution of hydrated $MnCl_2$ (11.3 mmol) with $Na(O_2CCMe_3)$ (5.05 mmol) and Na(OMe) (8.8 mmol) in MeOH (50 mL) for 48 h. After filtration the solution was placed in a freezer at −14 °C, and small crystals of **2** formed after 7 days in 6% yield.

The structure of **2** is best visualized as a central, distorted Mn_4O_4 cubane, with each face of this cubane shared with a further cubane, leading to a face-sharing heptacubane, $Mn_{16}O_{14}(OMe)_2$. Of the fourteen oxides, four act as μ_6-, two as μ_4-, and eight as μ_3-bridges; two of the μ_6-oxides are markedly asymmetric with one long and five shorter Mn−O bonds. The two methoxides are both μ_3-bridging. The sixteen manganese centers within the heptacubane are mixed-valent, with twelve showing distorted geometries typical of Mn(III) (four short Mn−O bonds ≤ 1.970 Å, and one medium and one long Mn−O contacts *trans* to one another), and four [Mn(13), Mn(14), Mn(15), and Mn(16)] with

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(5) Elemental analysis Found for **1**: C, 45.2; H, 4.0; N, 8.7. Calcd: C, 45.2; H, 4.2; N, 8.8. Analytical data for **2** were repeatedly low for both C and H, probably due to poor combustion of the molecule in the analyzer. This was the case even for samples where X-ray diffraction indicated that the same phase was present as found in the single crystal.

(6) Crystal data for **1**: triclinic, $P\bar{1}$, green plate developed in (101), $a = 13.750(5)$ Å, $b = 15.365(4)$ Å, $c = 30.695(9)$ Å, $\alpha = 100.88(3)°$, $\beta = 90.56(4)°$, $\gamma = 107.72(2)°$, $V = 6051(3)$ Å^3, $Z = 2$, $T = 220.0(2)$ K, $R1 = 0.0669$, GOF = 1.025. Crystal data for **2**: monoclinic, $P2_1/n$, dark red block, $a = 16.3826(14)$ Å, $b = 32.075(5)$ Å, $c = 22.797(3)$ Å, $\beta = 109.372(11)°$, $V = 11301(2)$ Å^3, $Z = 4$, $T = 160.0(2)$ K, $R1 = 0.0669$, GOF = 0.965. Data collection for **1** and structure solution and refinement for **1** and **2** were performed as detailed in ref 3c using the programs SHELXS-97 and SHELXL-93: Sheldrick, G. M., University of Göttingen, 1993. Data collection for **2** was performed using a Siemens SMART three-circle diffractometer equipped with a CCD detector attached to Station 9.8 at the CCLRC Daresbury synchrotron radiation source. Full details have been deposited as Supporting Information.

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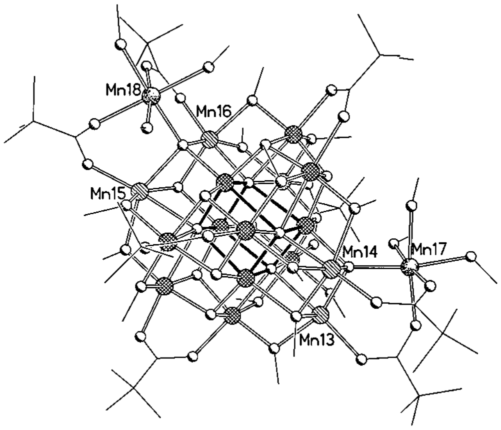

Figure 2. Structure of **2** in the crystal. Bond length ranges: (a) Mn(III) sites, Mn−O("short") 1.895−1.970, Mn−O("medium") 2.083−2.157, Mn−O("long") 2.287−2.539; (b) mixed-valent Mn(II)/(III) sites, Mn−O 1.861−2.415; (c) Mn(II) sites, Mn−O 2.105−2.224 Å (av esd 0.004 Å). [All unlabeled Mn atoms are Mn(III), cross-hatched circles; Mn(II) random dot pattern; Mn(II)/(III) sites shaded top left−bottom right].

an irregular distribution of bond lengths. Charge balance requires two of these sites to be Mn(II) and two Mn(III); however, there is no clear-cut metrical differentiation between these four sites. Some are markedly asymmetric, but the longest bonds are not trans to each other and the average Mn−O bond lengths are longer than for the Mn(III) sites. The best explanation we can offer is that these sites, which occupy a position in the structure between the Mn(III) and Mn(II) sites, are all delocalized Mn(II)/Mn(III).

The two additional Mn centers within **2** are clearly Mn(II), and are attached to the two μ_4-oxides [O(5) and O(6)]. Two O_2CCMe_3 ligands attach each of these Mn(II) to the central core, and in both cases their coordination spheres are completed by three MeOH molecules. These additional caps are attached to cubanes on opposite faces of the central cubane, with the result that these two cubanes are chemically distinct from the other four, which form an equatorial band within the cage. The remaining organic ligands are arranged symmetrically about the heptacubane. Each μ_2-methoxide bridges between Mn centers in neighboring cubanes, while the remaining four carboxylates bridge the external Mn···Mn vectors of the four equatorial cubanes in a 1,3-fashion.

Both **1** and **2** have structures which are clearly related to rock salt, which is in both cases the structure of the metal(II) oxide mineral, either NiO or MnO. In **2** the oxidation state of the manganese is more akin to that in Mn_3O_4, which contains mixed-valent Mn(II)/Mn(III) and which has a spinel structure. Fitting the metal core of **2** to the MnO lattice shows that while the sixteen Mn centers of the heptacubane match well to the Mn sites of MnO, the final two Mn sites [Mn(17) and Mn(18)] are near tetrahedral holes of the MnO array. These holes are occupied in the spinel structure. This may indicate that when larger mixed-valent Mn cages are characterized, the next "shell" of Mn centers may begin to resemble Mn_3O_4. A similar story may be true for Fe cages, as again FeO has the rock salt structure while Fe_3O_4 is an inverse spinel. If this is true, it has some implications for how such structures nucleate. Early stages of growth may involve rock salt cores which gain the defects required by charge balance as the particles become larger, eventually changing to spinel or inverse spinel lattices.

A number of other polynuclear structures have been reported which involve face-sharing cubanes. Face-sharing double cubanes such as **1** are found as part of the decavanadate structure,[7] which has also been reported for iron.[8] In these structures four additional metal sites lead to two further cubes which share edges with the central face-sharing bicubane. Christou and co-workers have reported an octanuclear triple-cubane structure involving cobalt,[9] and Hendrickson *et al.* a tridecanuclear manganese "super-cubane" which involves eight cubanes each sharing three faces with their neighbors, leading to a cube of cubanes.[10] The cubane array in **2** is a distorted extension of these previous structures.

Preliminary magnetic studies (SQUID susceptometer, Quantum Design) of both **1** and **2** are disappointing, showing predominantly antiferromagnetic exchange between the metal centers. For **1** the $\chi_m T$ value at 300 K of 13.1 emu K mol^{-1} (χ_m = the molar magnetic susceptibility) is consistent with eleven noninteracting $S = 1$ centers, and this value falls steadily to 2.9 emu K mol^{-1} at 1.8 K, which suggests a spin ground state no higher than $S = 2$. For **2** $\chi_m T$ at room temperature was found to be 56 emu K mol^{-1}, and the value falls steadily as the sample is cooled, reaching 6.0 emu K mol^{-1} at 1.8 K. This behavior can be rationalized in a manner similar to that adopted by Hendrickson and co-workers for the smaller Mn_{13} cage;[10] the assumption is ferromagnetic exchange within layers, but antiferromagnetic exchange between layers. In this case we would predict an $S = 1$ or 0 ground state for the heptacubane core of **2** depending on whether the two Mn(II) sites of the heptacubane are in the same layer. The presence of two additional Mn(II) sites in **2** makes it difficult to predict an overall ground state for the cage.

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Supporting Information Available: Crystallographic data for **1** and **2** (52 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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