JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 23
1991

Preparation and Characterization of $[Mn_{11}O_{10}Cl_2(OAc)_{11}(bpy)_2(MeCN)_2(H_2O)_2](ClO_4)_2{\cdot}8MeCN$, a Mixed-valence Manganese(III/IV) Aggregate with Rare Undecanuclearity (bpy = 2,2′-bipyridyl)

Spiros P. Perlepes, John C. Huffman and George Christou*

Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, IN 47405, USA

Treatment of $[Mn_4O_2(OAc)_7(bpy)_2](ClO_4){\cdot}3H_2O$ (bpy = 2,2′-bipyridyl) **1** with Me_3SiCl in MeCN leads to a disproportionation and nuclearity change to give $[Mn_{11}O_{10}Cl_2(OAc)_{11}(bpy)_2(MeCN)_2(H_2O)_2](ClO_4)_2{\cdot}8MeCN$ **2**; the crystal structure shows the core of this aggregate to comprise two $[Mn_4O_3Cl]^{6+}$ cubane units 'bridged' by a nearly linear $[Mn_3O_4]^+$ moiety.

Over the last few years, we have been reporting our efforts towards developing the chemistry of Mn at various nuclearities with primarily carboxylate ligation.[1] These studies have been stimulated by a variety of reasons, including Mn-containing biological systems[2] and the desire to prepare molecular species with large spin ground states.[3] Higher nuclearity Mn aggregates are particularly useful for the latter purpose, given their propensity to involve ferromagnetic interactions between at least some of the constituent metal centres.[3,4] There is a need to develop synthetic methodology to such species, because procedures to high nuclearity Mn aggregates are currently very limited. One procedure that has proven extremely useful at lower nuclearities is carboxylate-abstraction [eqn. (1)] with Me_3SiCl[5] from preformed Mn/O/RCO_2^- species.[4,6,7] We have described, for example, the conversion with Me_3SiCl of $[Mn_3O(OAc)_6(py)_3](ClO_4)$ (py = pyridine) to $Mn_4O_3Cl_4(OAc)_3(py)_3$ **3**;[4] this involves a transformation of the $Mn_3^{III}O$ planar unit to the $Mn_3^{III}Mn^{IV}O_3Cl$ cubane core *via* an undoubtedly complex mechanism involving disproportionation and nuclearity changes. We herein report that the reaction of $[Mn_4O_2(OAc)_7(bpy)_2]$-$(ClO_4){\cdot}3H_2O$ **1** with Me_3SiCl leads to a most remarkable high-nuclearity product, $[Mn_{11}O_{10}Cl_2(OAc)_{11}(bpy)_2$-$(MeCN)_2(H_2O)_2](ClO_4)_2{\cdot}8MeCN$ **2** with a quite unprecedented structure.

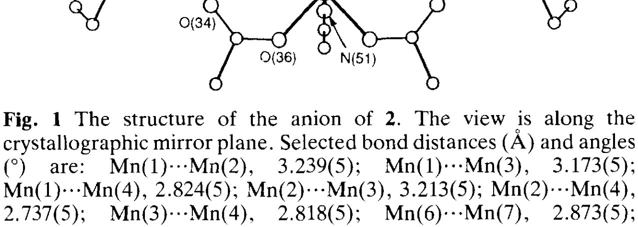

Fig. 1 The structure of the anion of **2**. The view is along the crystallographic mirror plane. Selected bond distances (Å) and angles (°) are: Mn(1)···Mn(2), 3.239(5); Mn(1)···Mn(3), 3.173(5); Mn(1)···Mn(4), 2.824(5); Mn(2)···Mn(3), 3.213(5); Mn(2)···Mn(4), 2.737(5); Mn(3)···Mn(4), 2.818(5); Mn(6)···Mn(7), 2.873(5); Mn(5)···Mn(6), 2.864(5); Mn(1)–Cl(8), 2.688(7); Mn(2)–Cl(8), 2.534(7); Mn(3)–Cl(8), 2.653(6); Mn(1)–O(11), 1.890(13); Mn(1)–O(12), 1.875(15); Mn(2)–O(9), 1.890(16); Mn(2)–O(10), 1.877(13); Mn(3)–O(10), 1.969(13); Mn(3)–O(11), 1.907(14); Mn(3)–O(13), 1.887(14); Mn(4)–O(9), 1.879(14); Mn(4)–O(10), 1.870(14); Mn(4)–O(11), 1.839(13); Mn(5)–O(12), 1.832(15); Mn(6)–O(12), 1.918(14); Mn(6)–O(13), 1.894(14); Mn(7)–O(13), 1.834(14); N(14)–Mn(2)–N(25), 80.4(9); Mn–Cl(8)–Mn, 72.89(17)–76.62(19).

$$M{-}O_2CR + Me_3SiCl \rightarrow M{-}Cl + Me_3SiO_2CR \qquad (1)$$

Treatment of a dark-red solution of complex **1** in MeCN with 3–4 equiv. of Me_3SiCl leads to a noticeable colour change to dark red–brown and the precipitation of some tan solid. The latter was removed by filtration, and the filtrate layered with hexanes. After several days, essentially black crystals of **2** had formed.† The structure‡ of the cation of **2** is shown in

---

† The layering also produces additional tan solid difficult to separate from the black crystals. IR bands and elemental analysis indicate $MnCl_2(bpy)$ to be the by-product, supporting disproportionation to have occurred.

‡ *Crystal data* for **2**: $C_{62}H_{83}N_{14}O_{42}Cl_4Mn_{11}$, $M = 2442.59$, monoclinic, $P2_1/m$, $a = 10.372(7)$, $b = 35.033(31)$, $c = 12.991(10)$ Å, $\beta = 104.73(4)$, $U = 4565.06$ Å^3, $Z = 2$, $D_c = 1.783$ g cm^{-3}, $\lambda = 0.71069$ Å, $T = -150$ °C, $6° \leq 2\theta \leq 45°$, $R(R_w) = 9.19(9.33)\%$ for 3299 unique reflections with $F > 2.33\sigma(F)$. Complex **2** loses solvent *extremely* rapidly and numerous attempts were made before a crystal was mounted and found to diffract. The structure was solved by MULTAN and Fourier techniques, and refined by full-matrix least-squares analysis. All non-hydrogen atoms of the anion and cation were readily located and refined with anisotropic thermal parameters, except for the solvent molecules and the acetate on the mirror plane; the latter were refined isotropically. The solvent molecules (both bound and free) also had fractional occupancies, with values in the 0.3–0.6 range. A final difference Fourier was satisfactorily featureless, the largest peaks being 1.5 e Å^{-3} near the disordered groups in the mirror plane.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

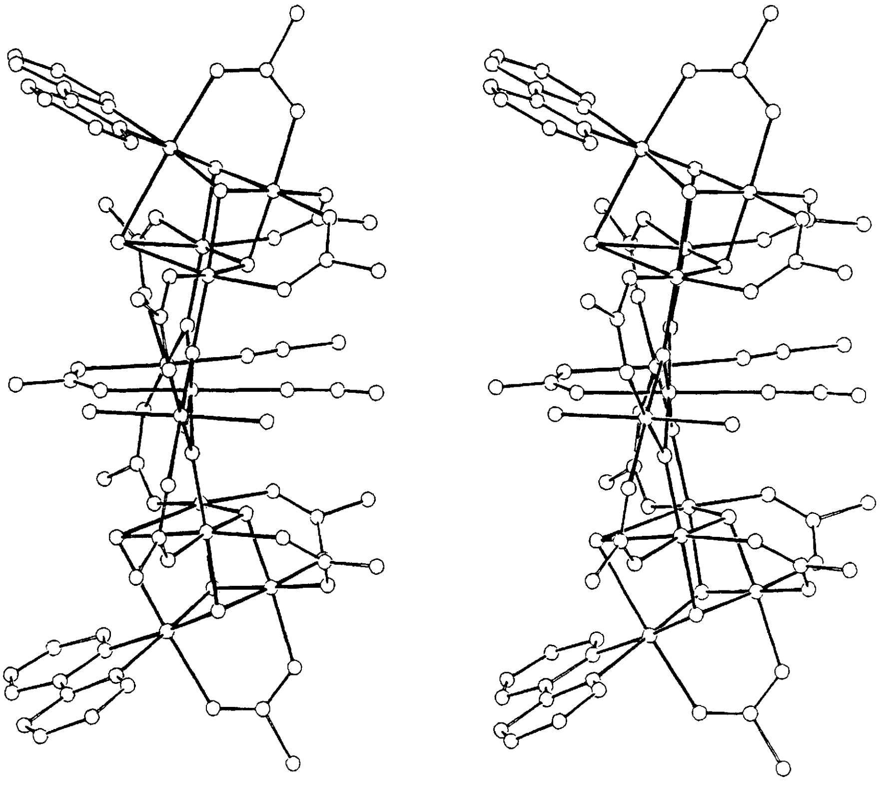

Fig. 2 A stereoview of the anion of **2**, from a viewpoint that emphasizes the non-planarity of the central Mn_3O_4 unit

Fig. 1 and a stereoview from a different viewpoint is provided in Fig. 2. The cation lies on a mirror plane bisecting the molecule and contains two $[Mn_4O_3Cl]^{6+}$ cubane-like units [Mn(1) to Mn(4)] that are similar to (although more distorted than) that in the discrete cubane complex **3** that has imposed C_3 symmetry;[4] the cubane units in **2** are similarly mixed-valence ($3Mn^{III}$, Mn^{IV}), and Mn(4) is assigned as the Mn^{IV} centre on the basis of metric parameters and the absence of a Jahn–Teller (JT) elongation expected for high-spin Mn^{III} and observed for Mn(1), Mn(2) and Mn(3). As for **3**, each $Mn^{III}Mn^{IV}$ pair is bridged by an AcO^- group, and three Mn^{III} ions are bridged by μ_3-Cl^- ion Cl(8) with long Mn–Cl bonds, 2.534(7)–2.688(7) Å; in C_3 complex **3**, the Cl^- bridges symmetrically [2.672(2) Å]. The two remaining terminal coordination sites on Mn(2) are occupied by a bpy group; the remaining two sites each on Mn(1) and Mn(3) are occupied by bridging groups to the central Mn_3 unit (*vide infra*). The asymmetry of the Mn_4O_3Cl core relative to that in **3** is emphasized by the Mn···Mn separations. The three Mn^{III}···Mn^{III} distances are in the range 3.173(5)–3.239(5) Å and are slightly shorter than in **3** [3.272(2) Å]; similarly the Mn^{III}···Mn^{IV} distances are in the range 2.737(5)–2.825(5), compared to 2.815(2) Å in **3**.

The two $[Mn_4O_3Cl]^{6+}$ cubanes are held together by the central Mn_3O_4 unit *via* linkages to O(12) and O(13) and two acetate groups [O(34), O(36), O(38), O(40)]. Oxygen (oxide) atoms O(12) and O(13) are thus triply bridging and only slightly out of their respective Mn_3 planes.§. Atoms Mn(5), Mn(6) and Mn(7) are not linear but slightly V-shaped with an angle of 162.91°. Metric parameters indicate Mn(5), Mn(6) and Mn(7) to be Mn^{III} centres with axially-elongated (JT) sites lying in the mirror plane. The Mn(5)···Mn(6) and Mn(6)···Mn(7) distances are 2.864(5) and 2.873(5) Å, respectively. Unlike the $[Mn_4O_3Cl]$ cubane units defined by Mn atoms Mn(1)–Mn(4), which have been found in discrete form in **3**, the central near-linear $[Mn_3O_4]^+$ unit has not been seen to date in a discrete trinuclear complex. The six axial sites are occupied by one AcO^-, two MeCN and two H_2O groups. Severe disorder and/or partial occupancy problems were encountered with these groups, the latter undoubtedly due to the observed solvent loss problems.¶ The molecule as shown in Fig. 1 represents the optimum model that was obtained.

Complex **2** joins a relatively small family of discrete aggregates of nuclearity eleven. The majority of known undecanuclear species are clusters with CO or phosphine ligands.[8] The nearest analogue to **2** is $Fe_{11}O_6(OH)_6(O_2CPh)_{15}$ which, however, has a structurally completely different Fe–O(OH) core.[9] As part of our search for molecules with large spin ground states, it will be of some interest to characterize the electronic structure and spin ground state of **2**, given that the discrete cubane complex **3** has already been

---

§ O(12) and O(13) are 0.022 and 0.046 Å, respectively, out of their Mn_3 planes.

¶ Difference Fourier maps at the latter stages of refinement showed the axial groups as depicted in Fig. 1 to be the majority peaks: the MeCN with N(51) was well behaved with 100% occupancy: the MeCN with N(54) had *ca.* 50% occupancy for all three atoms; the water with O(57) had *ca.* 30% occupancy; the water with O(50) had 100% occupancy; acetate oxygen atoms O(46) and O(48) had 100% occupancy but the acetate carbon atoms had *ca.* 50% occupancy. A difference Fourier phased on the cation as in Fig. 1 showed residual density in the space between O(48) and O(50). This suggested that the AcO^- group is disordered between bridging Mn(5)–Mn(6) and bridging Mn(6)–Mn(7); in the latter case, O(47) would be a H_2O group. A model including two carbon atoms between O(48) and O(50) did not refine well, however, and these carbon atoms were therefore removed in the final cycles. Many other attempts to model the disorder were also made but with little success. After the structure was completed, numerous attempts to find a better crystal were made, but to no avail.

shown to possess a rare $S = 9/2$ ground state. The presence of two such cubane units (albeit more distorted) in **2**, together with the presence of additional Mn^{III} sites, makes magnetochemical characterization of **2** an important future objective, but a challenging one, given the relatively low symmetry and large number of inequivalent Mn centres. Although, needless to say, the formation of **2** was totally unpredictable, and its mechanism of formation unclear and difficult to ascertain, the present result emphasizes the continuing utility of Me_3SiCl as a means to new and unusual Mn_x species and the novelty of structural types in this area. Further work with this reagent is in progress.

We thank Sheyi Wang for assistance with figure preparation. This work was supported by the NIH.

Received, 16th July 1991; Com. 1/03624F

References

1 G. Christou, *Acc. Chem. Res.*, 1989, **22**, 328.
2 K. Wieghardt, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1153.
3 P. D. W. Boyd, Q. Li, J. B. Vincent, K. Folting, H.-R. Chang, W. E. Streib, J. C. Huffman, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1988, **110**, 8537.
4 Q. Li, J. B. Vincent, E. Libby, H.-R. Chang, J. C. Huffman, P. D. W. Boyd, G. Christou and D. N. Hendrickson, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1731.
5 R. E. McCarley, T. R. Ryan and C. C. Torardi, *ACS Symp. Ser.*, 1981, **155**, 41; M. L. H. Green, G. Parkin, J. Bashkin, J. Fail and K. Prout, *J. Chem. Soc., Dalton Trans.*, 1982, 2519.
6 J. S. Bashkin, A. R. Schake, J. B. Vincent, H.-R. Chang, Q. Li, J. C. Huffman, G. Christou and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, 1988, 700.
7 J. S. Bashkin, W. E. Streib, J. C. Huffman, H.-R. Chang, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1987, **109**, 6502; E. Libby, R. J. Webb, W. E. Streib, K. Folting, J. C. Huffman, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1989, **28**, 4037; S. P. Perlepes, A. G. Blackman, J. C. Huffman and G. Christou, *Inorg. Chem.*, 1991, **30**, 1665.
8 D. M. P. Mingos and A. S. May, *The Chemistry of Metal Cluster Complexes*, eds. D. F. Shriver, H. D. Kaesz and R. D. Adams, Verlag Chemie, Weinheim, 1990, 11.
9 S. M. Gorun, G. C. Papaefthymiou, R. B. Frankel and S. J. Lippard, *J. Am. Chem. Soc.*, 1987, **109**, 3337.