

## Preparation and Characterization of $[\text{Mn}_{11}\text{O}_{10}\text{Cl}_2(\text{OAc})_{11}(\text{bpy})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 8\text{MeCN}$ , a Mixed-valence Manganese(III/IV) Aggregate with Rare Undecanuclearity (bpy = 2,2'-bipyridyl)

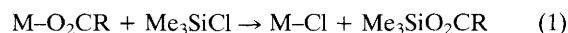
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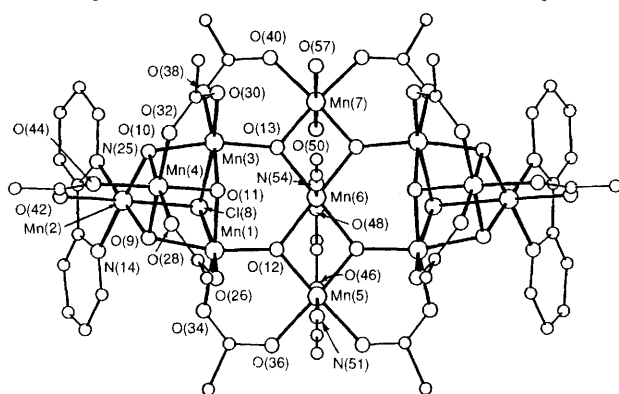
Treatment of  $[\text{Mn}_4\text{O}_2(\text{OAc})_7(\text{bpy})_2](\text{ClO}_4) \cdot 3\text{H}_2\text{O}$  (bpy = 2,2'-bipyridyl) **1** with  $\text{Me}_3\text{SiCl}$  in MeCN leads to a disproportionation and nuclearity change to give  $[\text{Mn}_{11}\text{O}_{10}\text{Cl}_2(\text{OAc})_{11}(\text{bpy})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 8\text{MeCN}$  **2**; the crystal structure shows the core of this aggregate to comprise two  $[\text{Mn}_4\text{O}_3\text{Cl}]^{6+}$  cubane units 'bridged' by a nearly linear  $[\text{Mn}_3\text{O}_4]^+$  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.<sup>1</sup> These studies have been stimulated by a variety of reasons, including Mn-containing biological systems<sup>2</sup> and the desire to prepare molecular species with large spin ground states.<sup>3</sup> 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.<sup>3,4</sup> 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  $\text{Me}_3\text{SiCl}$ <sup>5</sup> from preformed  $\text{Mn/O/RCO}_2^-$  species.<sup>4,6,7</sup> We have described, for example, the

conversion with  $\text{Me}_3\text{SiCl}$  of  $[\text{Mn}_3\text{O}(\text{OAc})_6(\text{py})_3](\text{ClO}_4)$  (py = pyridine) to  $\text{Mn}_4\text{O}_3\text{Cl}_4(\text{OAc})_3(\text{py})_3$  **3**;<sup>4</sup> this involves a transformation of the  $\text{Mn}_3^{\text{III}}\text{O}$  planar unit to the  $\text{Mn}_3^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_3\text{Cl}$  cubane core *via* an undoubtedly complex mechanism involving disproportionation and nuclearity changes. We herein report that the reaction of  $[\text{Mn}_4\text{O}_2(\text{OAc})_7(\text{bpy})_2](\text{ClO}_4) \cdot 3\text{H}_2\text{O}$  **1** with  $\text{Me}_3\text{SiCl}$  leads to a most remarkable high-nuclearity product,  $[\text{Mn}_{11}\text{O}_{10}\text{Cl}_2(\text{OAc})_{11}(\text{bpy})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 8\text{MeCN}$  **2** with a quite unprecedented structure.



Treatment of a dark-red solution of complex **1** in MeCN with 3–4 equiv. of  $\text{Me}_3\text{SiCl}$  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.<sup>†</sup> The structure<sup>‡</sup> of the cation of **2** is shown in



**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, 117.39(17)–76.62(19).

<sup>†</sup> The layering also produces additional tan solid difficult to separate from the black crystals. IR bands and elemental analysis indicate  $\text{MnCl}_2(\text{bpy})$  to be the by-product, supporting disproportionation to have occurred.

<sup>‡</sup> *Crystal data* for **2**:  $\text{C}_{62}\text{H}_{83}\text{N}_{14}\text{O}_{42}\text{Cl}_4\text{Mn}_{11}$ ,  $M = 2442.59$ , 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<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.783$  g cm<sup>-3</sup>,  $\lambda = 0.71069$  Å,  $T = -150$  °C,  $6^\circ \leq 2\theta \leq 45^\circ$ ,  $R(R_w) = 9.19(9.33)\%$  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  $1.5 \text{ e} \text{ \AA}^{-3}$  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.

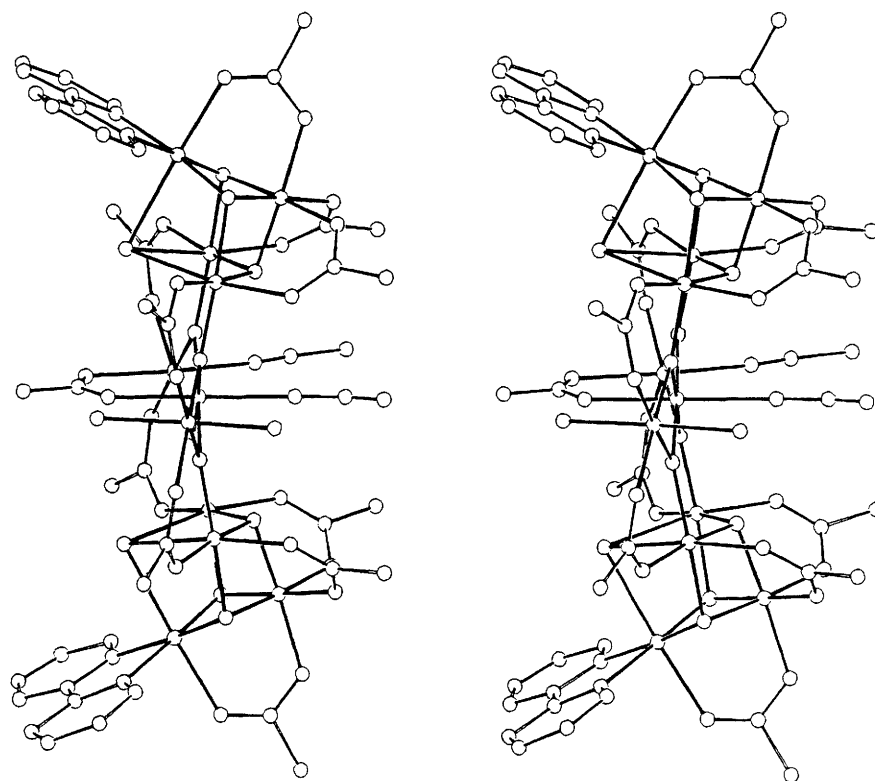


Fig. 2 A stereoview of the anion of **2**, from a viewpoint that emphasizes the non-planarity of the central  $\text{Mn}_3\text{O}_4$  unit

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  $[\text{Mn}_4\text{O}_3\text{Cl}]^{6+}$  cubane-like units  $[\text{Mn}(1)$  to  $\text{Mn}(4)]$  that are similar to (although more distorted than) that in the discrete cubane complex **3** that has imposed  $C_3$  symmetry;<sup>4</sup> the cubane units in **2** are similarly mixed-valence ( $3\text{Mn}^{\text{III}}$ ,  $\text{Mn}^{\text{IV}}$ ), and  $\text{Mn}(4)$  is assigned as the  $\text{Mn}^{\text{IV}}$  centre on the basis of metric parameters and the absence of a Jahn–Teller (JT) elongation expected for high-spin  $\text{Mn}^{\text{III}}$  and observed for  $\text{Mn}(1)$ ,  $\text{Mn}(2)$  and  $\text{Mn}(3)$ . As for **3**, each  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$  pair is bridged by an  $\text{AcO}^-$  group, and three  $\text{Mn}^{\text{III}}$  ions are bridged by  $\mu_3\text{-Cl}^-$  ion  $\text{Cl}(8)$  with long Mn–Cl bonds, 2.534(7)–2.688(7) Å; in  $C_3$  complex **3**, the  $\text{Cl}^-$  bridges symmetrically [2.672(2) Å]. The two remaining terminal coordination sites on  $\text{Mn}(2)$  are occupied by a bpy group; the remaining two sites each on  $\text{Mn}(1)$  and  $\text{Mn}(3)$  are occupied by bridging groups to the central  $\text{Mn}_3$  unit (*vide infra*). The asymmetry of the  $\text{Mn}_4\text{O}_3\text{Cl}$  core relative to that in **3** is emphasized by the  $\text{Mn}\cdots\text{Mn}$  separations. The three  $\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{III}}$  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  $\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{IV}}$  distances are in the range 2.737(5)–2.825(5), compared to 2.815(2) Å in **3**.

The two  $[\text{Mn}_4\text{O}_3\text{Cl}]^{6+}$  cubanes are held together by the central  $\text{Mn}_3\text{O}_4$  unit *via* linkages to  $\text{O}(12)$  and  $\text{O}(13)$  and two acetate groups [ $\text{O}(34)$ ,  $\text{O}(36)$ ,  $\text{O}(38)$ ,  $\text{O}(40)$ ]. Oxygen (oxide) atoms  $\text{O}(12)$  and  $\text{O}(13)$  are thus triply bridging and only slightly out of their respective  $\text{Mn}_3$  planes.<sup>§</sup> Atoms  $\text{Mn}(5)$ ,  $\text{Mn}(6)$  and  $\text{Mn}(7)$  are not linear but slightly V-shaped with an angle of  $162.91^\circ$ . Metric parameters indicate  $\text{Mn}(5)$ ,  $\text{Mn}(6)$  and  $\text{Mn}(7)$  to be  $\text{Mn}^{\text{III}}$  centres with axially-elongated (JT) sites lying in the mirror plane. The  $\text{Mn}(5)\cdots\text{Mn}(6)$  and

$\text{Mn}(6)\cdots\text{Mn}(7)$  distances are 2.864(5) and 2.873(5) Å, respectively. Unlike the  $[\text{Mn}_4\text{O}_3\text{Cl}]$  cubane units defined by Mn atoms  $\text{Mn}(1)$ – $\text{Mn}(4)$ , which have been found in discrete form in **3**, the central near-linear  $[\text{Mn}_3\text{O}_4]^+$  unit has not been seen to date in a discrete trinuclear complex. The six axial sites are occupied by one  $\text{AcO}^-$ , two MeCN and two  $\text{H}_2\text{O}$  groups. Severe disorder and/or partial occupancy problems were encountered with these groups, the latter undoubtedly due to the observed solvent loss problems.<sup>¶</sup> 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.<sup>8</sup> The nearest analogue to **2** is  $\text{Fe}_{11}\text{O}_6(\text{OH})_6(\text{O}_2\text{CPh})_{15}$  which, however, has a structurally completely different  $\text{Fe}-\text{O}(\text{OH})$  core.<sup>9</sup> 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

<sup>¶</sup> 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  $\text{AcO}^-$  group is disordered between bridging  $\text{Mn}(5)$ – $\text{Mn}(6)$  and bridging  $\text{Mn}(6)$ – $\text{Mn}(7)$ ; in the latter case, O(47) would be a  $\text{H}_2\text{O}$  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.

<sup>§</sup>  $\text{O}(12)$  and  $\text{O}(13)$  are 0.022 and 0.046 Å, respectively, out of their  $\text{Mn}_3$  planes.

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.

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