Preparation, Crystal Structure, Magnetic Properties, and Chemical Reactions of a Hexanuclear Mixed Valence Manganese Carboxylate

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The antiferromagnetic mixed valence manganese complex [$Mn_6O_2(Me_3CCO_2H)_4(Me_3CCO_2)_{10}$] has been prepared by the reaction of $MnCO_3$ with pivalic acid in toluene, and its molecular structure, determined by X-ray methods, comprises the new polynuclear cluster grouping of two tetrahedral oxygen-centred tetramanganese clusters sharing an edge; further cluster complexes have been prepared by reaction of this complex with donor molecules.

Previous work by ourselves[1] and others[2] has shown that mixed valence acetate complexes of manganese can readily be prepared. In order to extend the range of carboxylates studied in this area we refluxed fresh manganese(II) carbonate (0.1 mol) with pivalic acid (0.2 mol) in toluene (100 cm³) for 48 h. A red-brown precipitate of a mixed valence complex with apparent formula [$Mn_3O(Me_3CCO_2H)_2(Me_3CCO_2)_5$] is deposited, which can be recrystallised from toluene. Satisfactory C, H, Mn analyses have been obtained.

The above formulation is not easily reconciled with the trinuclear [$M_3L_3O(RCO_2)_6$] structure often found for carboxylates,[3] including those of manganese,[1] and a single crystal X-ray diffraction study was carried out to clarify the situation.†

The structure of the molecule is shown in Figure 1. It has a hexamanganese cluster structure [$Mn_6O_2(Me_3CCO_2)_{10}$-($Me_3CCO_2H)_4$] which is not derived from the familiar trinuclear structure but from the [$M_4O(RCO_2)_6$] structures already known for Be,[4] Zn,[5] and Co[6] carboxylates. The structure is best visualised as two Mn_4O tetrahedra sharing an edge. Pivalate ions bridge pairs of manganese atoms along each edge except that which is shared; two pivalates bridge edges connecting outer Mn atoms, four bridge edges connecting outer and inner Mn atoms in a normal bridging mode, whilst a further four pivalates bridge outer/inner Mn atoms in the normal way and further form monatomic bridges to Mn atoms on the other tetrahedron. The two centred oxygens are closer to the Mn atoms forming the shared edge [Mn–O = 1.89—1.91(3) Å] than to the outer Mn atoms [Mn–O = 2.10—2.19(3) Å], but there is no consistent trend in the Mn–O distances to the carboxylate oxygens with values between 1.90(3) and 2.39(3) Å. Finally a monodentate pivalic acid molecule co-ordinates each of the four outer manganese atoms. Thus there are no monodentate pivalate ligands and this agrees with the i.r. spectrum, which shows the $v(CO_2)$ antisymmetric frequency at 1585 and 1565 cm⁻¹ for the two types of bridging pivalate, and at 1690 cm⁻¹ for co-ordinated pivalic acid.

The complex shows antiferromagnetism, with a magnetic moment (per Mn atom) of 4.81 μ_B at 296 K and a Weiss constant of 34 K. The average oxidation state of the manganese atoms is $2^{1}/_{3}$, and it is attractive to consider the two
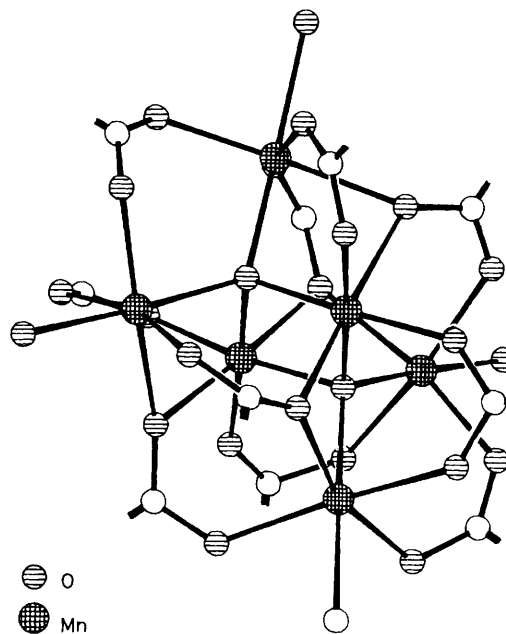
Figure 1. The central core of the hexanuclear cluster [Mn_6O_2-($Me_3CCO_2)_{10}(Me_3CCO_2H)_4$]. For the bridging carboxylates only the carboxylate function O–C–O is shown; for the terminal, monodentate carboxylates only the bonded oxygen is shown.

inner metal atoms as six-co-ordinate manganese(III) and the four outer ones as six-co-ordinate manganese(II).

The four monodentate pivalic acid molecules can be replaced by four pyridine (py) ligands to give [$Mn_6O_2(py)_4$-($Me_3CCO_2)_{10}$], but reaction with N,N-dimethylformamide (dmf) gives the tetranuclear manganese(II) cluster [$Mn_4O(dmf)_2(Me_3CCO_2H)_2(Me_3CCO_2)_6$], which we presume has the [$M_4O(RCO_2)_6$] structure with a pivalic acid or dimethylformamide ligand on each manganese atom.

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