Preparation, Crystal Structure, and Magnetic Properties of a Trinuclear Mixed-valence Manganese Carboxylate

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Summary The reaction of $[Mn(H_2O)_2(O_2CMe)_3]$ with pyridine (py) produces the antiferromagnetic trinuclear complex $[Mn_3(py)_3O(O_2CMe)_6]$, whose molecular structure, determined by *X*-ray methods, shows all three manganese atoms to be equivalent, with an average oxidation state of $2\frac{2}{3}$.

Recent electrochemical and reactivity studies[1] of trinuclear carboxylates and discussions of the role of changes in the oxidation state of manganese in biochemical electron-transfer processes[2] indicate the need for structural and physical investigations of polynuclear manganese carboxylates. We have found that the reaction of $[Mn(H_2O)_2(O_2CMe)_3]$ with pyridine (py), previously reported[3] to give $[Mn_4(py)_5O_2(O_2CMe)_8]$, gives the uncharged trinuclear complex $[Mn_3(py)_3O(O_2CMe)_6]$, for which satisfactory C, H, and N analyses have been obtained. This reduction to an average oxidation state of $2\frac{2}{3}$ contrasts with the oxidation to Mn($3\frac{1}{2}$) found when methanolic $[Mn_3(MeCO_2H)O(O_2CMe)_7]$ reacts with 2,2′-bipyridyl or 1,10-phenanthroline.[4]

The complex exhibits the expected weak antiferromagnetism, with the magnetic moment per Mn atom falling from 3·98 B.M. at 293 K to 3·21 B.M. at 90 K, although the maximum in the susceptibility commonly found in binuclear carboxylates[5] cannot be detected in the liquid nitrogen temperature range. The detailed interpretation of the magnetism will be reported elsewhere, but the reduction of the magnetic moment from the spin-only values of the Mn^{2+} and Mn^{3+} ions shows that this complex can be classified as a class III-A mixed-valence compound[6] in which the ions of formally different oxidation state interact strongly, in contrast to the separate roles of the Mn^{2+} and Mn^{3+} ions in the polymeric $[Mn^{II}(H_2O)_2\{Mn_3{}^{III}O(O_2CH)_9\}]^{2-}$ anion.[7]

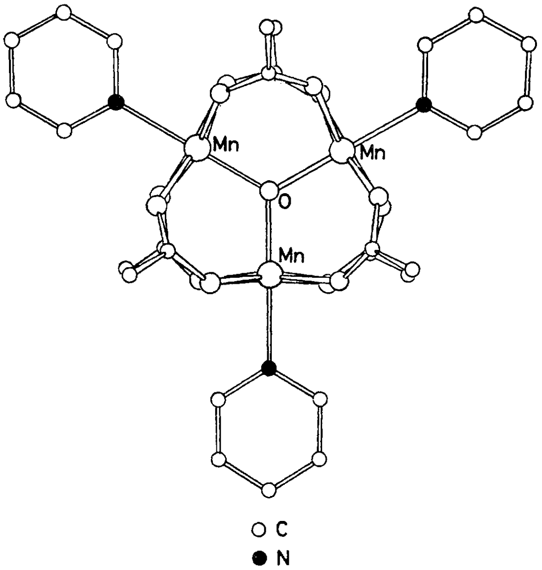

FIGURE. The molecule $[Mn_3(py)_3O(O_2CMe)_6]$.

Crystal Data: $C_{27}H_{33}Mn_3N_3O_{13}$, M = '772·37'. Rhombohedral, a = 10·794(4) Å, α = 108·94(5)° (hexagonal setting $a = b$ = 17·575, c = 11·077 Å), space group $R32$ (on the basis of successful analysis); D_c = 1·30 and Z = 3 (for no solvate), D_m = 1·48 g cm^{-3} (solvated crystals, corresponding to about 1·4 mol solvent py per mol complex); Mo-K_α radiation, λ = 0·71069 Å, μ = 9·44. Intensity data were collected using a Nonius CAD4 diffractometer and an $\omega/2\theta$ scan for a crystal sealed in a Lindemann capillary. Of the 715 data recorded, 500 obeyed the criterion $I > 1{\cdot}5\sigma(I)$ and were used for the structure solution (heavy-atom method) and refinement (full-matrix least-squares). R is currently 0·043. The structure refinement has been complicated by the presence of disordered solvent molecules and irregularities in the temperature-factor coefficients in some of the atoms of the co-ordinated pyridine molecule. These problems do not disappear when alternative space groups ($R3$, $R3m$) are tried, and both difficulties may be related to the fact that the crystals readily lose pyridine on standing. Nevertheless, with the low R value and sensible molecular geometry parameters obtained, we are convinced that the crystal structure is properly described by the space group $R32$.†

This requires that the molecule be assigned 32 (D_3) point symmetry, with three equivalent manganese atoms, each thus being assigned a formal oxidation state of $2\frac{2}{3}$. The Mn–Mn distance of 3·363(1) Å and Mn–O (central) distance of 1·941(1) Å are both a little longer than values for trinuclear Mn^{III} complexes[7,8] of the type $[M_3L_3O(O_2CR)_6]^{x+}$, and this is consistent with the small drop in average metal oxidation state. The Mn–O(carboxy) distances of 2·068(3) and 2·129(3) Å fall within the range found for Mn^{II}–O and Mn^{III}–O distances.

The Mn–N distance of 2·125 Å implies fairly strong co-ordination of the bonded pyridine and it is therefore probable that the pyridine loss involves only the solvating molecules. The slight disorder effects found for the bonded pyridines could be due to the grossly disordered situation for the solvating molecules, since the latter occupy channels bounded by the former.

We have also found that the iron compound, $[Fe_3(py)_3O(O_2CMe)_6]$ is isostructural with this manganese analogue.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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