Discrete Oxidation States and *X*-Ray Crystal Structure of the Trinuclear Manganese Carboxylate $[Mn_3(3\text{-}ClC_5H_4N)_3O(O_2CMe)_6]$

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Summary The antiferromagnetic $Mn^{II,III,III}$ complex $[Mn_3(3\text{-}Clpy)_3O(O_2CMe)_6]$, prepared by the reaction of 3-chloropyridine with $[Mn(H_2O)_2(O_2CMe)_3]$, possesses a molecular structure, determined by *X*-ray methods, in which a manganese(II) atom can be clearly distinguished from two manganese(III) atoms.

IN earlier work on polynuclear manganese carboxylates we reported[1] the preparation, magnetic properties, and crystal structure of $[Mn_3(py)_3O(O_2CMe)_6]$, (py = pyridine) in which the three manganese atoms were equivalent and had the mixed oxidation state $2^2/_3$. We have now found that black crystals of $[Mn_3(3\text{-}Clpy)_3O(O_2CMe)_6]$ (**1**) are deposited when a heated solution of $[Mn(H_2O)_2(O_2CMe)_3]$ in 3-chloropyridine is allowed to cool. Satisfactory C, H, N, Cl, and Mn analyses have been obtained.

Like the pyridine analogue, the new complex is antiferromagnetic; the magnetic moment per Mn atom is $4{\cdot}59\,\mu_B$ at 292 K and $3{\cdot}36\,\mu_B$ at 78 K. (A detailed analysis of the magnetism will be presented elsewhere.) The compound thus appears to be less antiferromagnetic than the pyridine complex, suggesting a difference in molecular structure. A single crystal *X*-ray diffraction study was therefore made to clarify this situation.

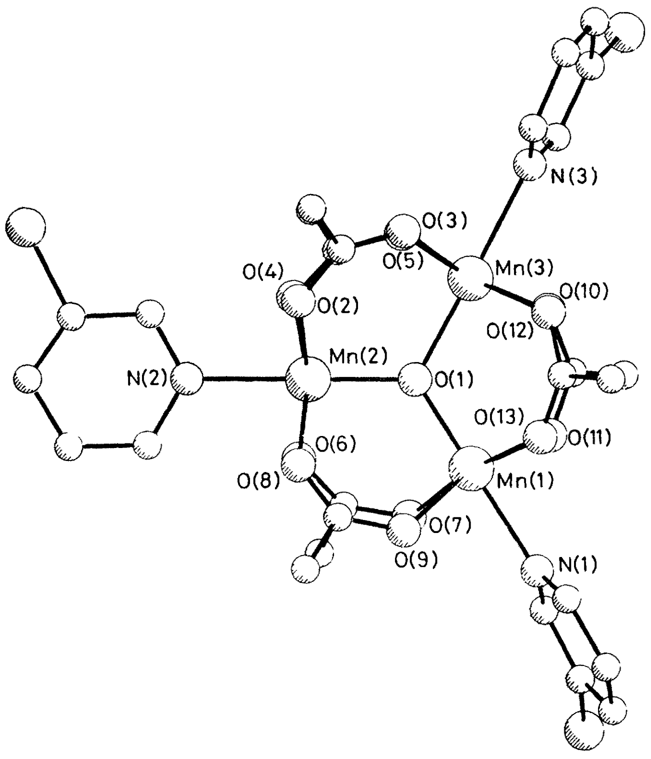

FIGURE. The molecular structure of $[Mn_3(3\text{-}Clpy)_3O(O_2CMe)_6]$(**1**). Important bond lengths (Å) are: Mn(1)–O(1) 1·863(4); Mn(2)–O(1) 1·864(4); Mn(3)–O(1) 2·034(4); Mn(1)–O(7) 2·065(8); Mn(1)–O(9) 2·101(8); Mn(1)–O(11) 2·072(5); Mn(1)–O(13) 2·037(8); Mn(2)–O(6) 2·091(7); Mn(2)–O(8) 2·065(8); Mn(2)–O(2) 2·062(5); Mn(2)–O(4) 2·083(5); Mn(3)–O(3) 2·098(5); Mn(3)–O(5) 2·129(5); Mn(3)–O(10) 2·090(5); Mn(3)–O(12) 2·140(5); Mn(1)–N(1) 2·151(7); Mn(2)–N(2) 2·135(5); Mn(3)–N(3) 2·280(7).

Crystal data: $C_{27}H_{30}N_3O_{13}Cl_3Mn_3$, F.wt. 875·7, monoclinic, a = 23·598(3), b = 8·477(1), c = 20·998(3), β = 97·46(2)°, space group $P2_1/a$, D_m = 1·42, Z = 4, D_c = 1·40 g cm^{-3}; Mo-K_α radiation (λ = 0·71069 Å), μ = 10·75 cm^{-1}. The structure was solved (by direct methods) and refined (full matrix least-squares) using 5237 observed $[I > 1{\cdot}5\sigma(I)]$ intensities out of a total 7295 measured, to a current R value of 0·06.†

The structure of (**1**) is shown in the Figure, along with some of the most important bond lengths. It is similar to that of the parent pyridine compound but with one highly significant difference. The Mn_3 triangle is isosceles and clearly indicates that one of the manganese atoms [Mn(3)] is different from the other two. This is most logically interpreted in terms of identifying [Mn(3)] as having oxidation state +2 and Mn(1), Mn(2) as +3. The Mn–O distances conform to this idea with Mn(1,2)–O invariably shorter than Mn(3)–O.

The occurrence in the crystal of this identifiable (+2, +3, +3) structure probably arises as a result of using the unsymmetrical chloropyridine ligand, and whilst one is tempted to explain the averaged structure of the pyridine complex in terms of crystallographic disorder, this would not explain the differences in magnetic properties of the compound.

It is usually impossible to distinguish crystallographically separate oxidation states in polynuclear carboxylate clusters,[2] but in $[Co_4(OMe)_4(O_2CMe)_2(acac)_4]$ (Hacac = acetylacetone) the cobalt(II) atoms show Co–O distances not less than 1·99 Å and the cobalt(III) atoms show Co–O distances not greater than 1·94 Å, giving a clear distinction between oxidation states.[3] $[Mn_3L_3O(O_2CMe)_6]$ is the only carboxylate cluster in which some complexes have averaged and others have discrete oxidation states.

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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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[3] J. A. Bertrand and T. C. Hightower, *Inorg. Chem.*, 1973, **12**, 206.