Synthesis and Characterization of the Binuclear Mixed Valence Complex Di-μ-oxobis[tris(2-methylpyridyl)amine]dimanganese(III,IV) Dithionate Heptahydrate, $[(tpa)MnO]_2(S_2O_6)_{3/2}\cdot 7H_2O$

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A role for binuclear manganese complexes in biological oxidations has been suggested [1], but very few examples of binuclear manganese complexes in high oxidation states have been reported. Notable exceptions to this statement, of course, are the 2,2′-bipyridine (bpy) complex $[(bpy)_2MnO]_2^{3+}$ and its 1,10-phenanthroline (phen) analogue. These complexes have been isolated as stable solids in the Mn(III)/Mn(IV) state and have been studied in solution in the fully oxidized Mn(IV)/Mn(IV) state [2]; the phen complex has also been isolated as a solid in the IV/IV form [3], and this fully oxidized species has recently been structurally characterized [4]. Recent work has also shown that these systems can act as powerful oxidants, electrochemically oxidizing benzyl alcohols and ethers [5] and (in the presence of chemical oxidants such as Ce(IV)) oxidizing water [6]. McAuliffe and coworkers have also demonstrated the photooxidation of coordinated water in a complex which they formulate as a binuclear manganese species [7].

In view of this apparent utility, it is surprising that related systems have not been synthesized. Very recently, we reported the synthesis and characterization of a new complex of this general type in which the two bidentate bpy (or phen) groups are replaced by a single tetradentate *N*,*N*′-bis(2-methylpyridyl)-1,2-ethanediamine (bispicen) ligand [8]; we here report the synthesis and properties of a related species in which each manganese center is bonded to a tetradentate tris(2-methylpyridyl)amine (tpa) ligand, the resulting complex being the $[(tpa)MnO]_2^{3+}$ ion.

Experimental

The tpa ligand was synthesized by a minor modification of the method of Anderegg and Wenk [9]. To a suspension of 1.5 g (5.2 mmol) tpa in approximately 20 ml H_2O was added 0.87 g (5.2 mmol) $MnSO_4\cdot H_2O$; the resulting mixture was stirred for a few minutes, until all of the material had dissolved to produce a pale pink solution. Hydrogen peroxide (30%) was added until the solution turned very dark green. Sodium dithionate (12.6 g) was added with stirring. Excess sodium dithionate which crystallized was removed by filtration, and then the deep green crystals which separated were filtered and recrystallized from water. The crystals analysed well for the heptahydrate of the dithionate salt of the complex.

Crystal data: Dark green prisms of $[(tpa)MnO]_2(S_2O_6)_{3/2}\cdot 7H_2O$ crystallize in the monoclinic space group $P2_1/n$ with four binuclear species in a cell of dimensions $a = 12.812(5)$, $b = 19.733(8)$, $c = 18.691(5)$ Å, and $\beta = 92.69(3)°$. The data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation, and the structure was solved by direct methods. At the present stage of refinement, the values of the conventional agreement factors R_1 and R_2 are 0.070 and 0.078. The structure refinement is presently hindered by apparent disorder of one of the anions, but the essential structural features of the binuclear cation are very clear.

Results and Discussion

The geometry of the binuclear cation $[(tpa)MnO]_2^{3+}$ is depicted in Fig. 1. The geometry at each Mn

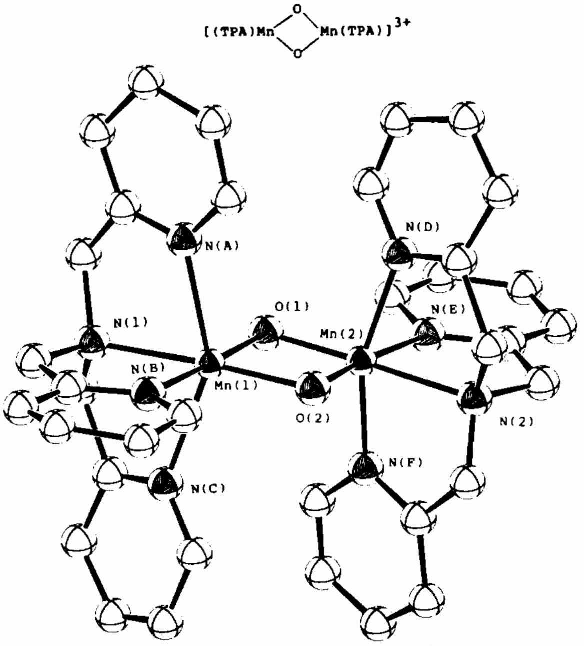

Fig. 1. View of the binuclear $[(tpa)MnO]_2^{3+}$ cation in the complex. Carbon atoms are shown as unshaded atoms.

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center is roughly octahedral, the coordination spheres consisting of the four nitrogen atoms from a single tpa ligand and the two *cis* bridging oxo ligands. The Mn(1)–Mn(2) separation of 2.643(1) Å is considerably shorter than the values of 2.716 and 2.700(1) Å in the bpy [2b] and phen [4] complexes, and slightly shorter than that of 2.659(2) Å in the bispicen analogue [8]. The geometries at the two metal centers are strikingly different, the bond lengths suggesting that the complex is best described as a fully localized Mn(III)/Mn(IV) system. Thus, the bond lengths at Mn(2) are all shorter than the chemically equivalent bonds at Mn(1). The Mn(2)–O(1) and Mn(2)–O(2) distances of 1.782(3) and 1.771(3) Å [average, 1.776(8) Å] are approximately 0.06 Å shorter than the corresponding values of 1.835(3) and 1.839(3) Å at Mn(1), and the equatorial Mn(2)–N(2) and Mn(2)–N(E) distances of 2.080(4) and 2.026(4) Å are shorter than the corresponding Mn(1)–N(1) and Mn(1)–N(B) values of 2.114(4) and 2.044(4) Å. Similarly, the axial Mn–N bonds at Mn(2) are shorter than those at Mn(1), but here the effect is much greater, the values of 2.014(4) and 2.012(4) Å at Mn(2) being approximately 0.22 Å smaller than the distances of 2.206(4) and 2.260(5) Å at Mn(1). Hence, the geometry at Mn(2) is roughly symmetric if we assume that the equatorial Mn(2)–N bonds are lengthened by approximately 0.04 Å due to the strong *trans* effect of the oxo ligands. At Mn(1), however, the geometry shows significant axial elongation suggestive of a Jahn–Teller distortion, the differences between corresponding bond lengths at Mn(1) and Mn(2) being very similar to those found in the bpy complex [2b]. Hence, the atom labelled Mn(2) is well described as a d^3 Mn(IV) center while atom Mn(1) is a Jahn–Teller distorted d^4 Mn(III) ion. In the bispicen complex which we reported earlier [8], the extent of localization was clearly less marked than in the present case, and in the phen complex the two sites are crystallographically equivalent as the result of a static or dynamic disorder [4].

A cyclic voltammogram of the complex in aqueous medium (pH = 6.86) shows a quasi-reversible oxidation wave at $E_{1/2}$ = 0.90 V *versus* SSCE which presumably represents the reversible oxidation of the III/IV dimer to the IV/IV form. This oxidation potential is apparently intermediate between the values of 1.32 and 0.81 V reported (in acetonitrile) for the bpy and bispicen complexes, respectively [8, 10]. Consequently, it appears that the present tpa complex is easier to oxidize to the IV/IV form than the bpy or phen complexes, but slightly harder than the bispicen complex. Reduction to the III/III form is observed (E_{peak} = 0.20 V), but in the present medium in the presence of dithionate ion this wave is not reversible; this value suggests that reduction to the III/III form occurs at higher potentials than in the bispicen, where $E_{1/2}$ is 0.10 V in acetonitrile and 0.14 V in water. This result is consistent with our observation that while the bispicen complex can be isolated as the iodide salt, the tpa complex apparently oxidizes iodide ion to iodine.

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