Synthesis and Characterization of the Binuclear Complex Di-μ-oxo-bis[*N,N′*-bis(2-methylpyridyl)ethane-1,2-diamine]dimanganese(III,IV) Perchlorate Trihydrate, $[(\text{bispicen})\text{MnO}]_2(\text{ClO}_4)_3.3\text{H}_2\text{O}$

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The title complex, a new binuclear di-μ-oxo complex of manganese-(III) and -(IV) with a single tetradentate ligand in place of the previously reported bidentate bpy or phen ligands, has been synthesised and characterised by *X*-ray crystallography and cyclic voltammetry.

The synthesis[1] and characterization[2] of the binuclear manganese complex ion $[(\text{bpy})_2\text{MnO}]_2{}^{3+}$ (bpy = 2,2′-bipyridine) and its 1,10-phenanthroline (phen) analogue have led to intense research activity, and two recent reports demonstrate that these systems can act as powerful oxidants in the IV/IV state. Gref *et al.*[3] have electrochemically oxidized benzyl alcohols and ethers in the presence of both the bpy and phen complexes, and Ramaraj *et al.*[4] have shown that the bpy complex oxidizes water in the presence of a chemical oxidant such as cerium(IV) ion. It is, therefore, surprising that no other di-μ-oxo complexes of manganese(III) or manganese(IV) have been reported to date. Here we report the synthesis and characterization of a new complex of this general type, in which the two bidentate bpy or phen ligands at each manganese centre are replaced by a single tetradentate *N,N′*-bis(2-pyridylmethyl)ethane-1,2-diamine (bispicen) ligand.

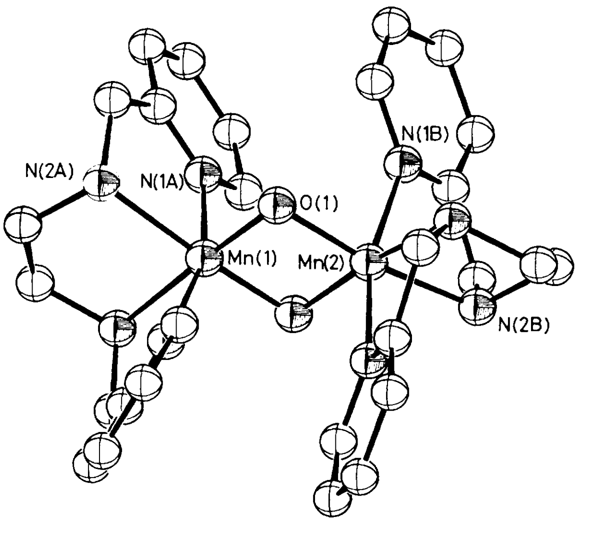

Figure 1. View of the binuclear cation $[(\text{bispicen})\text{MnO}]_2{}^{3+}$. Unlabelled atoms are related to labelled atoms by the C_2 axis passing through Mn(1) and Mn(2).

$\text{MnCl}_2{\cdot}4\text{H}_2\text{O}$ (200 mg) was added to a solution containing the tetrahydrochloride salt of the ligand, $(\text{bispicenH}_4)\text{Cl}_4{\cdot}2\text{H}_2\text{O}$ (2.6 ml, 0.38 M), and sodium carbonate (to pH = 8.5). A solution of hydrogen peroxide (30%) was very slowly added dropwise with stirring until the initial precipitate redissolved and the solution was dark olive-green in colour. After 1 h the solution was filtered and a solution of NaClO_4 (1 g in 1.5 ml) was added with stirring and ice cooling. The crystals which separated were filtered off and washed with ethanol; the crude product was recrystallized from boiling water (5 ml) to give 0.21 g of lustrous green-black crystals. The crystals analysed for 5 or 6 moles of water per mole of binuclear complex, but the subsequent crystallographic analysis† (*vide infra*) revealed the presence of only 3 moles of water in the crystallographic sample.

The complex cation lies on the crystallographic two-fold axis, which passes through the two crystallographically independent manganese centres and through the middle of the C–C bonds in the diaminoethane moieties of the ligands; one of the perchlorate groups [involving atom Cl(1)] is in a general position but with an occupancy factor of 0.5, while the other is

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† *Crystal data:* $\text{C}_{28}\text{H}_{36}\text{Cl}_3\text{N}_8\text{O}_{14}\text{Mn}_2{\cdot}3\text{H}_2\text{O}$, green-black prisms, M = 978.9, monoclinic, space group $C2/c$, a = 15.448(4), b = 12.271(2), c = 23.726(4) Å, β = 106.88(2)°, U = 4304(3) Å^3, Z = 4, D_c = 1.511 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 8.805 cm^{-1}, crystal dimensions 0.36 × 0.26 × 0.12 mm. Data were collected at 22 °C on an Enraf-Nonius CAD-4 diffractometer using Zr-filtered Mo-K_α radiation. 3491 unique data were collected, of which 1701 with $I > 3\sigma(I)$ were used in the analysis. The structure was solved by Patterson techniques and refined to final values of R and R_w of 0.076. All programs used were from the Enraf-Nonius SDP package. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

in a fully occupied site. The half-occupied position is evidently subject to significant thermal motion or to some disorder which we are not yet able to unravel with the present data set. Nonetheless, the principal features of the structure of the cationic moiety are well resolved and can be reported with confidence.

The geometry of the binuclear cation is depicted in Figure 1. As is required by the C_2 symmetry, the isomer observed here is the α,α isomer in which the pyridine nitrogen atoms are *trans* about both metal centres. This is, of course, only one of numerous isomers possible with this ligand, and is different from the isomers which we isolated for the di-μ-hydroxochromium(III) complexes of this ligand[5] and of the related ligand bispitn in which the 1,2-diaminoethane moiety is replaced by 1,3-diaminopropane.[6]

The Mn(1)–Mn(2) separation of 2.659(2) Å in the complex is shorter than the values of 2.716 and 2.700(1) Å reported[2] for the bpy and phen analogues, respectively, and is considerably shorter than 2.748(2) Å found for the oxidized form of the phen complex.[2a] The Mn(1)–O(1) bond of 1.793(4) Å is shorter than the Mn(2)–O(1) distance of 1.833(4) Å, suggesting that Mn(1) may be more highly oxidized than Mn(2) in this formally mixed valence complex. This assertion is also borne out by the axial metal–nitrogen bond lengths, the Mn(1)–N(1A) distance of 2.092(5) Å being considerably shorter than the Mn(2)–N(1B) length of 2.169(5) Å. It is also noteworthy that the Mn–N bond lengths at Mn(1) are symmetric, as expected for a d^3 Mn^{IV} ion, while those at Mn(2) show the axial elongation anticipated for a Jahn–Teller distorted high spin d^4 Mn^{III} ion. Thus, while all the differences between the geometries at Mn(1) and Mn(2) are small, they all show the same trend indicating a more highly oxidized metal centre at Mn(1). The description of the complex as a *completely* localized Mn^{III}/Mn^{IV} complex, however, is not consistent with all the structural data. Firstly, it should be noted that the equatorial Mn–N distances at the two metal centres are equal, and secondly, it is apparent that the magnitude of the differences between the bond lengths alluded to earlier are much smaller than would be expected for a fully localized system. Thus, in the bpy complex the differences between the Mn–O, Mn–N(axial), and Mn–N(equatorial) bond lengths are 0.071, 0.194, and 0.057 Å, respectively;[2a] in the complex presented here these values are 0.040, 0.077, and 0.00 Å, respectively. Consequently, while the structural data suggest that Mn(1) is more highly oxidized than Mn(2), they are more consistent with a partially delocalized model than with either a fully localized model as in the bpy complex or a fully delocalized model as is found in mixed valent μ-oxo complexes of ruthenium.[7] It is noteworthy that Bürgi and co-workers[2b] have interpreted the structure of the phen analogue as a disordered system with discrete Mn^{III} and Mn^{IV} sites.

A cyclic voltammogram in water (pH 7) with $NaClO_4$ electrolyte (0.1 M) shows two *quasi* reversible one-electron waves with $E_{\frac{1}{2}}$ values of 0.75 and 0.14 V *vs.* a saturated standard calomel electrode. The one-electron couple at 0.75 V presumably represents the reversible oxidation of the III/IV dimer to the IV/IV form, while the process at 0.14 V is the reduction of the III/IV dimer to the III/III form. In acetonitrile, the peaks are shifted slightly to 0.81 and 0.10 V, respectively. This $E_{\frac{1}{2}}$ value of 0.81 V can be contrasted to the values of 1.33 and 1.32 V reported for the phen and bpy complexes, respectively.[8] Consequently, it appears that the new complex is much easier to oxidize to the IV/IV form than the bpy and phen complexes.

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