

## Mixed Valence Manganese-(II, III) and -(III, IV) Dinuclear Complexes: Preparation, Structure, Magnetochemistry, and E.S.R. Spectra of $\text{Mn}_2(\text{biphen})_2(\text{biphenH})(\text{bpy})_2$ and $\text{Mn}_2\text{O}_2\text{Cl}_2(\text{OAc})(\text{bpy})_2$ ( $\text{biphenH}_2 = 2,2'$ -biphenol, $\text{bpy} = 2,2'$ -bipyridine)

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The preparation and properties of two new mixed valence Mn complexes,  $\text{Mn}_2(\text{biphen})_2(\text{biphenH})(\text{bpy})_2$  (**3**) and  $\text{Mn}_2\text{O}_2\text{Cl}_2(\text{OAc})(\text{bpy})_2$  (**2**) ( $\text{bpy} = 2,2'$ -bipyridine,  $\text{biphenH}_2 = 2,2'$ -biphenol) are reported; complex (**3**) has a rare  $S = 9/2$  ground state confirmed by magnetization studies.

The realization that a number of biological molecules contain Mn atoms in higher ( $\geq \text{II}$ ) oxidation states has prompted much research into the chemistry of this metal with biologically relevant oxidation levels and ligands. Of particular topical interest are the photosynthetic water oxidation enzyme<sup>1</sup> and the bacterial pseudocatalase<sup>2</sup> which contain 2–4 and 2 Mn atoms, respectively. To date we have concentrated mainly on tri- and tetra-nuclear species,<sup>3,4</sup> but we herein describe two new mixed valence dinuclear Mn complexes together with their interesting magnetic and e.s.r. properties.

A stirred slurry of 'Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O' (4.0 mmol) in MeCN (200 ml) was treated under N<sub>2</sub> with Me<sub>3</sub>SiCl (6.0 mmol, added dropwise), followed by addition of 2,2'-bipyridine (bpy) (4.5 mmol) in MeCN (25 ml). The resulting deep red–brown solution was separated by filtration from a tan precipitate giving analytical data consistent with MnCl<sub>2</sub>(bpy) (**1**).<sup>†</sup> The filtrate yielded, after 2 days, red–brown crystals of [Mn<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>(OAc)(bpy)<sub>2</sub>·2MeCN] (**2**).<sup>†</sup> The structure of (**2**) was

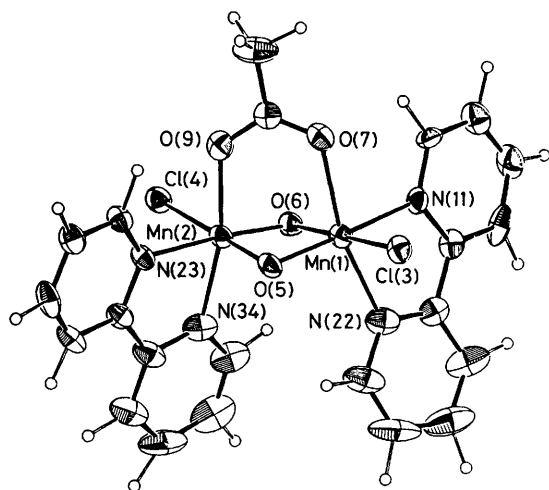
determined by X-ray crystallography<sup>‡</sup> (Figure 1). The molecule contains an [Mn<sub>2</sub>(μ-O)<sub>2</sub>(μ-OAc)]<sup>2+</sup> core, with each Mn terminally co-ordinated to a Cl atom and a bpy group completing distorted octahedral geometry. The complex is mixed valence (Mn<sup>III</sup>Mn<sup>IV</sup>), with Mn(1) assigned as the Mn<sup>III</sup>

<sup>‡</sup> Crystal Data for (**2**): C<sub>26</sub>H<sub>25</sub>N<sub>6</sub>O<sub>4</sub>Cl<sub>2</sub>Mn<sub>2</sub>,  $M_r = 666.31$ , monoclinic, space group Cc,  $Z = 4$ ,  $a = 11.798(4)$ ,  $b = 30.354(13)$ ,  $c = 10.014(3)$  Å,  $\beta = 125.45(1)^\circ$ ,  $U = 2921.27$  Å<sup>3</sup>,  $T = -155^\circ\text{C}$ .

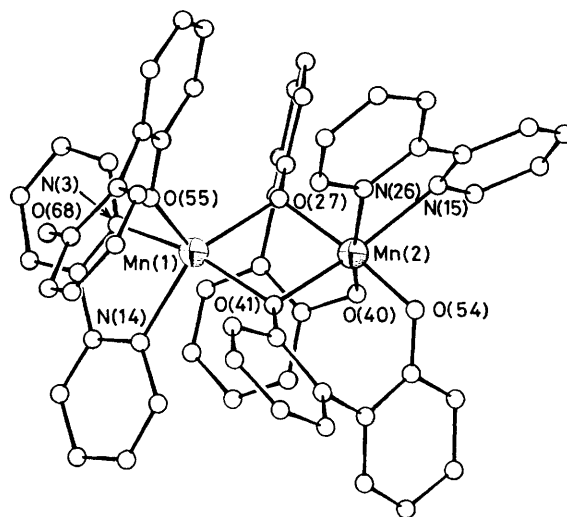
For (**3**): C<sub>59</sub>H<sub>47</sub>N<sub>4</sub>O<sub>6</sub>Cl<sub>2</sub>Mn<sub>2</sub>,  $M_r = 1230.63$ , monoclinic, space group P2<sub>1</sub>/c,  $Z = 4$ ,  $a = 13.373(5)$ ,  $b = 10.508(4)$ ,  $c = 39.005(22)$  Å,  $\beta = 90.65(2)^\circ$ ,  $U = 5480.59$  Å<sup>3</sup>,  $T = -155^\circ\text{C}$ .

Data (Mo-K<sub>α</sub> radiation) were collected in the range  $6 \leq 2\theta \leq 45^\circ$ . The structures were solved by a combination of direct methods (MULTAN) and Fourier techniques, and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. A total of 1756 [ $F > 3\sigma(F)$ ] and 2607 [ $F > 2.33\sigma(F)$ ] unique reflections were refined to  $R(R_w)$  values of 3.81 (3.77) and 7.19 (6.83), for (**2**) and (**3**), respectively. 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.

<sup>†</sup> Satisfactory elemental analyses have been obtained.

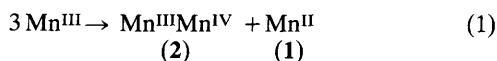


**Figure 1.** ORTEP projection of (2) at the 50% probability level. Selected bond distances (Å) and angles (degrees): Mn(1) ··· Mn(2) 2.6674(18), Mn(1)–Cl(3) 2.3265(26), Mn(1)–O(5) 1.827(5), Mn(1)–O(6) 1.843(5), Mn(1)–O(7) 2.203(6), Mn(1)–N(11) 2.106(7), Mn(1)–N(22) 2.155(8), Mn(2)–Cl(4) 2.3414(26), Mn(2)–O(5) 1.805(6), Mn(2)–O(6) 1.793(5), Mn(2)–O(9) 2.047(6), Mn(2)–N(23) 2.092(7), Mn(2)–N(34) 2.050(8) Å; Mn(1)–O(5)–Mn(2) 94.52(25), Mn(1)–O(6)–Mn(2) 94.35(25), O(5)–Mn(1)–O(6) 83.15(24), O(5)–Mn(2)–O(6) 85.22(24)°.



**Figure 2.** Structure of (3). Selected bond distances (Å) and angles (degrees): Mn(1)–O(27) 2.124(10), Mn(1)–O(41) 2.112(10), Mn(1)–O(55) 2.037(11), Mn(1)–N(3) 2.237(13), Mn(1)–N(14) 2.219(13), Mn(2)–O(27) 1.956(10), Mn(2)–O(40) 1.878(10), Mn(2)–O(41) 2.134(10), Mn(2)–O(54) 1.866(10), Mn(2)–N(15) 2.268(12), Mn(2)–N(26) 2.130(13) Å; Mn(1)–O(27)–Mn(2) 102.4(4), Mn(1)–O(41)–Mn(2) 97.1(4), O(27)–Mn(1)–O(41) 78.0(4), O(27)–Mn(2)–O(41) 81.3(4), O(55)–Mn(1)–O(41) 106.1(4), O(55)–Mn(1)–N(3) 93.3(4), O(55)–Mn(1)–N(14) 114.6(5), O(27)–Mn(2)–O(54) 171.2(5), O(40)–Mn(2)–N(26) 164.8(5); O(41)–Mn(2)–N(15) 166.5(4)°.

centre, based on inspection of structural parameters which indicate a trapped valence situation akin to that in  $[\text{Mn}_2\text{O}_2(\text{bpy})_4]^{3+}$  to which (2) bears some structural correspondence.<sup>5</sup> The extremely rare  $[\text{Mn}_2\text{O}_2(\text{OAc})]^{2+}$  bridging unit<sup>6</sup> has a Mn ··· Mn separation of 2.667(2) Å, similar to that deduced by EXAFS studies to be present in the photosynthetic water oxidation enzyme [2.69(3) Å].<sup>7</sup> The terminal Cl groups in (2) suggest that potentially useful ligand substitution reactions at these positions may be possible, a matter currently under investigation. The isolation of (2) from a reaction mixture containing only  $\text{Mn}^{\text{III}}$  indicates that a disproportionation occurred, and the isolated yields of (2) and (1) correspond to 40 and 80%, respectively, of those predicted by equation (1).



A brown solution of  $(\text{Et}_3\text{NH})_2[\text{Mn}^{\text{III}}(\text{biphen})_2(\text{biphenH})]$  (0.31 mmol)<sup>8</sup> in  $\text{CH}_2\text{Cl}_2$  (20 ml) was treated with solid bpy (0.96 mmol) to give a black solution. Layering with hexanes and storage at  $-20^\circ\text{C}$  (2 weeks) gave  $[\text{Mn}_2(\text{biphen})_2(\text{biphenH})(\text{bpy})_2] \cdot 3\text{CH}_2\text{Cl}_2$  (3)<sup>†</sup> (Figure 2). The Mn atoms are bridged by two oxygen atoms from two biphen groups whose other oxygen atoms bind terminally to Mn(2). Octahedral co-ordination to Mn(2) is completed by a bpy group. Ligation to Mn(1) is completed by a bpy and a monodentate biphenH whose second oxygen atom, O(68), is protonated and hydrogen bonded to O(55) [O(68) ··· O(55) 2.493 Å]. Mn(1) is thus five co-ordinate and approximately square pyramidal with O(55) at the apex. Complex (3) is again mixed-valence ( $\text{Mn}^{\text{II}}$ ,  $\text{Mn}^{\text{III}}$ )§ and Mn(1) is assigned as the  $\text{Mn}^{\text{II}}$  site on consideration of structural parameters. Mn(2) also shows the Jahn–Teller distortion expected for  $\text{Mn}^{\text{III}}$  ( $d^4$ ) with O(41) and

N(15) occupying axial positions. The Mn(1) ··· Mn(2) distance is 3.182(6) Å.

Variable-temperature solid-state magnetic susceptibility studies were performed on powdered samples of (2) and (3) in the range 5–300 K. The effective magnetic moment ( $\mu_{\text{eff}}$ ) of (2) varies gradually from 3.24  $\mu_{\text{B}}$  per  $\text{Mn}_2$  at 301 K to 2.40  $\mu_{\text{B}}$  at 91 K, below which  $\mu_{\text{eff}}$  changes only slightly, reaching 2.35  $\mu_{\text{B}}$  at 5 K. These data were fitted to the expression for an isotropic exchange interaction between an  $\text{Mn}^{\text{III}}$  ( $S_1 = 2$ ) and an  $\text{Mn}^{\text{IV}}$  ( $S_2 = 3/2$ ) ion to give an exchange parameter of  $J - 114 \text{ cm}^{-1}$  ( $\hat{H} = 2J\hat{S}_1\hat{S}_2$ ). The antiferromagnetic interaction is somewhat weaker than found in other  $[\text{Mn}_2\text{O}_2]^{3+}$ -containing complexes ( $|J|$  148–220  $\text{cm}^{-1}$ ).<sup>6,9</sup>

For compound (3),  $\mu_{\text{eff}}$  per  $\text{Mn}_2$  increases gradually from 7.82  $\mu_{\text{B}}$  at 302 K to 9.19  $\mu_{\text{B}}$  at 5 K. The data were fitted to the expression for an isotropic exchange interaction between an  $\text{Mn}^{\text{II}}$  ( $S_1 = 5/2$ ) and an  $\text{Mn}^{\text{III}}$  ( $S_2 = 2$ ) ion. The ferromagnetic interaction in (3) is characterized by  $J + 0.89 \text{ cm}^{-1}$ . The complex has a resulting  $S = 9/2$  ground state; this was confirmed by determining magnetization vs.  $H/T$  data. The external field was maintained at four different values in the range 10–43.5 kG, and at each field the temperature was varied in the range 1.7–40 K. The  $M$  vs.  $H/T$  plot shows a saturation value of 9.3  $\mu_{\text{B}}$ . The data fit well to an  $S = 9/2$  Brillouin function.

The few other dinuclear  $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$  complexes which have been structurally characterized also contain  $\mu$ -phenoxide bridges, but all have weakly antiferromagnetic interactions ( $|J|$  1.7–7.7  $\text{cm}^{-1}$ ).<sup>10</sup>

Variable-temperature X-band e.s.r. spectra were run for powdered samples and glasses of (2) and (3). A microcrystalline sample of (2) showed only a  $g = 2$  feature at 77 K or below, in agreement with the susceptibility data which show that (2) is totally in its  $S = 1/2$  ground state in this temperature range. An EtOH glass at  $\sim 7 \text{ K}$  gives a  $g = 2$  signal structured

§ The high yield of isolated (3) (90%) argues against a disproportionation to yield  $\text{Mn}^{\text{II}}$  and for metal reduction by excess biphenoxide.

with 16 Mn hyperfine lines<sup>¶</sup> as seen in an isolated form of *Thermus thermophilus* catalase.<sup>11</sup> The 7.5 K powder spectrum of (3) exhibits an intense signal at  $g \approx 5.0$  and a weaker signal at  $g = 1.98$ . A CH<sub>2</sub>Cl<sub>2</sub>-toluene glass at 7.5 K exhibits a moderate-intensity signal at  $g = 12.0$ , a strong Mn-hyperfine-structured signal at  $g = 5.1$ , and weaker signals at  $g = 2.01$  and  $1.47$ . These various features are probably explicable only in terms of the  $S = 9/2$  ground state which experiences a small zero-field splitting.

This work was supported by N.S.F. (G. C.) and N.I.H. (D. N. H.).

Received, 19th January 1988; Com. 8/00198G

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<sup>¶</sup> Weak broad signals are also seen at ~700, ~2000, and ~4500 G which, at this stage, are attributable to reaction of (3) with the EtOH solvent or impurities therein. Further studies are in progress to clarify this.