Mixed Valence Manganese-(II, III) and -(III, IV) Dinuclear Complexes: Preparation, Structure, Magnetochemistry, and E.S.R. Spectra of $Mn_2(biphen)_2(biphenH)(bpy)_2$ and $Mn_2O_2Cl_2(OAc)(bpy)_2$ (biphenH_2 = 2,2′-biphenol, bpy = 2,2′-bipyridine)

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The preparation and properties of two new mixed valence Mn complexes, $Mn_2(biphen)_2(biphenH)(bpy)_2$ (**3**) and $Mn_2O_2Cl_2(OAc)(bpy)_2$ (**2**) (bpy = 2,2′-bipyridine, 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 (≥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[1] and the bacterial pseudocatalase[2] which contain 2—4 and 2 Mn atoms, respectively. To date we have concentrated mainly on tri- and tetra-nuclear species,[3,4] 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 '$Mn(OAc)_3{\cdot}2H_2O$' (4.0 mmol) in MeCN (200 ml) was treated under N_2 with Me_3SiCl (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 $MnCl_2(bpy)$ (**1**).† The filtrate yielded, after 2 days, red-brown crystals of $[Mn_2O_2Cl_2(OAc)(bpy)_2]{\cdot}2MeCN$ (**2**).† The structure of (**2**) was determined by *X*-ray crystallography‡ (Figure 1). The molecule contains an $[Mn_2(\mu\text{-}O)_2(\mu\text{-}OAc)]^{2+}$ core, with each Mn terminally co-ordinated to a Cl atom and a bpy group completing distorted octahedral geometry. The complex is mixed valence ($Mn^{III}Mn^{IV}$), with Mn(1) assigned as the Mn^{III}

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† Satisfactory elemental analyses have been obtained.

‡ *Crystal Data* for (**2**): $C_{26}H_{25}N_6O_4Cl_2Mn_2$, $M_r = 666.31$, monoclinic, space group *Cc*, $Z = 4$, $a = 11.798(4)$, $b = 30.354(13)$, $c = 10.014(3)$ Å, $\beta = 125.45(1)°$, $U = 2921.27$ Å^3, $T = -155$ °C.

For (**3**): $C_{59}H_{47}N_4O_6Cl_6Mn_2$, $M_r = 1230.63$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 13.373(5)$, $b = 10.508(4)$, $c = 39.005(22)$ Å, $\beta = 90.65(2)°$, $U = 5480.59$ Å^3, $T = -155$ °C.

Data (Mo-K_α radiation) were collected in the range $6 \leqslant 2\theta \leqslant 45°$. 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.

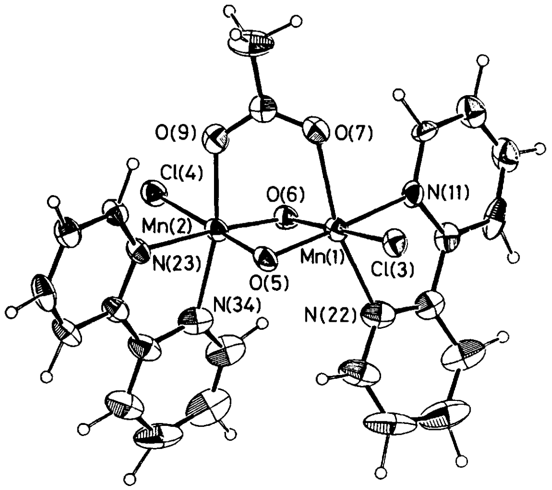

Figure 1. ORTEP projection of (**2**) at the 50% probability level. Selected bond distances (Å) and angles (degrees): Mn(1) · · · Mn(2) 2.6674(18), Mn(1)–Cl(3) 2.3265(26), Mn(1)–O(5) 1.827(5), Mn(1)–O(6) 1.843(5), Mn(1)–O(7) 2.203(6), Mn(1)–N(11) 2.106(7), Mn(1)–N(22) 2.155(8), Mn(2)–Cl(4) 2.3414(26), 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)°.

centre, based on inspection of structural parameters which indicate a trapped valence situation akin to that in $[\mathrm{Mn_2O_2(bpy)_4}]^{3+}$ to which (**2**) bears some structural correspondence.[5] The extremely rare $[\mathrm{Mn_2O_2(OAc)}]^{2+}$ bridging unit[6] 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].[7] 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 $\mathrm{Mn^{III}}$ 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).

$$3\,\mathrm{Mn^{III}} \rightarrow \underset{(\mathbf{2})}{\mathrm{Mn^{III}Mn^{IV}}} + \underset{(\mathbf{1})}{\mathrm{Mn^{II}}} \qquad (1)$$

A brown solution of $(\mathrm{Et_3NH})_2[\mathrm{Mn^{III}(biphen)_2(biphenH)}]$ (0.31 mmol)[8] in $\mathrm{CH_2Cl_2}$ (20 ml) was treated with solid bpy (0.96 mmol) to give a black solution. Layering with hexanes and storage at −20 °C (2 weeks) gave $[\mathrm{Mn_2(biphen)_2(biphenH)(bpy)_2}]\cdot3\mathrm{CH_2Cl_2}$ (**3**)† (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 ($\mathrm{Mn^{II}}$, $\mathrm{Mn^{III}}$)§ and Mn(1) is assigned as the $\mathrm{Mn^{II}}$ site on consideration of structural parameters. Mn(2) also shows the Jahn–Teller distortion expected for $\mathrm{Mn^{III}}$ (d^4) with O(41) and N(15) occupying axial positions. The Mn(1) · · · Mn(2) distance is 3.182(6) Å.

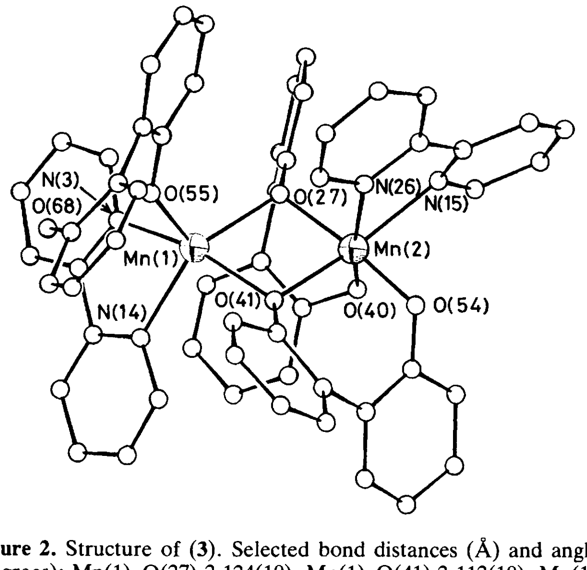

Figure 2. Structure of (**3**). Selected bond distances (Å) and angles (degrees): Mn(1)–O(27) 2.124(10), Mn(1)–O(41) 2.112(10), Mn(1)–O(55) 2.037(11), Mn(1)–N(3) 2.237(13), Mn(1)–N(14) 2.219(13), Mn(2)–O(27) 1.956(10), Mn(2)–O(40) 1.878(10), Mn(2)–O(41) 2.134(10), Mn(2)–O(54) 1.866(10), Mn(2)–N(15) 2.268(12), 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)°.

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 (μ_{eff}) of (**2**) varies gradually from 3.24 μ_B per $\mathrm{Mn_2}$ at 301 K to 2.40 μ_B at 91 K, below which μ_{eff} changes only slightly, reaching 2.35 μ_B at 5 K. These data were fitted to the expression for an isotropic exchange interaction between an $\mathrm{Mn^{III}}$ ($S_1 = 2$) and an $\mathrm{Mn^{IV}}$ ($S_2 = 3/2$) ion to give an exchange parameter of J −114 cm^{-1} ($\hat{H} = 2J\hat{S}_1\cdot\hat{S}_2$). The antiferromagnetic interaction is somewhat weaker than found in other $[\mathrm{Mn_2O_2}]^{3+}$-containing complexes ($|J|$ 148—220 cm^{-1}).[6,9]

For compound (**3**), μ_{eff} per $\mathrm{Mn_2}$ increases gradually from 7.82 μ_B at 302 K to 9.19 μ_B at 5 K. The data were fitted to the expression for an isotropic exchange interaction between an $\mathrm{Mn^{II}}$ ($S_1 = 5/2$) and an $\mathrm{Mn^{III}}$ ($S_2 = 2$) ion. The ferromagnetic interaction in (**3**) is characterized by J +0.89 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 μ_B. The data fit well to an $S = 9/2$ Brillouin function.

The few other dinuclear $\mathrm{Mn^{II}Mn^{III}}$ complexes which have been structurally characterized also contain μ-phenoxide bridges, but all have weakly antiferromagnetic interactions ($|J|$ 1.7—7.7 cm^{-1}).[10]

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 ~7 K gives a $g = 2$ signal structured

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

with 16 Mn hyperfine lines¶ as seen in an isolated form of *Thermus thermophilus* catalase.[11] 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_2Cl_2–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.

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¶ 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.