A Novel Mixed-valent Mn^{III}–Mn^{IV}-Dimer, $[L_2Mn_2(\mu\text{-}O)_2(\mu\text{-}MeCO_2)][BPh_4]_2\cdot MeCN$: Crystal Structure, Magnetic Properties, and E.S.R. Spectrum (L = 1,4,7-triazacyclononane)

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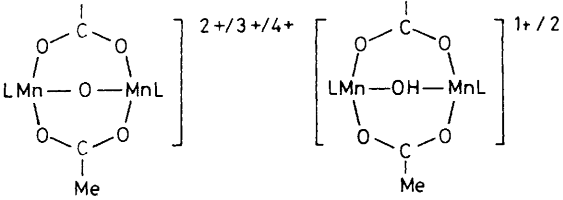
The green mixed-valence dimer $[L_2Mn_2(\mu\text{-}O)_2(\mu\text{-}MeCO_2)]$ $[BPh_4]_2\cdot MeCN$ (L = 1,4,7-triacacyclononane) is formed on hydrolysis of $[L_2Mn_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2]^{2+}$ in water in the presence of air; characterization by *X*-ray crystallography showed the presence of the di-μ-oxo-μ-acetato-dimanganese(III,IV) core, and temperature dependent magnetic susceptibility measurements indicate an $S = 1/2$ ground state and very strong intramolecular antiferromagnetic coupling (J −440 cm^{-1}).

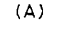
Witt and co-workers have recently reported that incubation of photosystem II particles with acetate resulted in an inhibition of oxygen evolution and a retardation of the chlorophyll-a_{II}^{+} reduction kinetics. Removal of acetate restored both the oxygen evolution and the reduction kinetics.[1] They proposed that the inhibition may be due to a replacement of Cl^- by $MeCO_2^-$ within the water-splitting enzyme. It is also conceivable that the acetate is reversibly co-ordinated to two co-ordination sites for water molecules (Scheme 1). This model requires the acetato bridge to be quite substitution labile. We have recently described a series of binuclear acetate bridged manganese(II,III,IV) complexes of the types (A) and (B),[2,3] where L represents the tridentate saturated amines 1,4,7-triazacyclononane (L) and *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L′). Similar neutral complexes of type (A) containing tris(pyrazolyl)borate(1−) ligands have also been characterized.[4] These complexes have potential biological significance for photosystem II and a recently characterized Mn catalase of *Lactobacillus plantarum*, which contains two manganese centres per subunit.[5]

During our investigation of the reactivity of these complexes it became apparent[6] that the acetate bridges are quite labile. We have now found that hydrolysis of red $[L_2Mn_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2](ClO_4)_2$ (**1**) (2 g) in H_2O (40 ml) in the presence of air yielded a green solution. Addition of sodium tetraphenylborate (0.5 g) dissolved in 10 ml of acetonitrile initiated the precipitation of green crystals of $[L_2Mn^{III}Mn^{IV}(\mu\text{-}O)_2(MeCO_2)][BPh_4]_2\cdot MeCN$ (**2**) (yield 2.8 g), which could be recrystallized from MeCN–EtOH. Crystals of (**2**) suitable for *X*-ray diffration studies and elemental analysis were obtained by this method.†‡

The structure (Figure 1) consists of binuclear cations $[L_2Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}MeCO_2)]^{2+}$, tetraphenylborate anions, and one molecule of unco-ordinated acetonitrile per formula unit. The mixed-valent cation possesses crystallographically imposed C_2 symmetry. The two manganese centres are crystallographically equivalent. The only indication that the valences of the Mn ions are localized and the Mn^{III} and Mn^{IV}-centres are inequivalent (*i.e.* a disorder of the cations in the unit cell prevails) may be deduced from the fact that the μ-acetato-bridge is not quite symmetrical. The methyl carbon atom C(8) is not located on the crystallographic two-fold axis; a split-atom model with two locations for this atom was refined yielding a slightly lower *R* factor, and, more importantly, reasonable anisotropic temperature factors for C(8) were found. The Mn · · · Mn distance in (**2**) is 2.588(2) Å, which is in good agreement with the proposed average Mn · · · Mn distance

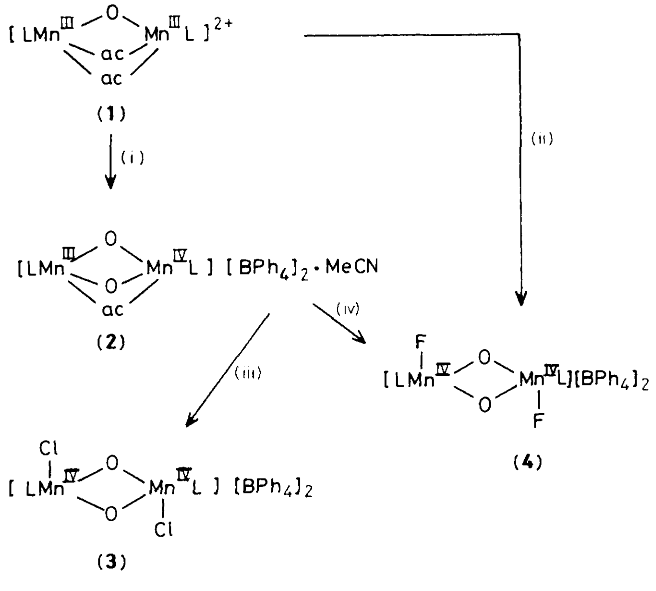


Scheme 1



(A)

(B)



Scheme 2. Reactions of (1) with (i) oxygen in H_2O, (ii) oxygen in H_2O and $NaBF_4$; and of (2) with (iii) oxygen and conc. HCl in acetone and (iv) $NaBF_4$ in H_2O. ac = $MeCO_2^-$.

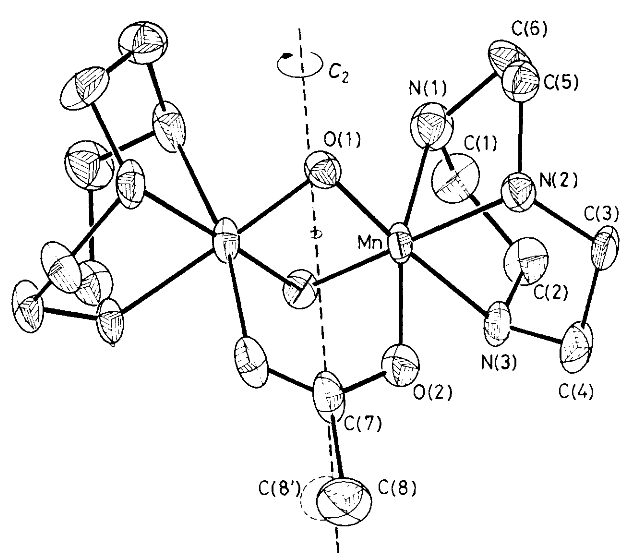


Figure 1. Structure of the cation $[L_2Mn_2(\mu\text{-}O)_2(\mu\text{-}MeCO_2)]^{2+}$ with 40% probability thermal ellipsoids and showing the atom labelling scheme. The crystallographic two-fold axis (dashed line) and the split-atom model for C(8) are shown. Selected interatomic distances (Å) and angles(°) for the $N_6Mn_2O_2(\mu\text{-}MeCO_2)$-core are as follows: Mn–O(1) 1.817(5); Mn–O(1') 1.808(4); Mn–O(2) 2.079(5); Mn–N(1) 2.135(6); Mn–N(2) 2.105(5); Mn–N(3) 2.110(5); Mn ··· Mn' 2.588(2); C(7)–O(2) 1.262(7); C(7)–C(8) 1.56(2); Mn–O(1)–Mn' 91.1(1); O(1)–Mn–O(1') 87.2(2); N(1)–Mn–N(2) 81.8(2); N(1)–Mn–N(3) 82.1(2); N(2)–Mn–N(3) 82.1(2); O(1)–Mn–N(2) 94.4(2); O(1)–Mn–N(3) 175.6(2); N(3)–Mn–O(1') 96.3(2); O(2)–Mn–N(1) 167.0(2); O(2)–Mn–O(1) 93.5(2); O(2)–Mn–N(2) 87.7(2); O(2)–Mn–N(3) 89.0(2).

~2.7 Å in photosystem II as has been determined by EXAFS studies[7] on spinach chloroplasts.

The electronic spectrum of (**2**) measured in acetonitrile exhibits two bands at 628 nm (ε 345 l mol^{-1} cm^{-1}) and 546 (394) and a shoulder at ~440 nm.

Temperature dependent magnetic susceptibility measurements for a powdered sample of (**2**) revealed an $S = 1/2$ ground state. The data were fitted using an isotropic Heisenberg model $H = -JS_1\cdot S_2$ ($S_1 = 4/2$; $S_2 = 3/2$; fixed $g = 2.0$; temperature independent paramagnetism = 0). The spin-exchange coupling constant J was found to be -440 cm^{-1}, indicating a very strong intramolecular antiferromagnetic coupling of the Mn^{III} (d^4 high-spin) and Mn^{IV} (d^3) centres in (**2**). Interestingly, for the analogous $[L'_2Mn^{III}Mn^{IV}(\mu\text{-}O)(\mu\text{-}MeCO_2)_2]^{3+}$ cation,[3] the exchange coupling is much weaker (J -80 cm^{-1}), and for the well characterized $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ (bpy = 2,2'-bipyridine) and its phenanthroline analogues J values of -300 and -268 cm^{-1}, respectively, have been reported.[19]

Owing to the presence of the large counterion, $[BPh_4]^-$, of (**2**) a powdered sample yielded a well resolved e.s.r. spectrum at low temperatures (Figure 2a). 16 Hyperfine lines were observed around $g = 2$. This g value is expected for a spin doublet ground state. When the temperature was raised, the spectrum broadened and above 160 K only one broad band

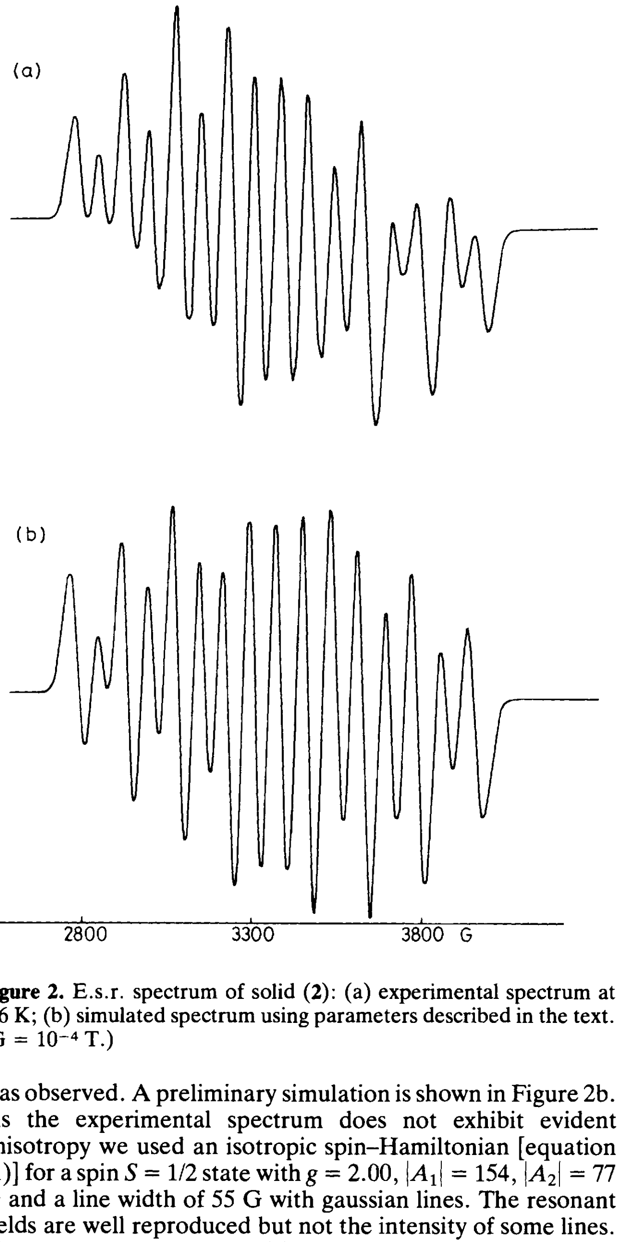


Figure 2. E.s.r. spectrum of solid (**2**): (a) experimental spectrum at 8.6 K; (b) simulated spectrum using parameters described in the text. (G = 10^{-4} T.)

was observed. A preliminary simulation is shown in Figure 2b. As the experimental spectrum does not exhibit evident anisotropy we used an isotropic spin–Hamiltonian [equation (1)] for a spin $S = 1/2$ state with $g = 2.00$, $|A_1| = 154$, $|A_2| = 77$ G and a line width of 55 G with gaussian lines. The resonant fields are well reproduced but not the intensity of some lines. The e.s.r. spectrum of (**2**) is quite similar to that of $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ ($|A_1| = 167$, $|A_2| = 79$ G).[9]

$$\mathcal{H} = g\cdot\beta\cdot HS_z + A_1\vec{I}_1\vec{S}_1 + A_2\vec{I}_2\vec{S}_2 \qquad (1)$$

The reaction of (**2**) (2 g) dissolved in acetone (20 ml)–water (5 ml) with *ca.* five drops of conc. HCl in the presence of air yielded immediately yellow–brown microcrystals of $[L_2Mn^{IV}{}_2(\mu\text{-}O)_2Cl_2][BPh_4]_2$ (**3**) (yield: 0.25 g). Complexes (**1**) or (**2**) (~1 g) dissolved in water (50 ml) yielded a green solution. Upon addition of $Na[BF_4]$ (~3 g) in the presence of air the colour changed to yellow–brown. Addition of $Na[BPh_4]$ (0.5

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† Satisfactory elemental analyses were obtained for complexes (**2**), (**3**), and (**4**). (C, H, N, Cl, Mn); i.r. data for $[L_2Mn_2(\mu\text{-}O)_2(\mu\text{-}MeCO_2)][BPh_4]_2$ MeCN (KBr-disc): $\nu_{as}(CO_2)$: 1555 cm^{-1}, $\nu_s(CO_2)$: 1385 cm^{-1}.

‡ *Crystal data:* $C_{64}H_{76}N_7B_2Mn_2O_4$, monoclinic, space group $C2/c$, $a = 26.73(3)$, $b = 14.40(1)$, $c = 18.97(2)$ Å, $\beta = 126.77(7)°$, $U = 5845(10)$ Å^3, $Z = 4$, $R = 0.070$ for 2636 observed $I \geqslant 2.0\,\sigma(I)$ diffractometer-collected reflections (Mo-K_α radiation, 233 K). 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.

g) dissolved in acetone (10 ml) initiated the precipitation of yellow–brown microcrystals of $[L_2Mn_2(\mu\text{-}O)_2F_2][BPh_4]_2$ (**4**) (Scheme 2). Both (**3**) and (**4**) are binuclear manganese(IV) complexes containing two μ-oxo bridges. Preliminary temperature dependent magnetic susceptibility measurements indicate quite strong intramolecular antiferromagnetic coupling of the Mn^{IV} centres in (**3**) and (**4**). These results indicate that the acetato bridges in (**1**) and (**2**) are quite labile, even though the manganese centres are in the oxidation states III and IV.

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