A New Mixed-valence Binuclear Complex containing the $[\mathrm{Mn^{IV}}(\mu\text{-O})_2(\mu\text{-O_2CMe})\mathrm{Mn^{III}}]^{2+}$ Core: Synthesis, Magnetism, Electron Paramagnetic Resonance and Redox Properties†

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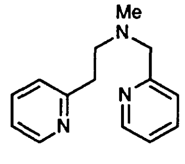
The complex $[\mathrm{Mn_2}(\mu\text{-O})_2(\mu\text{-O_2CMe})\mathrm{L_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O}$ **1** {L = methyl[2-(2-pyridyl)ethyl](2-pyridylmethyl)amine} has been synthesised and isolated in the solid state. In MeCN solution complex **1** exhibits absorption spectral features characteristic of the $[\mathrm{Mn_2}(\mu\text{-O})_2(\mu\text{-O_2CMe})]^{2+}$ core. Variable-temperature (19.8–300 K) solid-state magnetic susceptibility data are consistent with a doublet ground state with $J = -144$ cm^{-1}. The X-band EPR spectrum at 77 K exhibits a sixteen-line pattern centred at $g = 2$. This spectrum is attributed to the overlap of hyperfine splitting of two chemically distinct manganese nuclei ($I = \frac{5}{2}$) with one hyperfine coupling constant being roughly twice the magnitude of the other. Cyclic voltammetry of **1** shows a quasi-reversible one-electron oxidation [$E_{\frac{1}{2}} = +1.0$ V *vs.* saturated calomel electrode (SCE)] to the $\mathrm{Mn^{IV}}_2$ species as well as an irreversible one-electron reduction ($E_{\mathrm{pc}} = -0.10$ V *vs.* SCE) to the $\mathrm{Mn^{III}}_2$ species. Coulometric or perchloric acid oxidation generates the orange $\mathrm{Mn^{IV}}_2$ species. The redox stability and the absorption spectral properties of this oxidised species have been investigated.

Interest in $[\mathrm{Mn^{IV}}(\mu\text{-O})_2\mathrm{Mn^{III}}]^{3+}$ species[1,2] has grown enormously in recent years[3–8] largely from the involvement of such species in the water-oxidation photosystem II (PS II) of the photosynthetic apparatus.[9] For the S_2 state in PS II, the multiline signal at $g \approx 2$ in the EPR spectrum and the short Mn ··· Mn separation (2.70 Å, as indicated by extended X-ray absorption fine structure analysis) are both consistent[10] with, minimally, a binuclear formulation for the manganese centre. These characteristic physical properties are modelled remarkably well by a group of synthetic complexes having a $[\mathrm{Mn^{IV}}(\mu\text{-O})_2\mathrm{Mn^{III}}]^{3+}$ core structure. The di-μ-oxo complexes with an additional carboxylato bridge $[\mathrm{Mn^{IV}}(\mu\text{-O})_2(\mu\text{-O_2CMe})\mathrm{Mn^{III}}]^{2+}$ have also been devised as model complexes for the S_2 state.[11–13] Although so far three bis(μ-oxo)(μ-carboxylato)dimanganese(III,IV) complexes have been reported, there has been no report on the existence of bis(μ-oxo)(μ-carboxylato)dimanganese(IV,IV) species.

Our own interest in complexes of these general types stems from our ongoing research activity[14,15] on complexes containing $[\mathrm{M}(\mu\text{-O})(\mu\text{-O_2CMe})_2\mathrm{M}]^{2+,3+}$ cores (M = Fe or Ru). In these studies we have used two tridentate nitrogen-donor ligands with inherent chelate-ring asymmetry to block the terminal co-ordination sites of these cores. Herein, we describe a new mixed-valence binuclear manganese complex and its one-electron oxidation product, containing $[\mathrm{Mn_2}(\mu\text{-O})_2(\mu\text{-O_2CMe})]^{2+,3+}$ units respectively and utilising methyl[2-(2-pyridyl)ethyl](2-pyridylmethyl)amine L as the capping ligand. The magnetic, EPR and redox properties of the system have been investigated.

Experimental

Chemicals and Starting Materials.—Reagents were obtained from commercial sources and used without further purification. Purification/preparation of acetonitrile, diethyl ether and tetrabutylammonium perchlorate were done as described previously.[16,17] Ligand L was prepared as reported.[14]



L

Synthesis of $[\mathrm{Mn_2}(\mu\text{-O})_2(\mu\text{-O_2CMe})\mathrm{L_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O}$ **1**.—A suspension of $[\mathrm{Mn(O_2CMe)_3}]\cdot 2\mathrm{H_2O}$ (400 mg, 1.49 mmol) and $\mathrm{NaClO_4\cdot H_2O}$ (210 mg, 1.49 mmol) in degassed MeCN (5 cm^3) was stirred for 1 h. The ligand methyl [2-(2-pyridyl)ethyl](2-pyridylmethyl)amine (L) (340 mg, 1.49 mmol) also in degassed MeCN (5 cm^3) was then added slowly over a period of 5 min and the mixture was stirred at room temperature for 2 h. The brownish green solution mixture was filtered through a G-4 frit and layering of the filtrate with $\mathrm{Et_2O}$ (5 cm^3) initiated the precipitation of a green microcrystalline complex $[\mathrm{Mn_2}(\mu\text{-O})_2(\mu\text{-O_2CMe})\mathrm{L_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O}$ in 42% yield. To obtain the pure compound strict exclusion of air was critical at all stages of reaction and work-up (Found: C, 41.20; H, 4.60; N, 9.70. Calc. for $\mathrm{C_{30}H_{39}Cl_2Mn_2N_6O_{13}}$: C, 41.30; H, 4.50; N, 9.65%). IR (KBr, selected peaks): 3420 [ν(OH)], 1550 [ν_{asym}(OCO)], 1440 [ν_{sym}(OCO)], 1100 and 620 [ν(ClO$_4$)] and 670 cm^{-1} [ν(Mn$_2$O$_2$)]. UV/VIS [MeCN solution, λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 800 (sh) (150), 640 (350), 548 (300), 440 (sh) (750), 400 (sh) (1100) and 259 (21 000). Conductivity (MeCN, 298 K): $\Lambda_{\mathrm{M}} = 295\ \Omega^{-1}$ cm^2 mol^{-1}.

CAUTION: This complex contains perchlorate as counter ion and therefore should be handled with care.

Measurements.—Infrared spectra were recorded as KBr pellets on a Perkin Elmer 1320 IR spectrophotometer and electronic spectra with a Perkin Elmer Lambda 2 spectrophotometer. Solution electrical conductivity was measured on acetonitrile solutions with a type CM-82 T Elico conductivity bridge (Hyderabad, India) and solute concentration of $\approx 10^{-3}$ mol dm^{-3}. Solution magnetic susceptibility was determined by the conventional NMR method[18] in acetonitrile with a PMX-60 JEOL (60 MHz) spectrometer. Solvent susceptibility[19a] and diamagnetic corrections[19b] were taken from published data.

X-Band EPR spectra were recorded with a Varian E-109 C

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† *Non-SI unit employed:* G = 10^{-4} T.

spectrometer fitted with a quartz Dewar for measurements at liquid-nitrogen temperature. The spectra were calibrated with diphenylpicrylhydrazyl (dpph) ($g = 2.0037$).

Cyclic voltammetry and coulometric measurements were performed using a PAR model 370-4 electrochemistry system incorporating the following: model 174A polarographic analyser; model 175 universal programmer; model 173 potentiostat/galvanostat; model 179 digital coulometer and model RE-0074 *x–y* recorder. Details of the electrochemical measurements are the same as described previously.[14,16,17]

Variable-temperature magnetic susceptibility measurements were made on powdered samples over the temperature range 19.8–300 K by the Faraday method as described previously.[15] A total of 20 data points was taken over this temperature range with each data point a mean of three measurements. Effective magnetic moments per manganese centre were calculated using the formula $\mu_{eff}^2 = (7.998/2)\chi_M T$, where χ_M is the corrected molar susceptibility. The susceptibility of the sample holder was measured at the same temperatures and subtracted from the observed susceptibility with sample present. The diamagnetic contributions were calculated by using a value[19b] of -351×10^{-6} cm^3 mol^{-1} for **1**. All measurements were made at a fixed field strength and field dependence of the magnetic susceptibility was not studied. The data were fitted to the appropriate theoretical expression for two interacting high-spin manganese-(III) and -(IV) ions developed under the usual isotropic spin Hamiltonian $H_o = -2JS_1S_2$.[19b] Inclusion of terms for the temperature-independent paramagnetism (t.i.p.) and for possible sample contamination by a paramagnetic manganese(III) impurity exhibiting Curie behaviour yields equation (1) where $x = J/kT$, N, g and k have their usual

$$\chi_{calc} = \frac{Ng^2\beta^2}{kT}\left(\frac{1 + 10e^{3x} + 35e^{8x} + 84e^{15x}}{4 + 8e^{3x} + 12e^{8x} + 16e^{15x}}\right) + \frac{Ng^2\beta^2S(S+1)}{3kT}\chi_{para} + \text{t.i.p.} \quad (1)$$

meaning and χ_{para} is the mole fraction of manganese(III) contaminant. A non-linear least-squares fitting computer program was used to fit the observed data to equation (1).

Results and Discussion

Synthesis of the $[Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)Mn^{III}]^{2+}$ *Core.*—In the present work, the spontaneous self-assembly method[20] has been adopted to synthesise $[LMn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)Mn^{III}L][ClO_4]_2\cdot H_2O$ **1**, which consists essentially of adding the tridentate pyridine-rich capping ligand L to a stirred suspension of $[Mn(O_2CMe)_3]\cdot 2H_2O$ in MeCN in the presence of perchlorate. This is the second example where the terminal co-ordination sites of the bis(μ-oxo)(μ-carboxylato)dimanganese-(III,IV) unit have been capped by this kind of ligand and is the fourth example of this type of core structure. At present the mechanism of the formation of the $[Mn_2O_2(O_2CMe)]^{2+}$ core is not well understood.

The $[Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)Mn^{III}]^{2+}$ core formulation results in a dipositively charged complex, which is consistent with the conductivity data.[21] The green solid **1** exhibited characteristic IR bands assignable to bridging acetate, the Mn_2O_2 core, water of crystallisation and ClO_4^-. The similarities between the absorption spectrum of **1** (Fig. 1) and known structurally authenticated binuclear complexes containing $[Mn^{IV}(\mu\text{-}O)_2Mn^{III}]^{3+}$ or $[Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)Mn^{III}]^{2+}$ units[2–8,13] suggests that the manganese atoms in **1** have similar electronic structure. It should be emphasised that the electronic spectra of these complexes is dominated by the $[Mn^{IV}(\mu\text{-}O)_2Mn^{III}]^{3+}$ unit. Solution magnetic susceptibility measurements using the Evans method[19] (MeCN, 300 K) gave a magnetic moment of 2.34 per Mn. This is well below the spin-only values expected for magnetically isolated d^3 Mn^{IV} (3.87) or high-spin d^4 Mn^{III} (4.90). The present result agrees well with values expected[4,11–13] for an antiferromagnetically coupled Mn^{IV} ($S = \frac{3}{2}$)–Mn^{III} ($S = 2$) pair.

Magnetism and EPR Spectrum.—We have so far been unsuccessful in determining the three-dimensional X-ray structure of **1** owing to the poor quality of the single crystals obtained. We thus decided to study the temperature dependence of the magnetic susceptibility and EPR spectral behaviour to elucidate its electronic structure.

The antiferromagnetic coupling in **1** proposed from room-temperature solution magnetic moment data (see above) is confirmed by the variable-temperature magnetic susceptibility measurements (Faraday method) in the range 19.8–300 K on solid samples (Fig. 2). The effective magnetic moment decreases gradually from a value of 3.05 per dimer at room temperature to 1.98 at 19.8 K. The experimental data were fitted to the expression[19b] for an isotropic exchange interaction between Mn^{IV} ($S = \frac{3}{2}$) and Mn^{III} ($S = 2$) ions. The spin-exchange coupling constant J was found to be -144 cm^{-1} [$g = 2.0$ (fixed); t.i.p. $= 1.11 \times 10^{-3}$ cm^3 mol^{-1}; paramagnetic impurity as monomeric Mn^{III} $\approx 1\%$]. The observation of a large antiferromagnetic interaction in the present complex is consistent with the reported interactions in all known mixed-valence dimanganese(III,IV) complexes. The J value for **1** is comparable to that obtained by Armstrong and co-workers for a similar system with *N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethane-1,2-diamine as the terminal ligand.[13]

The frozen-solution EPR spectrum of **1** (Fig. 3) at 77 K exhibiting a sixteen-line ^{55}Mn hyperfine pattern centred near $g \approx 2.0$ is representative of binuclear Mn^{III,IV} systems[10] including the S_2 state of the manganese centre of PS II.[10] The

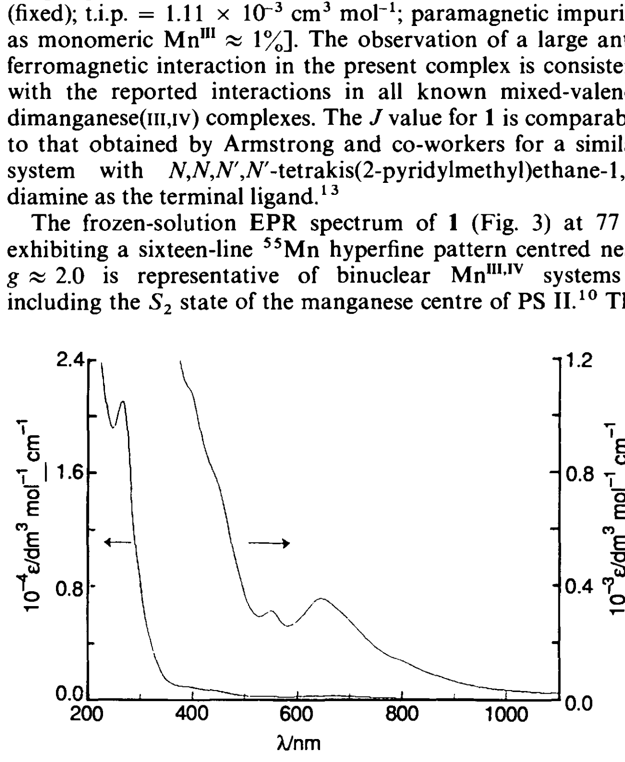

Fig. 1 Electronic spectrum of **1** in acetonitrile

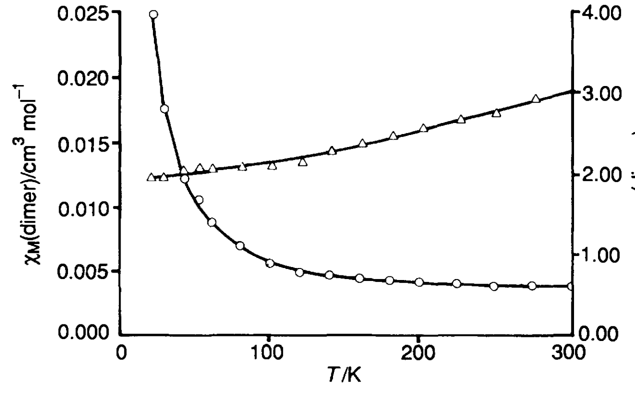

Fig. 2 Molar susceptibility (○) and effective magnetic moment per dimer (△) of **1** as a function of temperature. The solid lines are the theoretical fits using equation (1)

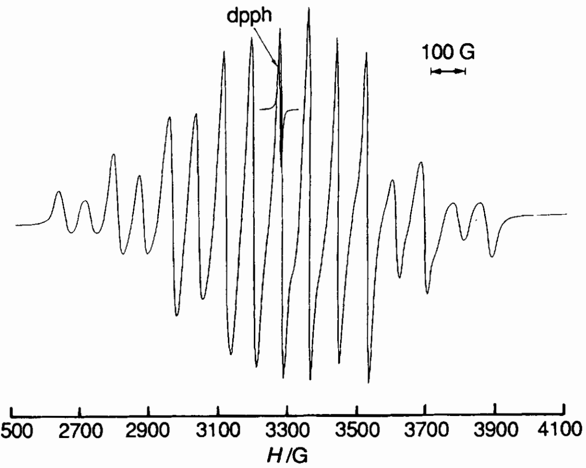

Fig. 3 X-Band EPR spectrum of **1** in dichloromethane at 77 K

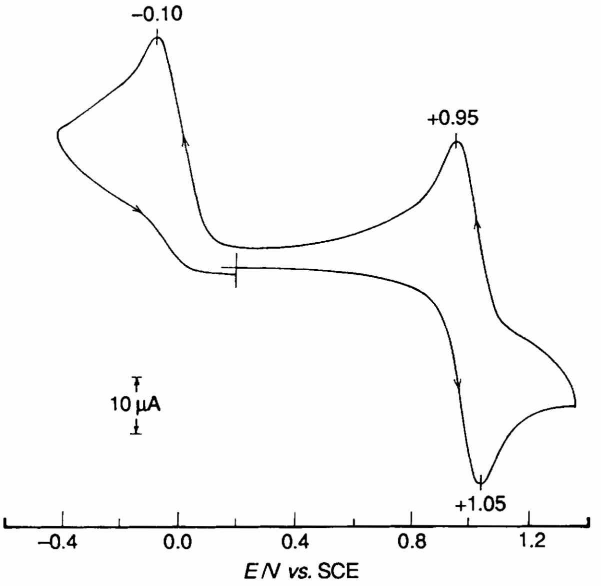

Fig. 4 Cyclic voltammogram (scan rate 50 mV s^{-1}) of a 10^{-3} mol dm^{-3} solution of **1** in MeCN (0.15 mol dm^{-3} $[NBu^n_4]ClO_4$) at a platinum working electrode

observed spectrum comes exclusively from the doublet ground state of two inequivalent manganese ions. The observed spectral pattern is indicative of a situation in which one of the ions has about twice the hyperfine coupling constant of the other.

Redox Properties.—An important test for the merit of any PS II model system is the thermodynamics of its redox reaction. The cyclic voltammogram of a 10^{-3} mol dm^{-3} MeCN solution of **1** in 0.15 mol dm^{-3} $[NBu^n_4]ClO_4$ shows (Fig. 4) a well-behaved quasi-reversible (ΔE_p = 100 mV, scan rate = 0.05 mV s^{-1})[14] oxidative response at 1.00 V and an irreversible reduction wave at −0.10 V *vs.* saturated calomel electrode (SCE). The $E_{\frac{1}{2}}$ value of 1.00 V corresponds to the one-electron Mn^{IV}_2–$Mn^{III}Mn^{IV}$ couple (see below) and the reduction wave is assigned to the $Mn^{III}Mn^{IV}$–Mn^{III}_2 couple. Interestingly, the $E_{\frac{1}{2}}$ value of the oxidative couple for **1** is identical to that of the $[Mn^{IV}(\mu\text{-}O)_2Mn^{III}]^{3+}$ species with 1,4,8,11-tetraazacyclotetradecane as the terminal ligand.[6] From the separation of $E_{\frac{1}{2}}$ (oxidative response) and $E_{\frac{1}{2}}$ [reductive response; as this is not a reversible response we have added 0.05 V to E_{pc} (cathodic peak potential)] values for **1**, the comproportionation constant (K_c at 25 °C) of reaction (2) is calculated to be 6.26×10^{17}, indicating that the mixed-valence complex is considerably stabilised with respect to the Mn^{III}_2 and Mn^{IV}_2 species. In fact complex **1** is the most stable species among all mixed-valence dimanganese(III,IV) complexes reported so far.[4e,5a,7,13] Of the three other compounds containing the $[Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)Mn^{III}]^{2+}$ core which have been synthesised previously, the redox behaviour of only one of these has been reported[13] and is similar to that found for **1**.

$$[Mn^{IV}\text{–}Mn^{IV}] + [Mn^{III}\text{–}Mn^{III}] \rightleftharpoons 2[Mn^{IV}\text{–}Mn^{III}] \quad (2)$$

Synthesis and Properties of $[Mn_2(\mu\text{-}O)_2(\mu\text{-}O_2CMe)L_2]^{3+}$.—Controlled-potential electrolysis at 1.24 V gave n = 0.92 for the net electrochemical oxidation of **1** generating the dimanganese(IV,IV) complex which is stable in MeCN solution. The orange solution of $[Mn^{IV}_2(\mu\text{-}O)_2(\mu\text{-}O_2CMe)L_2]^{3+}$ can also be generated chemically by oxidation of **1** with perchloric acid. The one-electron oxidised species displays an identical cyclic voltammogram to **1** (this time however, as expected, both the responses are reductive in nature). The absorption spectrum of the Mn^{IV}_2 species is less complex than that of the $Mn^{III}Mn^{IV}$ dimer, containing only one peak in the visible region at 620 nm ($\varepsilon \approx 400$ dm^3 mol^{-1} cm^{-1}). Unlike **1** the oxidised product showed no EPR spectrum at 77 K. Isolation of the Mn^{IV}_2 complex in the solid state thus far has been unsuccessful. This is for the first time that a stable Mn^{IV}_2 species containing the $[Mn^{IV}_2(\mu\text{-}O)_2(\mu\text{-}O_2CMe)]^{3+}$ core has been generated.

Conclusion

The fourth example of a complex containing a $[Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)Mn^{III}]^{2+}$ core has been reported. Complex **1** in its oxidised form appears especially attractive for use as a reagent for one-electron oxidations in non-aqueous media. Interestingly, the $E_{\frac{1}{2}}$ value for the oxidative couple is above the water-oxidation threshold. Since the release of four electrons is required for the formation of an oxygen molecule ($2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$), water oxidation[22] cannot be achieved if the oxidative process is not efficiently coupled, and the search for such systems is a principal aspect of our work. This is the first time that redox and spectral properties of a dimanganese(IV,IV) complex containing a bis(μ-oxo)(μ-acetato) core has been examined. The presence of the bridging acetate group in **1** gives us an opportunity to study ligand-exchange reactions at these sites. The results of such studies will be published elsewhere.

Acknowledgements

This work was supported by the Department of Science and Technology and the Council of Scientific and Industrial Research, New Delhi, India. Our thanks are also due to Professors A. Chakravorty and S. Mitra and Mr. B. T. Kansara for EPR and variable-temperature magnetic susceptibility measurements.

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Received 21*st August* 1992; *Paper* 2/04513C