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Synthesis, Characterization, and Novel Redox Properties of a New Triply Bridged Dimanganese(III) Complex with a $\{Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2\}^{2+}$ Core†

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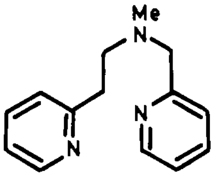
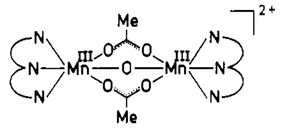
Oxo-bridged clusters of manganese[1,2] have been shown to occur in the active sites of the catalases, *pseudo*catalases, ribonucleotide reductases, and the photosynthetic water oxidation center. The synthetic complexes with structural units $\{Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2\}^{2+}$ [3–5] and $\{Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CCH_3)\}^{2+}$ [6,7] are of current interest since they are good models for these enzymes. It has been shown[3,4a,b,6a,8] that (μ-oxo)bis(μ-acetato)dimanganese(III) complexes could be oxidized by following two pathways: (i) sequential electrochemical oxidation to $Mn^{III}Mn^{IV}$ and Mn^{IV}_2 oxidation levels and (ii) chemical transformations to $\{Mn^{III}Mn^{IV}(\mu\text{-}O)(\mu\text{-}ac)_2\}^{3+}$ and $\{Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}ac)\}^{2+}$ species. It is interesting to note that while disproportionation of the $\{Mn^{III}Mn^{IV}(\mu\text{-}O)_2\}^{3+}$ core under acidic conditions has been postulated previously,[9,10] to our knowledge isolation of a $Mn^{III}_2(\mu\text{-}O)(\mu\text{-}ac)_2\}^{2+}$ species from a $\{Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}ac)\}^{2+}$ species has not so far been achieved.

We recently reported[7] an antiferromagnetically coupled dimanganese complex $[Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CMe)(MeL)_2](ClO_4)_2\cdot H_2O$ (**1**) using MeL as a facially capping ligand [MeL = (2-pyridylethyl)(2-pyridylmethyl)methylamine].[11] The present work originated from our search for $\{Mn^{III}_2(\mu\text{-}O)(\mu\text{-}ac)_2\}^{2+}$ species. When glacial acetic acid was added to the reaction medium conducive to the synthesis of **1**, formation of a dimanganese(III) complex $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2(MeL)_2](PF_6)_2\cdot H_2O$ (**2**) of the bridging type was noted. Here we present a novel oxidative transformation of $\{Mn^{III}_2(\mu\text{-}O)(\mu\text{-}ac)_2\}^{2+}$ to a lower potential species $\{Mn^{IV}_2(\mu\text{-}O)_2(\mu\text{-}ac)\}^{3+}$ via electrochemically generated $\{Mn^{III}Mn^{IV}(\mu\text{-}O)(\mu\text{-}ac)_2\}^{3+}$ species.



MeL



The synthetic reaction requires under dinitrogen atmosphere stirring of $Mn(O_2CCH_3)_3\cdot 2H_2O$ (400 mg, 1.49 mmol), NH_4PF_6 (243 mg, 1.49 mmol), and MeL (339 mg, 1.49 mmol) in MeCN (10 mL) for 2 h at 298 K. The product is isolated in 60% yield (by adding glacial acetic acid (3 mL) and ethyl acetate (10 mL) and allowing the mixture to stand for 24 h at 273 K) as purplish brown microcrystals.[12] The (μ-oxo)bis(μ-carboxylato)dimanganese(III) core formulation[14] seems reasonable, given the available characterization data.[12] In fact, the absorption spectral feature of **2** is similar to[3–5a,b] those of the related structurally characterized binuclear manganese(III) complexes with the $\{Mn^{III}_2(\mu\text{-}O)(\mu\text{-}ac)_2\}^{2+}$ chromophore.

In the temperature range 52–300 K molar magnetic susceptibilities and effective magnetic moments per manganese of powdered sample of **2** (4.91 μ_B/Mn at 300 K; 5.17 μ_B/Mn at 52

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† Dedicated to Professor Richard H. Holm on the occasion of his 60th birthday.

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(12) Satisfactory elemental analysis was obtained for **2** dried under vacuum. Anal. Calcd for $C_{32}H_{42}N_6O_6F_{12}P_2Mn_2$: C, 38.15; H, 4.17; N, 8.35. Found: C, 37.96; H, 4.10; N, 8.82. IR spectrum of **2** (KBr), mass spectra (FAB) of **1** and **2**, and absorption spectrum of **2** (MeCN) are in Figures S1–S3 (supplementary material). Conductivity measurements showed that it is a 1:2 electrolyte ($\Lambda_M = 293\ \Omega^{-1}\ mol^{-1}\ cm^2$ in MeCN).[13]

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(14) We have not succeeded so far in solving the X-ray structure of **2** since single crystals thus obtained have turned out to be twinned!

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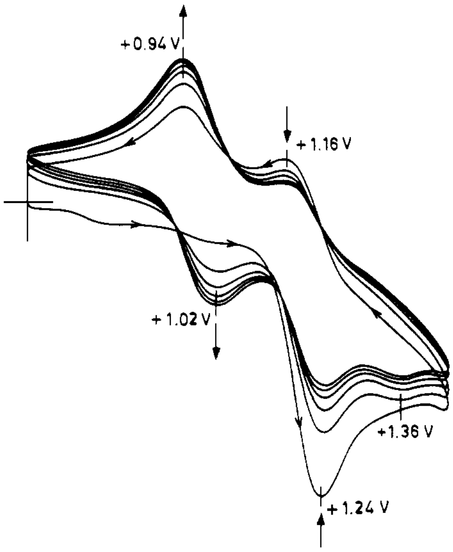

Figure 1. Repetitive scan cyclic voltammograms of **2** at a scan rate of 50 mV s^{-1}.

K) are consistent with two isolated[15] high-spin manganese(III) centers. This behavior is similar to that encountered with related binuclear manganese(III) systems.[3,4a,5c]

When examined by cyclic voltammetry[11] [MeCN; Pt electrode; vs SCE], **2** exhibits at a scan rate[17] of ≥1000 mV/s a reversible[11] oxidative response at 1.20 V and an irreversible reductive response at 0.00 V. The electrode reactions for **1**[7] and **2** are in eqs 1 and 2 and eqs 3 and 4, respectively. The CV results of **2** are comparable to those of the reported compounds of similar core unit.[3,4a,b,5b]

$$[\mathrm{Mn^{IV}}_2(\mu\text{-O})_2(\mu\text{-ac})(\mathrm{MeL})_2]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})_2(\mu\text{-ac})(\mathrm{MeL})_2]^{2+} \quad (E_{1/2} = 1.00\ \mathrm{V}) \quad (1)$$

$$[\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})_2(\mu\text{-ac})(\mathrm{MeL})_2]^{2+} \xrightarrow{+e^-} [\mathrm{Mn^{III}}_2(\mu\text{-O})_2(\mu\text{-ac})(\mathrm{MeL})_2]^{1+} \quad (E_{\mathrm{p,c}} = -0.10\ \mathrm{V}) \quad (2)$$

$$[\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})(\mu\text{-ac})_2(\mathrm{MeL})_2]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Mn^{III}}_2(\mu\text{-O})(\mu\text{-ac})_2(\mathrm{MeL})_2]^{2+} \quad (E_{1/2} = 1.20\ \mathrm{V}) \quad (3)$$

$$[\mathrm{Mn^{III}}_2(\mu\text{-O})(\mu\text{-ac})_2(\mathrm{MeL})_2]^{2+} \xrightarrow{+e^-} [\mathrm{Mn^{III}Mn^{II}}(\mu\text{-O})(\mu\text{-ac})_2(\mathrm{MeL})_2]^{1+} \quad (E_{\mathrm{p,c}} = 0.00\ \mathrm{V}) \quad (4)$$

An estimate of the thermodynamic stability of **2** can be easily obtained from the comproportionation constant (K_{com} at 298 K; ~1.0 × 10^{21})[18] of reaction 5.

$$[\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})(\mu\text{-ac})_2(\mathrm{MeL})_2]^{3+} + [\mathrm{Mn^{III}Mn^{II}}(\mu\text{-O})(\mu\text{-ac})_2(\mathrm{MeL})_2]^{+} \rightleftharpoons 2[\mathrm{Mn^{III}}_2(\mu\text{-O})(\mu\text{-ac})_2(\mathrm{MeL})_2]^{2+} \quad (5)$$

For **2** on repetitive scanning of the potential between the limits 0.60–1.50 V, at the expense of the higher potential response (eq 3) a new redox wave (eq 1) is being formed (Figure 1). If after holding the potential at 1.50 V for 30 s (in order to oxidize all of the manganese(III) complex in the double layer) scanning (at 50 mV/s scan rate) is done cathodically up to 0.60 V, an identical behavior is observed (Figure S4, supplementary material). It is to be noted that in both Figures 1 and S4, an additional irreversible response is observed at 1.36 V which is associated with the formation of the lower potential response. On scanning of the potential further down to –0.40 V, two irreversible reductive responses corresponding to electrode processes (eqs 2 and 4) are observed (Figure S4).

The above two experiments point toward redox transformation of **2** to the one-electron oxidized form of **1** under oxidative conditions. This is a clear case of an ECE mechanism[19,20] where removal of the second electron occurs with greater facility than removal of the first (compare eqs 1 and 3). Thus, as the potential scanning is made up to the oxidative couple of **2** (eq 3), $[\mathrm{Mn^{III}}_2(\mu\text{-O})(\mu\text{-ac})_2(\mathrm{MeL})_2]^{2+}$ is oxidized to $[\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})(\mu\text{-ac})_2(\mathrm{MeL})_2]^{3+}$, which in turn transforms[21] to $[\mathrm{Mn^{IV}}_2(\mu\text{-O})_2(\mu\text{-ac})(\mathrm{MeL})_2]^{3+}$. The same reasoning holds good for the results in Figure S4. The species generated after two-electron coulometric oxidation[21] of **2**, $[\mathrm{Mn^{IV}}_2(\mu\text{-O})_2(\mu\text{-ac})(\mathrm{MeL})_2]^{3+}$, has been confirmed by its redox behavior when compared with[7] that obtained from the chemically or coulometrically oxidized form of **1**.

An interesting observation of the present work is the transformation of **1** to **2** brought about by glacial acetic acid (the synthetic reaction). Controlled experiments suggest the mechanism of this reaction is as shown in eqs 6[22] and 7. The manganese(IV) dimer thus generated[24] decomposes under the reaction conditions. In essence, the synthesis of $[\mathrm{Mn^{III}}_2(\mu\text{-O})(\mu\text{-ac})_2(\mathrm{MeL})_2]^{2+}$ has been achieved by the reaction between glacial acetic acid and $[\mathrm{Mn^{III}Mn^{IV}}_2(\mu\text{-O})_2(\mu\text{-ac})(\mathrm{MeL})_2]^{2+}$ following a disproportionation reaction.

$$[\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})_2(\mu\text{-O_2CCH_3})(\mathrm{MeL})_2]^{2+} + \mathrm{CH_3CO_2H} \rightleftharpoons [\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})(\mu\text{-OH})(\mu\text{-O_2CCH_3})(\mathrm{MeL})_2]^{3+} + \mathrm{CH_3CO_2^-} \quad (6)$$

$$[\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})(\mu\text{-OH})(\mu\text{-O_2CCH_3})(\mathrm{MeL})_2]^{3+} + [\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})_2(\mu\text{-O_2CCH_3})(\mathrm{MeL})_2]^{2+} \xrightarrow[-\mathrm{OH^-}]{+\mathrm{CH_3CO_2^-}} [\mathrm{Mn^{III}}_2(\mu\text{-O})(\mu\text{-O_2CCH_3})_2(\mathrm{MeL})_2]^{2+} + [\mathrm{Mn^{IV}}_2(\mu\text{-O})_2(\mu\text{-O_2CCH_3})(\mathrm{MeL})_2]^{3+} \quad (7)$$

The structures of **1**, **2**, and the $\mathrm{Mn^{IV}}_2$ species and their redox interconversion properties are now under investigation.

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Supplementary Material Available: Figures S1–S4, showing a segmented IR spectrum of **2**, FAB mass spectra of **1** and **2**, absorption spectrum of **2**, and a cyclic voltammogram of **2**, and a table of magnetic susceptibility data for **2** (6 pages). Ordering information is given on any current masthead page.

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[15] The magnetic data adhere closely to the Curie–Weiss law (μ = 5.03 μ_B; Θ = –9.92 K; correlation coefficient = 0.9992). When the experimental χ_M^{-1} vs T data were fitted to the appropriate expression[16] for Mn^{III}–Mn^{III} (S = 2/S = 2) pairs, only very weak ferromagnetic exchange coupling (~+1 cm^{-1}) was obtained.

[16] O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

[17] When the potential scan rates were in the range 20–500 mV/s, after initial anodic scanning to monitor the oxidative response at 1.20 V during cathodic scan an additional ill-defined wave was observed at 0.94 V.

[18] The anodic wave for the reductive response of **2** was not observed on scan reversal: the $E_{1/2}$ value is a rough estimate (cathodic peak potential +40 mV[11]).

[19] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980.

[20] The chemical reaction after removal of the first electron from **2** could be as follows:

$$[\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})(\mu\text{-O_2CMe})_2(\mathrm{MeL})_2]^{3+} \xrightarrow[-\mathrm{MeCO_2H},\,-\mathrm{H^+}]{+\mathrm{H_2O}} [\mathrm{Mn^{III}Mn^{IV}}(\mu\text{-O})_2(\mu\text{-O_2CMe})(\mathrm{MeL})_2]^{2+}$$

[21] In fact, coulometric oxidation of **2** at 1.50 V gives rise to an effective 2-e$^-$ transfer. For complete oxidation (at 1.50 V) of 5.29 × 10^{-6} mol of **2**, 0.99 C was observed. The value calculated for n = 2 is 1.02 C.

[22] The protonation of a bridging oxo group would make the Mn^{III}Mn^{IV} complex a much stronger[23] oxidant (irreversible oxidation at 1.36 V (in Figures 1 and S4).

[23] Thorp, H. H.; Sarneski, J. E.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 9249.

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