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Formation of a high valent di-μ-oxo manganese dimer in aqueous solution

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Abstract

We find an unusual example in which different clusters can be isolated from the same reaction mixture depending on the choice of counter-ion. The complex $[(bipy)_2Mn(III)(\mu\text{-}O)_2Mn(IV)(bipy)_2]^{3+}$ (**1**) (bipy = 2,2′-dipyridyl) is isolated from Mn(II) and permanganate in acetate buffer with ClO_4^-, but $[(bipy)(H_2O)Mn(III)(\mu\text{-}O)(\mu\text{-}OAc)_2Mn(III)(bipy)(H_2O)]^{2+}$ (**2**) with NO_3^-. $1e^-/2H^+$ or $1e^-/1H^+$ proton-coupled electron transfer chemistry is found for **2** according to the type of buffer used. The new complex $[(bipy)(H_2O)Mn(III)(\mu\text{-}O)_2(\mu\text{-}OAc)Mn(IV)(bipy)(H_2O)]^{2+}$ (**3**) is also postulated as an intermediate in the formation of **1**.

Introduction

A striking feature of the chemistry of the higher valence states of Mn is the unexpected facility of the ligand redistribution and metal redox reactions that can take place. This means that a species that is isolated and crystallographically characterized from a reaction mixture may be only a minor species in that solution. The species isolated may depend on the counter-ion used if changing the counter-ion alters the relative solubilities of two species. For example, $[(bipy)_2Mn(III)(\mu\text{-}O)_2Mn(IV)(bipy)_2]^{3+}$ (**1**) (bipy = 2,2′-dipyridyl) is isolated [1] from solutions containing $Mn(II)/MnO_4^-/AcO^-$ and dipyridyl (bipy) with ClO_4^- as counter-ion. Previously, Ménage *et al.* [2] reported a synthesis of $[(bipy)(H_2O)Mn(III)(\mu\text{-}O)(\mu\text{-}OAc)_2Mn(III)(bipy)(H_2O)]^{2+}$ (**2**) which involved a different procedure from the synthesis of **1** [2]. But we find that **2** can be isolated from the reaction mixture involved in the synthesis of **1** by addition of NO_3^- to the reaction mixture.

In studies related to modeling the Mn_4 cluster of the oxygen evolving center (OEC) of Photosystem II, we have been looking at species of this sort in some detail to try to develop syntheses of higher nuclearity Mn clusters relevant to the OEC [3, 4]. In the buildup of the Mn_2 cluster of **1**, the acetate bridged cluster **2** may be an intermediate. The uninegative acetates appear to stabilize Mn(IV) less well than the dinegative oxo groups. Logically it seemed as if there might be an intermediate with a higher oxo:acetate ratio between **2** and **1**, and that this might be a III,IV species like **1**. In this paper we describe the observation of such an intermediate and conditions under which this intermediate is stable.

Experimental

The procedure of Cooper and Calvin [1] was followed for the synthesis of **1**. The synthesis of **2** was essentially the same as for **1** but NO_3^- was used as a counter-ion instead of ClO_4^-. *Anal.* Calc. for $C_{24}H_{36}N_6O_{18}Mn_2$: C, 35.74; H, 4.50; N, 10.42; Mn, 13.62. Found: C, 35.86; H, 4.52; N, 10.11; Mn, 13.42%. The nitrate salt **2** is isolated as a pentahydrate. The chemical microanalysis was conducted by Galbraith Labs., Inc. Knoxville, TN (USA). Electrochemistry was carried out on a PAR 273 instrument. The concentration of **2** in the solutions was ~1–2 mM. The solutions were buffered in either 0.1 M acetate, 0.1 M phosphate or 0.05 M bipy buffer. A typical three electrode cell was employed with a polished glassy carbon working electrode, Pt wire auxiliary electrode and a saturated calomel electrode as reference. The working electrode was activated as described elsewhere [5]. UV–Vis measurements were carried out on a Perkin–Elmer 283 spectrophotometer. IR spectra were recorded on a Nicolet 5-SX FT-IR system. Pellets were made in dehydrated KBr.

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Results and discussion

Chemical studies

The formation of **1** from the aqueous solutions containing Mn(II), acetate and Mn(VII) seems to go via the formation of a di-μ-acetato complex, **2**. Previously, a separate procedure for the preparation of **2** was reported [2]. We find that in the synthesis of **1** addition of NO_3^- as a counter-ion precipitates **2** quantitatively. This procedure offers evidence for **2** being present as an intermediate in the formation of **1**. This is an unusual example of a reaction product being determined by the counter-ion used. In each case, the least-soluble cluster precipitates but the solubility is determined by the anion used.

Christou [6] has shown that Me_3SiCl is a useful reagent for abstracting acetate bridges. We find that the reaction of **2** with Me_3SiCl yields the known di-μ-oxo dimer, **1**. The UV–Vis spectrum shows characteristic bands at 684 and 550 nm for **1** [1]. In addition, in the presence of excess bipy, **2** yields **1** as detected by UV–Vis and IR (1632, 1447, 1080, 1040, 768, 688, 668, 621 cm^{-1}) [1].

An alternate reagent for acetate abstraction, NEt_3, gave only MnO_2, however, so the success of Wieghardt *et al.* with the corresponding tacn and Me_3tacn systems [7] depends for its success on the presence of the tridentate tacn ligands. Also, the dimer formed contained a $(\mu\text{-oxo})_3$ bridge [7]. This would imply that the formation of a di-μ-oxo dimer species proceeds via another intermediate bridged complex. To further investigate the aqueous chemistry of **2** in different buffers under electrolytic conditions, cyclic voltammetry was conducted.

Electrochemical studies

Only broad waves are observed in the cyclic voltammogram (CV) for **2** in MeCN, so we moved to aqueous solution, where sharper, better-resolved waves were seen in phosphate, acetate or bipy buffers. We have previously [8–10] obtained useful information from the pH dependence of the potentials of di-μ-oxo complexes. Mn oxo clusters of this sort tend to undergo proton-coupled electron transfer (PCET) in which reduction of the metal is accompanied by protonation of a μ-oxo group and oxidation by deprotonation of a μ-OH group. There is only one couple observed in the CV of **2** in acetate buffer (Fig. 1). We see a 120 mV/pH dependence of the potential (E_0) which indicates that the $1e^-/2H^+$ proton-coupled electron transfer (PCET) process is involved (Fig. 2). Zero current potential (ZCP) studies confirm that the starting oxidation state is (III,III) (data not shown). The strong implication is that the process shown in eqn. (1) is taking place, in which the proton source is the coordinated water, and two not one protons are lost because this water becomes a doubly deprotonated μ-oxo in the product **3**.

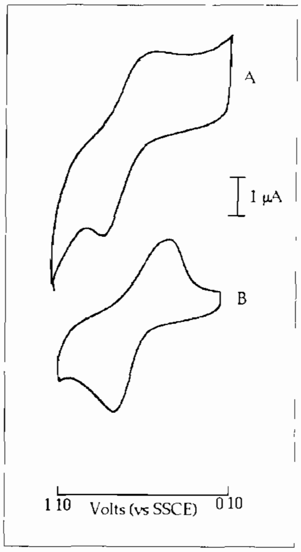

Fig. 1. Cyclic voltammogram of $[Mn_2III,III(O)(OAc)_2(H_2O)_2(bipy)_2]^{2+}$ (**2**): (A) in 0.1 M phosphate buffer (pH = 4.25); (B) in 0.1 M acetate buffer (pH = 3.95).

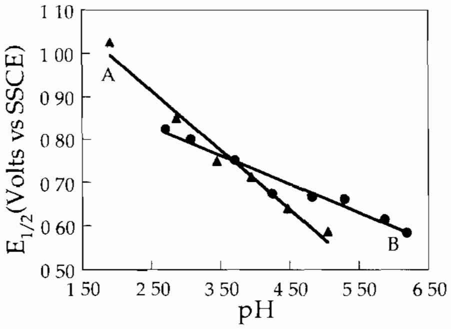

Fig. 2. Pourbaix diagram for $[Mn_2III,III(O)(OAc)_2(H_2O)_2(bipy)_2]^{2+}$ (**2**) in: (A) 0.1 M acetate buffer with slope = 0.12 V/pH; (B) 0.1 M phosphate buffer with slope = 0.069 V/pH Scan rate = 50 mV/s.

$$
\begin{aligned}
&[(bipy)(H_2O)Mn(III)(\mu\text{-}O)(\mu\text{-}OAc)_2\\
&\quad Mn(III)(bipy)(H_2O)]^{2+} + H_2O \longrightarrow\\
&\qquad\qquad [(bipy)(H_2O)Mn(III)(\mu\text{-}O)_2(\mu\text{-}OAc)\\
&\quad Mn(IV)(bipy)(H_2O)]^{2+} + e^- + 2H^+ + AcO^- \qquad (1)
\end{aligned}
$$

In phosphate or bipy buffer, the situation is different. Two waves are seen at 700 and 0 mV (versus SCE), respectively. The peak at 700 mV is assigned to the (III,III) to (III,IV) oxidation (Fig. 1), based on comparison with the CV of the pure (III,IV) dimer **1** [8, 11]. The peak at 0 mV is assigned to the oxidation of the Mn(II) species [11]. The pH dependence of 70 mV/pH suggests a $1e^-/1H^+$ PCET process (Fig. 3) that we assign to eqn. (2).

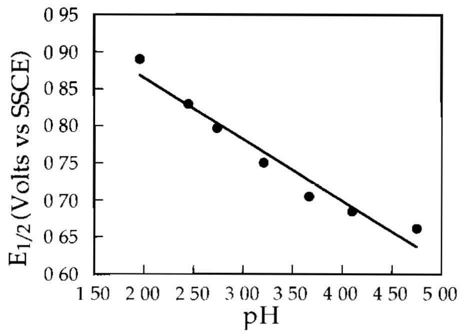

Fig. 3. Pourbaix diagram for $[Mn_2III,III(O)(OAc)_2(H_2O)_2(bipy)_2]^{2+}$ (2) in 0.05 M bipy buffer. Slope = 0.08 v/pH.

$$\begin{aligned}&[(bipy)_2Mn(III)(\mu\text{-}O)_2\\&\quad Mn(IV)(bipy)_2]^{3+} + e^- + H^+ \longrightarrow\\&[(bipy)_2Mn(III)(\mu\text{-}O)\text{-}(\mu\text{-}OH)Mn(III)(bipy)_2]^{3+}\end{aligned} \quad (2)$$

In phosphate or bipy buffer, the complex **2** disproportionates spontaneously via eqn. (3) to give **1** and the CVs observed are those of complex **1**.

$$\begin{aligned}&3[(bipy)(H_2O)Mn(III)(\mu\text{-}O)\text{-}(\mu\text{-}OAc)_2\\&\quad Mn(III)(bipy)(H_2O)]^{2+} + H_2O + 2bpy \longrightarrow\\&\qquad 2[(bipy)_2Mn(III)(\mu\text{-}O)_2Mn(IV)(bipy)_2]^{3+}\\&\quad + 2Mn(II) + 6AcO^- + 2H^+\end{aligned} \quad (3)$$

These results for **2** can be compared to those previously published [11] for $[Mn(III)(bipy)(H_2PO_4)(HPO_4)]_x$ (**4**), which also disproportionates in an analogous way, but $[(bipy)(H_2PO_4)Mn(IV)(\mu\text{-}O)_2(\mu_2\text{-}HPO_4)Mn(IV)(bipy)(H_2PO_4)]$ (**5**), behaves in a similar fashion in phosphate buffer [11] to **2** in acetate buffer. In these cases, an electrolytic step, reduction or oxidation, is needed to carry out the chemistry and we do not see a spontaneous disproportionation. It may be noted that the electrolytic processes involved in these reactions are occurring at the electrode surface and, thus, do not necessarily imply that the bulk solution is also undergoing a similar transformation [11]. Bulk electrolysis of **2** in acetate buffer failed to produce **3** in measurable quantities, MnO_2 was formed instead.

Conclusions

We see an unusual anion dependence on the product formed from Mn(II) and a permanganate in acetate buffer: **1** with ClO_4^- and **2** with NO_3^-. The role of the acetate seems to be to bring the dimer unit together. The acetate subsequently departs to be replaced by the $(\mu\text{-}O)_2$ group of **1**. In previous cases, we have found that phosphate forms a stable (μ-phosphato) complex [12], so the facile decomplexation of acetate is important. We find several examples of PCET, including the unusual $1e^-/2H^+$ process of eqn. (1). Thus, **3** is only generated electrochemically from **2** in acetate buffer whereas in the presence of other buffers it yields **1** as a thermodynamically stable product.

Acknowledgements

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