Synthesis and Properties of Two Bimetallic Mixed-Valence Di-μ-oxo Manganese Complexes with Different Tetra-aza Macrocyclic Ligands

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Mixed-valence di-μ-oxo complexes of the form $[LMnO]_2(ClO_4)_3$ (L = 1,4,8,11-tetra-azacyclotetradecane or 1,4,7,10-tetra-azacyclododecane) have been synthesized; their electrochemical properties in 1.5% water–acetonitrile indicate that the oxidized forms interact with water.

Our interest in compounds involving cyclic aliphatic amines and manganese ions is based on their potential use as homogeneous, multiple-electron redox catalysts, particularly for the oxidation of water to molecular oxygen. The dioxygen-evolving site of photosystem II has manganese ions in close proximity to one another. It is thought that oxygen and/or nitrogen are the atoms attached to the metal.[1] Reaction of either 1,4,8,11-tetra-azacyclotetradecane (cyclam) or 1,4,7,10-tetra-azacyclododecane (cyclen) with manganese(2+) ions in the presence of dioxygen yields Mn^{III}–Mn^{IV} mixed-valence dimers. These species, especially the complex containing the twelve-membered macrocyclic ligand (cyclen), are reasonably inert in aqueous solution in air; the cyclen complex is essentially unchanged after 24 h at pH 7. These properties are in marked contrast to those of mixed-valence Mn di-μ-oxo dimers (*e.g.* containing bipyridyl) previously reported.[2] The macrocycle effect present in a tetraco-ordinate ligand may contribute to this stability.[3] The complexes were prepared by air oxidation of an aqueous solution containing ligand and $Mn(ClO_4)_2$. After several days a green microcrystalline product was obtained which was collected by vacuum filtration and washed with diethyl ether to remove excess of water. (**Caution**: The solid explodes upon heating.) Both the cyclam and cyclen products give analytical figures in accord with $[LMnO]_2(ClO_4)_3 \cdot 2H_2O$.

Spectroscopic evidence supports identification of the two complexes as di-μ-oxo bridged species. The i.r. spectra show bands in the region expected for an oxo bridge between Mn^{III} and Mn^{IV}[3] (cyclam 680 cm^{-1}; cyclen 689 cm^{-1}). The *X*-band e.p.r. spectra of the cyclam and cyclen complexes in 2:1 ethylene glycol–water glasses at 8 K both exhibit 16 lines centred at *g* 1.99. Both spectra are very similar to that of the well characterized $[(bpy)_2MnO]_2^{3+}$ dimer.[4]

Preliminary *X*-ray data[5] confirm that the cyclen complex is a di-μ-oxo species and has very nearly octahedral geometry around the manganese. Initial results show crystallographically equivalent manganese atoms, but final refinement has been difficult. We think this difficulty is due to disorder of the Mn^{III}, Mn^{IV} centres in the crystal lattice. A similar situation has been observed for the *o*-phenanthrolinemanganese di-μ-oxo dimer.[6]

Although the i.r. and low-temperature e.p.r. spectra of the cylam and cyclen complexes show great similarity, the visible spectra in water are significantly different. Both the cyclam and cyclen dimers exhibit a d-d band characteristic of Mn^{III} ($\lambda_{max.}$ 550 nm, ε 760 $dm^3\ mol^{-1}\ cm^{-1}$ cyclam; $\lambda_{max.}$ 556 nm, ε 700 $dm^3\ mol^{-1}\ cm^{-1}$ for cyclen). Also, both complexes show a broad band at 650 nm (ε 780 for cyclam, 890 $dm^3\ mol^{-1}\ cm^{-1}$ for cyclen) tailing into the near i.r. These bands are similar to those observed previously for $[L_2MnO]_2(ClO_4)_3$ (where L = 2,2′-bipyridine or 1,10-phenanthroline).[3] The cyclen complex has a more dominant feature at lower energy ($\lambda_{max.}$ 740 nm, ε 880 $dm^3\ mol^{-1}\ cm^{-1}$), of uncertain origin. It is possible that the cyclen complex is partially protonated in aqueous solution, forming a μ-hydroxo-μ-oxo complex.[7] This band at 740 nm is not due to decomposition; the cyclic voltammograms show no such evidence.

The cyclic voltammogram of the cyclam complex in rigorously dry acetonitrile is shown in Figure 1. For both complexes reduction from the III, IV to the III, III level and oxidation to the IV, IV level are reversible (ΔE_p 59 mV). The $E_{1/2}$ value for the first reduction of the cyclam complex is −0.35 V, and for the cyclen complex is −0.20 V; the $E_{1/2}$ values for the first oxidation are +0.65 and +0.55 V, respectively.‡ Thus, the cyclen complex is both easier to oxidize and easier to reduce than the cyclam complex. The electrochemical properties may be influenced by steric factors such as the ability of one of the macrocycles to accommodate a larger metal centre more easily. Attempts to grow suitable

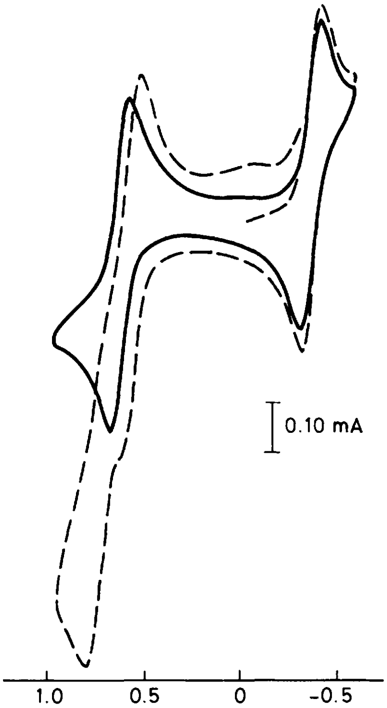

Figure 1. Cyclic voltammogram of $[(cyclam)MnO]_2(ClO_4)_3$ at 100 mV s^{-1} at a glassy carbon disc electrode with 0.1 M $Bu^n{}_4NPF_6$ as supporting electrolyte; ref. to Ag/Ag⁺. Solid line dry MeCN, dashed line 1.5% v/v H_2O–MeCN.

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‡ For our Ag/Ag⁺ reference electrode: *E vs.* normal hydrogen electrode(n.h.e.) = 0.57 V + *E vs.* Ag/Ag⁺; *E vs.* saturated calomel electrode(s.c.e.) = 0.35 V + *E vs.* Ag/Ag⁺.

crystals of the cyclam complex for *X*-ray analysis are in progress.[5]

The dashed line in the cyclic voltammogram of the cyclam complex (Figure 1) represents the electrochemical behaviour when water is added to the acetonitrile solution to make it 1.5% v/v water–acetonitrile. The oxidative peak current ($i_p{}^a$) for the wave at +0.70 V has increased substantially. In the absence of the manganese complex, the cyclic voltammogram of the mixed solvent does not show peaks in this region. For the complex, $[(\text{cyclam})\text{MnO}]_2{}^{3+}$, plots of the peak current *v.s.* water concentration and peak current *versus* (scan rate)$^{1/2}$ (Ilkovic equation) are indicative of an *ECE* mechanism.[8] The first electrochemical step apparently involves the oxidation of the III, IV complex to the IV, IV level. The effect of water in the subsequent chemical step is to produce a species which has an equal or lower oxidation potential than the III, IV complex. The product of the chemical step is then oxidized in the final electrochemical process. Thus, the observed peak current is substantially larger than that expected for a one-electron oxidation of the manganese complex. The cyclic voltammograms are consistent with water being oxidized in the chemical step at the electrode.

Elemental analysis and i.r., visible, and e.p.r., spectroscopic data all support the formulation of the two macrocyclic manganese complexes as di-μ-oxo Mn^{III}, Mn^{IV} species. Differences in oxidation potentials and in electronic spectra indicate that changing from a fourteen- to a twelve-membered macrocycle has a marked effect on the properties of these complexes, most interestingly their interaction with water. We plan therefore to investigate the eleven-, thirteen-, and fifteen-membered macrocycles as ligands, as well as the effect of water on electrochemical properties.

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