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

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The mixed-valence di- μ -oxo complexes of the form $[\text{LMnO}]_2(\text{ClO}_4)_3$ (L = 1,4,8,11-tetraazacyclotetradecane or 1,4,7,10-tetraazacyclododecane) have been synthesized, various of their spectroscopic and structural properties are outlined, and their electrochemical properties indicate that in their oxidized forms they interact with water.

Our interest in compounds involving aliphatic cyclic 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 of attachment to the metal.¹ Reaction of either 1,4,8,11-tetraazacyclotetradecane (cyclam) or 1,4,7,10-tetraazacyclododecane (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 12-member macrocyclic

ligand (cyclen), are reasonably inert in aqueous solution in air; the cyclen complex is essentially unchanged after 24 hours at pH 7. This property is in marked contrast to mixed-valence Mn di- μ -oxo dimers (e.c. containing bipyridyl) previously reported in the literature.² The macrocycle effect present in a tetracoordinate ligand may contribute to this stability.³ Under similar synthetic conditions the linear triethylenetetraamine does not form stable manganese complexes. We observe that the cyclam and cyclen dimeric species exhibit unusual electrochemical properties in acetonitrile when water is added. Both dimers apparently interact with water when they are oxidized above the III-IV level.

The complexes were prepared as follows. A solution of 0.42 g (2.1 mmols) of cyclam in 10 mL of water was added to a solution of 0.73 g (2.9 mmols) of $\text{Mn}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ in 8 mL of water. A small quantity of reddish-brown hydrous manganese oxide formed and was removed by vacuum filtration. The resulting yellow-brown solution was allowed to remain undisturbed in contact with the atmosphere for several days. A green microcrystalline product forms which was collected by vacuum filtration and washed with diethyl ether to remove excess water. (CAUTION: The solid explodes upon heating. Perchlorate salts are often explosive under such conditions as mild shock or heat.) The green microcrystalline product analyses well for $[(\text{Cyclam})\text{MnO}]_2(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$. An analogous procedure was used for the preparation of the cyclen complex, $[(\text{Cyclen})\text{MnO}]_2(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$. A slight variation is needed since the cyclen ligand is used as the hydrochloride salt. The pH must be adjusted from ca. 2.3 to 6.8 after the addition of the metal salt to the solution containing the ligand. Also, no reddish-brown precipitate is

formed, and thus no filtration step is needed until the final isolation of the product of interest.

Various characteristics of the two complexes reported herein and of the previously reported bipyridine and phenanthroline analogues are compared below.

The infrared spectra of the two complexes support the assignment of a di- μ -oxo bridged dimer. The cyclam dimer has a band at 680 cm^{-1} , which is split as expected into two bands at 680 and 670 cm^{-1} when the synthesis is performed in 53% atom ^{18}O -labelled water. This is very similar to the behaviour of the well characterised $[(\text{bpy})_2\text{MnO}]_2^{3+}$ (bpy = 2,2'-bipyridine).³ The cyclen dimer also has a strong band at 689 cm^{-1} .

The X-band EPR spectra of the cyclam and cyclen complexes were both taken in 2:1 ethylene glycol:water glasses at 8°K . Both species exhibit a 16-line spectrum centered at $g = 2$. These spectra are again very similar to that of the bpy Mn(III,IV)di- μ -oxo dimer⁴ and are attributed to overlap of hyperfine splitting with two chemically different Mn nuclei ($I = 5/2$), one hyperfine coupling constant being roughly twice the magnitude of the other. A similar 16-line spectrum is seen at 8°K for photosystem II.⁵

Preliminary X-ray data 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) centers in the crystal lattice. A similar situation has been observed for the o-phenanthroline manganese di- μ -oxo dimer.⁶

While the IR and low temperature EPR spectra of the cyclam and cyclen complexes show great similarity, the visible spectra in water are significantly different. Figure 1 illustrates the visible and near infrared spectra of the cyclam and cyclen complexes. Both the cyclam and cyclen dimers exhibit a d-d band characteristic of Mn(III) ($\lambda_{\text{max}} = 550 \text{ nm}$, $\epsilon = 760 \text{ M}^{-1} \text{ cm}^{-1}$ cyclam; $\lambda_{\text{max}} = 556 \text{ nm}$, $\epsilon = 700 \text{ M}^{-1} \text{ cm}^{-1}$ cyclen). Also, both complexes show a broad band at 650 nm ($\epsilon = 780 \text{ M}^{-1} \text{ cm}^{-1}$ cyclam, $\epsilon = 890 \text{ M}^{-1} \text{ cm}^{-1}$ cyclen) tailing into the near IR. This band is assigned as a ligand-to-metal charge transfer band (LMCT) from the oxygen to the Mn(IV). The tailing of this band into the near infrared can be explained as due to an intervalence transition between the Mn(III) and Mn(IV) centers which underlies the O to Mn charge transfer band. These assignments are comparable to the ones made previously for $[\text{L}_2\text{MnO}]_2(\text{ClO}_4)_3$ (where L = 2,2'-bipyridine or 1,10-phenanthroline).³ The cyclen complex has a more dominant feature at lower energy ($\lambda_{\text{max}} = 740 \text{ nm}$, $\epsilon = 880 \text{ M}^{-1} \text{ cm}^{-1}$). Assignment of this band is less certain. A possibility is that the cyclen complex may partially protonate in aqueous solution forming a μ -hydroxo- μ -oxo complex.⁷ This band at 740 nm in the cyclen complex is not due to decomposition since the cyclic voltammograms show no such evidence.

The cyclic voltammogram of the cyclam complex in rigorously dry acetonitrile is shown in Figure 2. For both complexes reduction of the III,IV dimer to the III,III level as well as oxidation to the IV,IV level are reversible ($\Delta E_p = 59 \text{ mV}$). The $E_{1/2}$ for the first reduction of the cyclam complex is -0.35 V and for the cyclen complex is -0.20 V

while the $E_{1/2}$ values for the first oxidation are +0.65 V and +0.55 V, respectively.⁸ Thus, the cyclen complex is both easier to oxidize and easier to reduce than the cyclam complex. The electro-chemical properties may be influenced by steric factors such as the ability of one of the macrocycles to accommodate a larger metal center more easily. Attempts to grow suitable crystals of the cyclam complex for X-ray analysis are currently in progress.

The dashed line in the cyclic voltammogram of the cyclam complex (Figure 2) represents the electrochemical behavior 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 volts 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 versus water concentration and peak current versus (scan rate)^{1/2} (Ilkovic equation) are indicative of an ECE mechanism.⁹ The first electro-chemical 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.

Elemental analysis, IR, VIS and EPR spectroscopic data all support 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 simply changing from a 14-member to a

12-member macrocycle has a marked effect on the properties of these complexes, most interestingly their interaction with water. Hence we plan to investigate the 11-, 13-, and 15-member macrocycles as ligands, as well as the effect of water on electrochemical properties.

Acknowledgements

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Figure Captions

- Fig. 1 Electronic Spectra for $[(\text{Cyclam})\text{MnO}]_2(\text{ClO}_4)_3$ — and $[(\text{Cyclen})\text{MnO}]_2(\text{ClO}_4)_3$ - - - in water.
- Fig. 2. Cyclic Voltammogram of $[(\text{Cyclam})\text{MnO}]_2(\text{ClO}_4)_3$ at 100mV/sec at a Glassy Carbon Disk Electrode with 0.1 M $(n\text{-Bu})_4\text{NPF}_6$ as Supporting Electrolyte, References to Ag/Ag^+ CH_3CN . Solid Line Dry CH_3CN , Dashed Line 1.5% V:V H_2O , CH_3CN .

Fig. 1

Fig. 2

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