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Synthesis, Structure, and Characterization of a Mixed-Valence Manganese(III)–Manganese(IV) Bis(μ-oxo) Complex with a Macrocyclic Tetraaza Ligand

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The complex $[(14\text{-aneN}_4)\text{MnO}]_2^{3+}$ (14-aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane) has been prepared and characterized. The crystal structure of this mixed-valence (III,IV) compound shows discrete Mn(III) and Mn(IV) centers. Comparison of our crystallographic data with the data for the three previously reported Mn(III)–Mn(IV) bis(μ-oxo) complexes indicates that while the external ligands are varied, the Mn–O distances in the Mn_2O_2 core remain relatively unchanged (±0.03 Å). The X-band EPR experiments at 4 K exhibit a 16-line spectrum centered at $g = 2$. This 16-line spectrum is attributed to the overlap of hyperfine splitting with two chemically different Mn nuclei ($I = {}^5/_2$) with one hyperfine coupling constant being roughly twice the magnitude of the other. This complex is a Robin and Day class II mixed-valence species. Detailed studies of the formation of this binuclear Mn species indicate that the bridging oxygens come from solvent water and that the bridge formation occurs with both manganese ions in the III oxidation state. Cyclic voltammetry of the complex exhibits a reversible one-electron oxidation ($E_{1/2} = +1.0$ V vs SCE) to the IV,IV level as well as a reversible one-electron reduction ($E_{1/2} = -0.12$ V vs SCE) to the III,III level. Spectroelectrochemical experiments have been performed that help to establish the assignments of the electronic spectrum of the III,IV complex. The III,IV complex exhibits three main absorption maxima in the visible region (λ_{max}^{abs} = 538 (sh), 550, 650 nm) as well as a tail that extends into the near-infrared region. The bands at 538 and 550 nm are assigned to d–d transitions involving the Mn(IV) and Mn(III) centers, respectively. The band at 650 nm is assigned to a ligand-to-metal charge-transfer transition, oxo → Mn(IV). The tail into the near-infrared region is due to an intervalence transition, which underlies the intense 650-nm charge-transfer band. Complexes such as **1** are of interest as models for multiple-electron redox catalysts like the oxygen-evolving complex (OEC) in photosystem II.

Introduction

A dominant feature of the inorganic chemistry of manganese is the variety of complexes that can be made with different oxidation levels of the manganese. Complexes have been prepared that contain manganese in the 3−, 2−, 1−, 0, 1+, 2+, 3+, 4+, 5+, 6+, and 7+ oxidation states.[1] Living systems have utilized this property in that manganese-containing enzymes are involved in many diverse redox functions.[2] This has led to a great deal of recent work in attempting to develop synthetic model manganese compounds that mimic properties of natural systems.[3] Of particular interest has been the development of multinuclear manganese complexes. The biological function that has generated the most interest is the photosynthetic oxygen-evolving complex of photosystem II in which it is generally believed that four manganese atoms are involved.[4] These manganese atoms are in close proximity to one another. Much of the available data can be interpreted by a dimer of dimers structure[5] in which the two dimers are electronically isolated from each other. The first good model compounds for the short Mn–Mn distance and multiline signal in the EPR spectrum of photosystem II were the mixed-valence bis(μ-oxo) species $[L_2MnO_2MnL_2]^{3+}$ (L = bipyridine or phenanthroline).[6] Recently three new Mn(III)–Mn(IV) binuclear bis(μ-oxo) complexes have been reported.[7,8] In addition, a number of trinuclear[9] and tetranuclear[10] manganese compounds involving at least one bridging-oxo group have been described. Most of the synthetic procedures for these aggregated manganese species involve oxidation of manganese(II) precursors. No information about the mechanism of the formation of these multinuclear species has been presented, however. Also, the origin of the oxygen bridging atom in this type of compound has not previously been established because most synthetic routes have involved oxidants that can act as oxygen atom donors. Evidence is described herein that supports a scheme involving oxidation of Mn(II) to Mn(III), followed by dimer formation with water as the source for bridging oxygen.

We recently reported a new mixed-valence Mn(III)–Mn(IV) bis(μ-oxo) compound with a macrocyclic tetradentate ligand, 1,4,8,11-tetraazacyclotetradecane,[11] $[(14\text{-aneN}_4)\text{MnO}]_2^{3+}$ (**1**). Our interest in this and other mixed-valence binuclear manganese species is their potential as multiple-electron redox catalysts that may promote the oxidation of water. The electrochemical oxidation of complex **1** in dry acetonitrile produces the IV,IV complex. If water is then added, the oxidized form of the complex reacts with water with partial regeneration of the III,IV complex as evidenced by changes in the UV–vis spectra. The source of electrons for this reduction could be oxidation either of the solvent or of water. This chemistry is still being investigated.

Compound **1** is one of the few species that have been described with a cis configuration for a 14-membered macrocycle. While cis 14-aneN$_4$ complexes are known,[12a] the vast majority of complexes with this ligand have been previously prepared with the ligand in a planar or trans configuration. Even in the case of a large metal atom such as osmium(III), the ligand 14-aneN$_4$ adopts a planar, trans geometry to form *trans*-$[\text{Os}(14\text{-aneN}_4)\text{Cl}_2]^+$.[12b]

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Another interesting observation about the compound $[(14\text{-aneN}_4)\text{MnO}]_2^{3+}$ is that it self-assembles from dilute solution. In contrast to most synthetic procedures of multinuclear metal complexes, which require very concentrated solutions (ca. 0.1 mol L^{-1}), our complex can be prepared from millimolar solutions. These facts and other experiments described herein point out the remarkable tendency of the Mn_2O_2 core to form. This core is particularly stable with the Mn in the III and IV oxidation levels.

Experimental Section

Visible spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer with 2-nm resolution or on a Varian 2300 instrument. Solutions used for these measurements were millimolar solutions in acetonitrile solvent. Typical spectra on the 8450A instrument were the average of 10 scans.

X-Band EPR spectra were recorded on a Varian Model E109 spectrometer equipped with a low-temperature Dewar (Air Products, Ltd.). A dilute solution of the complex (ca. 10^{-5} mol L^{-1}) in 2:1 ethylene glycol–water (v/v) was frozen into a glass at 77 K in liquid nitrogen and then cooled to 4 K with helium. All EPR spectra were recorded at 4 K.

Infrared spectra were recorded on a Nicolet 5DX FT infrared spectrometer system. Solid samples were used as KBr pellets (2–4 wt %) prepared in a Wilk's minipress. Typical spectra were an average of 20 scans.

Electrochemistry was performed by using a PAR Model 175 potentiostat equipped with a PAR Model 173 controller. Dry acetonitrile was used as the solvent and tetrabutylammonium hexafluorophosphate (TBAH) (0.1 M) was used as the electrolyte. Solutions used for cyclic voltammograms were of millimolar concentration in the electroactive species. A nonaqueous Ag/Ag^+ electrode was used as the reference electrode (potential vs Ag/Ag^+ + 0.34 V = potential vs SCE). A glassy-carbon-disk working electrode and platinum-wire counter electrode were used for cyclic voltammetry.

Spectroelectrochemistry was performed in a cell constructed from a quartz cuvette with a quartz fritted compartment separating the working- and counter-electrode units (see Figure 1). The counter electrode was Pt foil and the working electrode was a Pt-mesh cylinder mechanically supported by two Pt strips. The light beam of the spectrometer passed between the two Pt strips. Stirring was accomplished by bubbling with argon. With this cell, one-electron controlled-potential oxidation or reduction of a 1 mM solution of **1** in acetonitrile (with 0.1 M TBAH as supporting electrolyte) could be obtained in 6 min. The potential of the cell was controlled by a PAR Model 175 potentiostat equipped with a PAR Model 173 controller and a Model 179 digital coulometer.

Materials and Methods

1,4,8,11-Tetraazacyclotetradecane was purchased from Strem Chemicals and used without further purification. Acetonitrile was UV grade from Burdick and Jackson dried over activated molecular sieves. Water was purified by using a Millipore-MilliQ system. All other solvents were HPLC grade or the best commercially available grade and were used without further purification. $Mn(ClO_4)_2 \cdot 6H_2O$ was purchased from Fluka and $Mn(CF_3SO_3)_2 \cdot CH_3CN$ was synthesized by the reaction of manganese powder with trifluoromethanesulfonic acid which was diluted in CH_3CN. (*Caution*! This reaction is extremely exothermic and produces hydrogen gas. The triflic acid should be diluted at least 100-fold in acetonitrile and the manganese powder added slowly under nitrogen flow to flush away hydrogen as it is formed.)

Synthesis of $[(14\text{-aneN}_4)\text{MnO}]_2(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ (1). A solution of 0.42 g (2.1 mmol) of 14-aneN$_4$ in 20 mL of water was added to a solution of 0.73 g (2.9 mmol) of $Mn(ClO_4)_2 \cdot 6H_2O$ 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 dark green microcrystalline product formed, 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 and heat.) Anal. Calcd for $[Mn(C_{10}H_{24}N_4)O]_2(ClO_4)_3 \cdot 2H_2O$: Mn, 12.53; C, 27.39; H, 5.98; N, 12.78; Cl, 12.13. Found: Mn, 12.2; C, 28.40; H, 5.65; N, 12.81; Cl, 12.06.

Crystal Growth and Analysis. Attempts to grow diffraction-quality crystals of the perchlorate salt of **1** produced blade-type crystals with insufficient thickness. Good crystals were obtained by adding a 10-fold excess of $Mn(CF_3SO_3)_2$ to an aqueous solution of the macrocyclic ligand and allowing the green solution to stand undisturbed in a refrigerator for a week. The resultant shiny dark green crystals rapidly lose water of crystallization in a dry atmosphere, and it was necessary to seal them in thin-wall capillaries with a small amount of the mother liquor to prevent decomposition. A crystal with dimensions 0.20 × 0.22 × 0.40 mm was mounted in an Enraf-Nonius CAD-4 diffractometer, and 5432 unique intensity data were collected at room temperature.

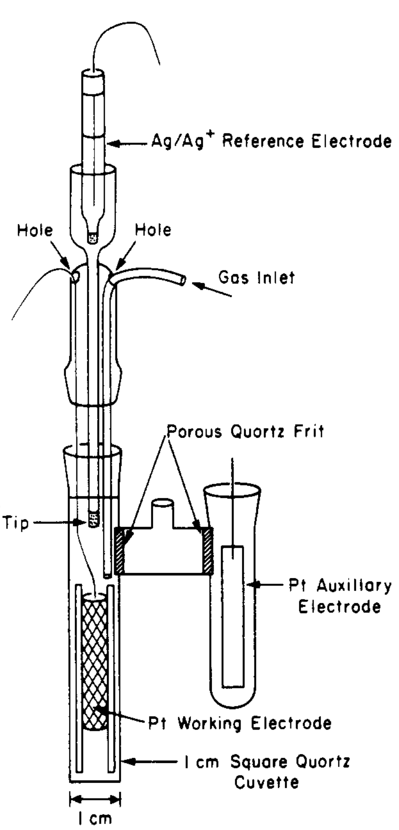

Figure 1. Spectroelectrochemical cell constructed of quartz utilizing a 1-cm quartz cuvette. The light beam of the spectrophotometer passes between two platinum strips and below the platinum-mesh cylinder of the large surface area working electrode. The counter-electrode compartment is separated by two quartz frits from the working-electrode compartment. The working-electrode compartment was deoxygenated by bubbling with argon through a Teflon needle, and the other compartments were deoxygenated by septum and needle techniques.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. One of the triflate anions was disordered through rotation around the carbon–sulfur bond, and this was modeled with a combination of isotropic and anisotropic motions. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of all of the hydrogen atoms on the ligands. Hydrogen atoms were assigned idealized locations. They were included in structure factor calculations, but not refined. The crystal was found to be monoclinic, belonging to space group $P2_1/n$, with a = 12.620 (2) Å, b = 14.442 (2) Å, c = 22.806 (2) Å, β = 91.651°, V = 4.155 Å^3, d_{calc} = 1.64 g/cm^3. The R index for the data for which $F^2 > 3\sigma(F^2)$ (4178 data) was 0.0481. The R value for all 5432 data was 0.0916. Additional crystallographic data, including bond angles, bond lengths, and atom coordinates, can be obtained as supplementary material.

Results and Discussion

Synthesis. Compound **1** is only the fifth species[6a,7a,7b] reported with a Mn_2O_2 core and with crystallographically discrete Mn(III) and Mn(IV) atoms. Also, several mixed-valence complexes with manganese atoms bridged by two oxo groups and one acetate group have recently been reported.[9,10,13] Various synthetic routes have been used to make these compounds, but most involve oxidation of Mn(II) precursors. Oxidation has been accomplished by persulfate, permanganate, hydrogen peroxide, or dioxygen. No suggestions have been put forward regarding the mechanism of formation of the Mn_2O_2 core. This four-membered ring appears to be particularly stable, and the steps in its assembly may have relevance to the nature of the oxygen-evolving center of photosystem II. Earlier work with ^{18}O-labeled water on the bipyridine analogue of **1**

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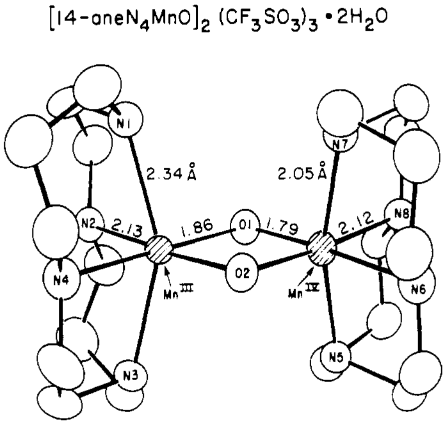
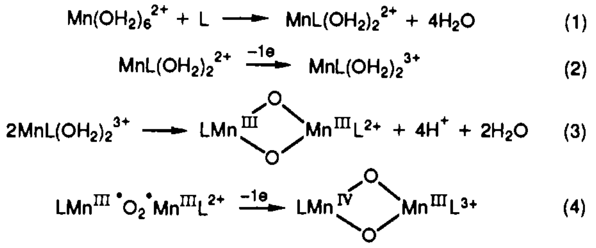


Figure 2. Structure of the cation $[(14\text{-aneN}_4)\text{MnO}]_2{}^{3+}$ with 50% probability ellipsoids and showing the atom labeling scheme. Hydrogen atoms were located but are not shown. Pertinent bond distances (Å) and angles (deg): Mn(III)-Mn(IV) = 2.741 (1), Mn(III)-O1 = 1.855 (2); Mn(III)-O2 = 1.868 (2), Mn(IV)-O1 = 1.786 (5); Mn(IV)-O2 = 1.790 (2), Mn(III)-N1 = 2.336 (3), Mn(III)-N2 = 2.129 (2), Mn(III)-N3 = 2.362 (3), Mn(III)-N4 = 2.116 (3), Mn(IV)-N5 = 2.051 (2), Mn(IV)-N6 = 2.111 (3), Mn(IV)-N7 = 2.049 (3), Mn(IV)-N8 = 2.115 (3); O1-Mn(III)-O2 = 80.6, O1-Mn(IV)-O2 = 84.6, Mn(III)-O1-Mn(IV) = 97.7, Mn(III)-O2-Mn(IV) = 97.1, O1-Mn(III)-N1 = 95.8, O1-Mn(IV)-N5 = 95.6.

Scheme I



indicated that the oxo groups can be exchanged with solvent water in aqueous solution by recrystallization at elevated (80 °C) temperature.[14] However, the original source of these bridging oxygens has previously not been established.

In the initial synthesis of the Mn_2O_2 unit, oxidizing agents (MnO_4^-, H_2O_2, O_2) have been used that could donate oxygen atoms to form the bridge. However, our work supports the synthetic mechanism given in Scheme I in which water is the source of the bridging oxygens.

In this scheme, the initial step involves ligation of the Mn^{2+} ion by the macrocycle. This ligation has a large effect on the oxidation potential of the metal. An aqueous solution containing 1:1 equiv of Mn^{2+} and macrocycle has a quasi-reversible oxidation wave in its CV at about −0.1 V, while an aqueous solution of $Mn(ClO_4)_2$ shows an irreversible oxidation at +0.8 V. A solution containing only the macrocycle exhibits a broad, multielectron irreversible wave at +1.0 V. A thoroughly deaerated solution of Mn^{2+} and the macrocyclic ligand is essentially colorless. Addition of dioxygen or other suitable oxidants produces a colored MnL^{3+} species.

Evidence establishing that the oxo bridges come from H_2O is provided by an electrochemical synthesis procedure. An acetonitrile solution was prepared that contained 2% by volume water, was 10 mM in $Mn(CF_3SO_3)_2$, 10 mM in ligand, and 100 mM in tetrabutylammonium hexafluorophosphate. This solution was deaerated and then oxidized at +0.34 V (Pt gauze electrode, SCE reference). The colorless solution developed a green color over about 2 h and gave the characteristic electronic spectrum of the III,IV bis(μ-oxo) binuclear complex (see Figure 3 and below). The only available source for the bridging oxo groups in this synthesis is water. In other experiments, the driest available acetonitrile (molecular-sieve dried), which contained 47 ppm H_2O (0.003 M), was used as the solvent. Solutions containing 0.001 M $Mn(CF_3SO_3)_2$ and 0.001 M 14-aneN$_4$ were saturated with dry O_2. The solution turned red, indicating oxidation of the Mn(II). Over 24 h, a peak at 650 nm appears that can be attributed to partial formation of the Mn(III)-Mn(IV) mixed-valence compound. When the experiment is done in 0.006 M H_2O, more of the Mn(III)-Mn(IV) complex is generated and the apparent rate of formation is doubled. These experiments indicate that the role of dioxygen or other potentially oxygen atom donating oxidants in a conventional synthesis is simply that of an oxidizing agent.

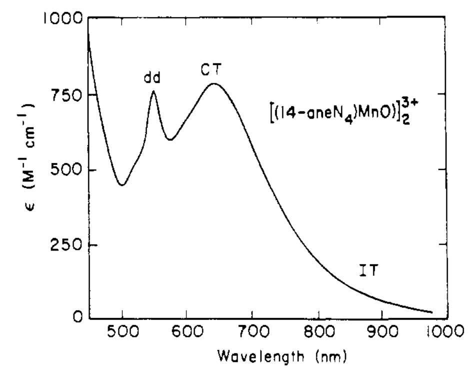


Figure 3. Electronic spectrum of $[(14\text{-aneN}_4)\text{MnO}]_2{}^{3+}$ in acetonitrile. Assignments are discussed in the text: IT, intervalence transition; CT, O → Mn(IV) charge transfer; d-d, probably Mn(III).

These experiments also highlight the unusual tendency for formation of the Mn_2O_2 core. It is remarkable that a binuclear species such as **1** will self-assemble from 10 mM solutions. The details of the actual bridge formation (step 3) remain unclear. Presumably the MnL^{3+} monomeric species contains two solvent molecules to raise the coordination number to six. In aqueous solution, these ligands would be water. At some point the water ligands must deprotonate to form the isolated complex **1**.

The isolated complex $[(14\text{-aneN}_4)\text{MnO}]_2{}^{3+}$ contains the 14-aneN$_4$ ligand coordinated in a cis fashion. In the literature, the vast majority of metal complexes isolated with the 14-aneN$_4$ macrocycle adopt the planar trans geometry.[15] Thus, it is quite surprising that we isolate a cis-coordinated 14-aneN$_4$ manganese complex. The bis(μ-oxo) Mn_2O_2 core must trap the ligand in a cis-coordinated geometry. This points once again to the exceptional stability of this Mn_2O_2 core.

An alternative route to the product of Scheme I might be to require oxidation of the monomeric MnL^{3+} to manganese +4 species, followed by dimerization involving Mn(III) and Mn(IV) monomers. Several observations argue against such a process. The first is that the cyclic voltammetry of **1** (see below) shows that it is much easier to oxidize the III,III dimer to the III,IV dimer than it is to oxidize the $Mn^{II}L$ monomer to the $Mn^{III}L$ monomer and to further oxidize the $Mn^{III}L$ monomer to the $Mn^{IV}L$ monomer. In fact, the electrochemistry of an aqueous solution containing $Mn(ClO_4)_2$ and L exhibits no oxidation waves attributable to the conversion of $Mn^{III}L$ to $Mn^{IV}L$ prior to +1.5 V vs SCE. Another observation consistent with Scheme I is the relative kinetic inertness of the III,III dimer. In a spectroelectrochemistry experiment it was possible to reduce **1** to the III,III level and then to reoxidize to the original III,IV dimer (see below). The rate of the reoxidation step was the same as the reduction, which implies that the III,III dimer remains intact and does not immediately dissociate into monomer.

Structure. Compound **1** is the fifth example[16] of a mixed-valence Mn(III), Mn(IV) bis(μ-oxo) species with crystallographically discrete Mn(III) and Mn(IV) atoms (Figure 2). The ligands occupying the other coordination sites of Mn in the known compounds are bipyridine (bpy),[6a] *N*,*N*-bis(2-methylpyridyl)ethane-1,2-diamine (bispicen),[7a] tris(2-methylpyridyl)amine[7b] (tpa), 2,2′,2″-triaminotriethylamine (tren),[8] and the present 14-aneN$_4$ macrocycle. A comparison of the bond distances and bond angles of the compounds reveals the structural integrity of the Mn_2O_2 core. The longest Mn(III)-oxo bond length is 1.861 Å in the present compound (Figure 2) while the shortest is 1.833 Å in the bispicen; the range of Mn(IV)-oxo bond lengths is from 1.793 Å in the bispicen to 1.774 Å in the tren. Thus, the Mn_2O_2 ring structure is not very sensitive to changes in the ligand environment of the Mn atoms. This fact is also reflected in the similarity of the optical and EPR spectra that have been reported for these complexes.

The structure of the $[Mn(14\text{-aneN}_4)O]_2{}^{3+}$ ion is shown in Figure 2. The structure is that of discrete Mn(III) and Mn(IV) ions with a planar bis(μ-oxo)dimanganese core. The three-carbon segments of the ligands for the two manganese atoms are eclipsed rather than staggered as might have been predicted from steric considerations. The average Mn(III)-O

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(15) See for example: Fabbrizzi, L. *Comments Inorg. Chem.* **1985**, *4*(1), 33-54. Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2968-2981. Thöm, V. J.; Shaikjee, M. S.; Hancock, R. D. *Inorg. Chem.* **1986**, *25*, 2992-3000 and references therein.

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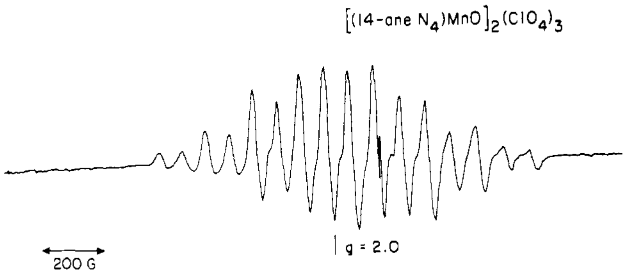

Figure 4. X-Band EPR spectrum of $[(14\text{-aneN}_4)MnO]_2^{3+}$ in 2:1 ethylene glycol–water at 8 K with the following instrument settings: Microwave power, 2mW; modulation amplitude, 10 G; modulation frequency, 100 kHz.

bond length is 1.862 versus 1.788 Å for Mn(IV)–O. There is a large difference between the axial Mn(III)–N bond distances, 2.349 Å (average), and the equatorial Mn(III)–N average of 2.122 Å. This reflects the expected Jahn–Teller distortion for a high-spin Mn(III) d^4 ion.[17] The axial Mn(III)–N bond is exceptionally long, probably because of the degree of flexibility inherent in the 14-member macrocycle. Interestingly, the average bond lengths for the equatorial nitrogens are very similar (Mn(III)–N_{eq} average 2.122 Å versus Mn(IV)–N_{eq} average 2.113 Å). This similarity[7a] has also been observed in the mixed-valence Mn(III)–Mn(IV) bis(μ-oxo) compound with *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine as a ligand. The authors claim that the similarity indicates partial delocalization in their compound. However, there are a number of factors that affect the equilibrium distances of the equatorial nitrogens of the two manganese atoms. The first is the oxidation state of the manganese; manganese(III)–nitrogen bonds are expected to be longer than manganese(IV)–nitrogen bonds. Further, the Jahn–Teller distortion of the Mn(III) will affect the equatorial as well as the axial bond lengths. With Jahn–Teller distortion, the axial bonds lengthen and the equatorial bonds shorten. Another factor present is the oxo effect, which acts to lengthen bonds trans to an oxygen group.[18] This trans-oxygen effect has been observed in the bpy[6a] and tren[8] compounds. The oxo effect is evident in the present case as manifested by the longer Mn(IV)–N bond trans to the μ-oxo groups (2.113 Å) compared to 2.065 Å for the average axial distance. A final factor affecting Mn–N equatorial distances is the fact that the coordinating nitrogens are incorporated into a macrocycle, which puts constraints on movement. With all these factors influencing the observed bond lengths, it does not seem necessary to invoke delocalization in the Mn_2O_2 core to explain similar Mn–N equatorial bond distances for the two Mn centers in **1**.

Infrared Spectrum. The infrared spectrum of **1** was taken in a KBr pellet and exhibits a strong band at 679 cm^{-1}. Bands in this region have been attributed to a vibration of the Mn_2O_2 core.[14] When the synthesis reaction was run in 51% ^{18}O-labeled water, the dark green crystalline product thus obtained showed a splitting of this band into two peaks, one at 681 cm^{-1} and the other at 670 cm^{-1}. This confirms assignment of the 679-cm^{-1} band as due to Mn_2O_2. The bpy analogue of **1** shows the same behavior.[14]

EPR Spectrum. The EPR spectrum of **1** in 2:1 ethylene glycol–water at 8 K is very similar, feature for feature, to those reported for the bpy and tren analogues of **1** (Figure 4). The 16-line spectrum is characteristic of strongly exchange-coupled ions of spin 2 [Mn(III)] and spin $^3/_2$ [Mn(IV)], where one of the ions has about twice the hyperfine coupling constant of the other. The spectrum also shows a small asymmetry and a resolution of additional lines at the high-field end of the spectrum because the hyperfine interaction is not small in comparison with the Zeeman interaction.[6b]

Electrochemistry. The cyclic voltammogram of **1** in dry CH_3CN is shown in Figure 5. There is a reversible oxidation at +1.00 V and a reversible reduction at −0.12 V vs SCE (ΔE_p = 59 mV; i_p^a/i_p^c = 1.0). These oxidation and reduction steps are more reversible than those reported for the bpy, phen, bispicen, and tren analogues of **1**. This increased reversibility is presumably due to the macrocyclic effect of the 14-aneN$_4$ ligand. The comproportionation constant K_c = $[III,IV]^2/[III,III][IV,IV]$ can be calculated[19] from the difference of the two potentials ($\log K_c = 16.9\ \Delta E_{1/2}$). The value for **1** is 10^{19}, which is exceptionally large. The value reported for the phenanthroline analogue is 10^{16}, and values of 10^{10} for the bispicen and 10^{13} for the tren can be calculated from reported electrochemical data.

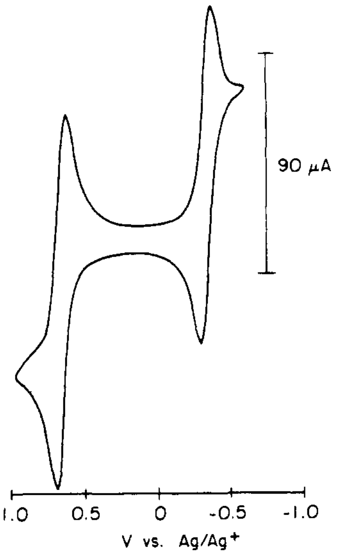

Figure 5. Cyclic voltammogram of $[(14\text{-aneN}_4)MnO]_2(CF_3SO_3)_3$ in CH_3CN containing 0.1 M $[(C_4H_9)_4N]PF_6$. Conditions: glassy-carbon-disk working electrode; Pt-wire counter electrode; Ag/Ag$^+$ reference electrode; scan rate = 100 mV/s.

Spectroelectrochemistry. The optical spectrum of **1** is given in Figure 3. This spectrum is similar in some features to that observed for the $[(bpy)_2MnO]_2^{3+}$ compound. Electronic spectra of completely localized mixed-valence binuclear compounds (class I)[20] are expected to be the sum of the individual spectra of the components. In class II, or partially delocalized compounds, a new low-energy band appears, which is frequently attributed to a metal-to-metal charge-transfer (intervalence) band.[21] A tentative assignment of the bands of **1** can be made from this classification scheme, spectra of monomeric Mn(III) and Mn(IV) complexes, and prior assignment of the spectrum of the bpy complex.[14] The intense absorption tailing from the UV is assigned to ligand-to-metal charge-transfer bands. There is a weak shoulder at roughly 560 nm and an asymmetric peak at 556 nm; somewhat similar features in the spectrum of the bpy complex have been attributed to d–d transitions.[14] A peak with an extinction coefficient of 760 M^{-1} cm^{-1} is observed at 646 nm. This peak compares in position and intensity to charge-transfer bands assigned to oxygen-to-Mn(IV) charge-transfer transitions in monomeric compounds.[22] However, a band in this region for the bpy dimer has been assigned to an oxo-to-Mn(III) CT transition.[14] The spectrum of the bpy dimer has a broad band at about 800 nm that has no parallel in either Mn(III) or Mn(IV) monomeric compounds and is attributed to an intervalence transition. Such a band is reported as being absent in the tren Mn(III)–Mn(IV) mixed-valence complex although no absorption spectrum is shown.[8] In the present case no distinct near-IR peak appears but the 646-nm peak has a broad tail extending into this region. Compound **1** has an extinction coefficient of 125 M^{-1} cm^{-1} at 800 nm. This broadened absorption may be due to an intervalence band that underlies other types of transitions.

Spectroelectrochemistry was employed to learn more about the electronic transitions and to investigate the stabilities of oxidized and reduced forms of **1**. In dry acetonitrile, it was possible both to reduce and to oxidize the III,IV mixed-valence compound by one equivalent. In both cases the process can be reversed by changing electrolysis potentials, and more than 95% regeneration of the original mixed-valence species can be obtained.

Reduction of a green 1 mM solution of **1** in CH_3CN at a platinum electrode (E = −0.26 V vs SCE, 0.1 M TBAH) leads to an essentially colorless solution after passage of 1 equiv of charge (Figure 6a). When the potential is changed to 0.34 V vs SCE, the current is reversed, and after 1 equiv of oxidation, the original spectrum of the III,IV compound is obtained. In our cell the reduction and reoxidation steps both take about 6 min. The ease of the reoxidation step is taken as evidence that

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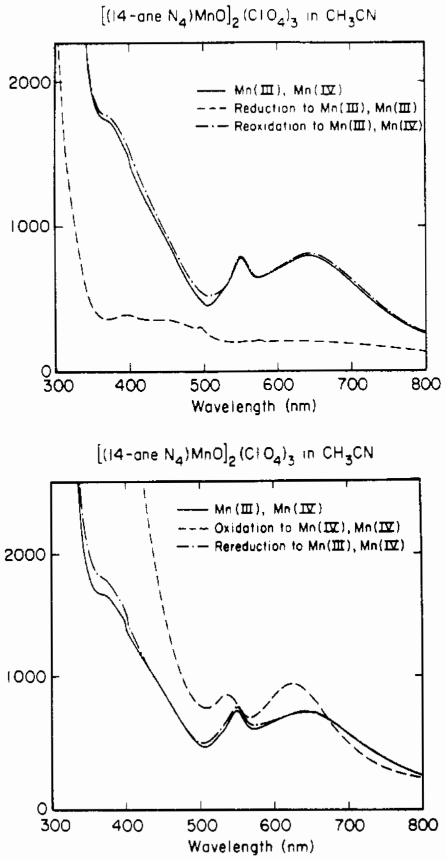

Figure 6. Spectroelectrochemical results for $[(14\text{-aneN}_4)\text{MnO}]_2(\text{CF}_3\text{SO}_3)_3$ in CH_3CN (0.1 M $[(\text{C}_4\text{H}_9)_4\text{N}]\text{PF}_6$). (a) Top: (—) original spectrum; (--) spectrum after reduction with 1.05 equiv at −0.5 V (Ag/Ag^+) at a Pt-mesh electrode (total elapsed time 8 min); (-·-) spectrum after reoxidation with 1.05 equivalent at 0.0 V (total elapsed time 6 min). (b) Bottom: (—) original spectrum; (--) spectrum after oxidation with 1.05 equiv at 0.95 V (Ag/Ag^+) at a Pt-mesh electrode (total elapsed time 6 min); (-·-) spectrum after rereduction with 1.05 equiv at 0.0 V (total elapsed time 6 min).

the reduced species retains the bridging oxo groups and is presumably the III,III compound. Oxidation of monomeric complexes to form the bis(μ-oxo) complex occurs on a much longer time scale under similar conditions (ca. 2 h). The much lower extinction coefficients for the III,III complex are consistent with d to d transitions and support the argument that the 648-nm band in the spectrum of **1** is an oxo-to-Mn(IV) CT transition.

This assignment of the 648-nm peak is supported by the spectrum that is obtained when a green 1.0 mM solution of the III,IV species is oxidized by 1 equiv at +1.29 V versus SCE (Figure 6b). A change from deep green to a more yellow green is discernible to the eye during the oxidation. This resulting solution can also be reduced rapidly to the original compound by lowering the potential to +0.34 V. The presumed IV,IV compound has lower intensity in the 650–800-nm region compared to the spectrum of **1**, which is consistent with a broad IT band being present in this region in the mixed-valence compound and disappearing in the isovalent IV,IV complex. The peak at 648 nm in **1** is shifted to 630 nm in the IV,IV compound and increases in intensity. This corroborates the assignment of the 648-nm band in **1** to an oxo-to-Mn(IV) charge transfer. In the process of the oxidation of the mixed-valence III,IV species, the peak at 555 nm decreases while a peak at 540 nm grows in. This feature at 540 nm is in the same region as transitions assigned as d–d in monomeric Mn(IV) Schiff-base complexes.[23] A shoulder near 540 nm is also observed in the spectrum of the Mn(III)–Mn(IV) mixed-valence compound, which is presumably due to a d–d transition associated with the Mn(IV) moiety.

The $[(\text{phen})_2\text{MnO}]_2(\text{ClO}_4)_4$ compound (IV,IV) has been isolated[24] and characterized by X-ray crystallography.[16] Interestingly this species is reddish brown in contrast to our observation that $[(14\text{-aneN}_4)\text{MnO})]_2^{4+}$ is green. We have confirmed in a spectroelectrochemical oxidation in acetonitrile that the visible spectrum of the red $[(\text{phen})_2\text{MnO}]_2^{4+}$ consists of an intense absorption at 400 nm with weak shoulders at about 440, 510, and 675 nm. The reversibility of the oxidation of the phen binuclear species is not as complete as that of the 14-aneN_4 macrocycle. The difference in the visible spectra of the two Mn(IV)–Mn(IV) species is presumably due to the differences in capping ligands. With the aliphatic secondary amine macrocycle (14-aneN_4) a ligand-to-metal charge-transfer (LMCT) band dominates the spectrum at wavelengths below 500 nm. With the more easily oxidized phenanthroline ligand, this LMCT band has moved to longer wavelengths (beginning at ca. 650 nm), and thus the observed color is different.

Our spectroelectrochemical experiments are then consistent with the following assignments: Charge transfer bands, probably L → Mn(IV), tail into the visible region from the UV. These appear in the spectrum of **1** and are shifted to lower energy in the oxidized IV,IV species. A peak at 540 nm for the IV,IV species (shoulder in spectrum of **1**) is attributable to a d–d transition for Mn(IV). A peak at 550 nm in the mixed-valence compound is probably a d–d transition centered at Mn(III). A prominent band at 648 nm in the spectrum of **1** (shifted to 630 nm in the IV,IV species) is assigned to an oxo-to-Mn(IV) LMCT transition. A broad, underlying intervalence band causes a long tail into the near-IR region for the mixed-valence compound. This absorption feature is lost in the spectrum of the IV,IV species.

Summary and Conclusions

The complex $[(14\text{-aneN}_4)\text{MnO}]_2^{3+}$ is the fifth mixed-valence complex prepared with a Mn_2O_2 core that shows crystallographically discrete Mn(III) and Mn(IV) metal centers.[6a,7a,7b] The Mn–O distances are nearly equal (±0.03 Å) in all the complexes, while the Mn–N distances vary (±0.2 Å). This points to the integrity of the Mn_2O_2 core. Other compounds with different capping ligands may be expected to be reported in the future. The tendency of manganese to form bis(μ-oxo) complexes of this type is quite interesting. The ligand 14-aneN_4 would normally coordinate in a planar trans geometry;[12b,15] however, in our reaction, the propensity of manganese to form the Mn_2O_2 core leads to the isolation of a complex with a cis-coordinated 14-aneN_4 ligand.

The electrochemistry of our complex $[(14\text{-aneN}_4)\text{MnO}]_2^{3+}$ is characterized by two reversible one-electron processes:

$$\text{Mn(III)–Mn(IV)} + e^- \rightarrow \text{Mn(III)–Mn(III)}$$

$$E_{1/2} = -0.12 \text{ V vs SCE}$$

$$\text{Mn(III)–Mn(IV)} \rightarrow \text{Mn(IV)–Mn(IV)} + e^-$$

$$E_{1/2} = +1.00 \text{ V vs SCE}$$

The 1.12-V range of stability of the mixed-valence complex is unusually large with respect to other examples in the literature.[25] Both the reduction of the III,IV complex to the III,III state and the oxidation to the IV,IV state are reversible in dry acetonitrile. This is in marked contrast to the electrochemical behavior of other binuclear Mn(III), Mn(IV) complexes in the literature.

The accessibility of the three oxidations states—III,III, III,IV, and IV,IV—makes it possible to perform spectroelectrochemical experiments and make assignments of the electronic spectra. The results of these experiments indicate that the intense band at 646 nm ($\epsilon = 760\ \text{M}^{-1}\ \text{cm}^{-1}$) in the III,IV complex is due to an oxygen-to-Mn(IV) ligand-to-metal charge-transfer (LMCT) transition. This is in contrast to its previous assignment as an oxygen-to-Mn(III) LMCT band in the bipyridine complex.[14] Additionally, spectroelectrochemical results indicate that the tail into the near-infrared region is due to an intervalence transition that underlies the charge-transfer band.

The complex $[(14\text{-aneN}_4)\text{MnO}]_2^{3+}$ is remarkably stable. The spectrum of the complex in aqueous solution is unchanged at pH = 7.0 for 30 min. Acetonitrile solutions of the complex are stable for days in contact with the atmosphere. The use of this macrocyclic ligand for the formation of Mn_2O_2 type complexes not only provides stability to the Mn(III), Mn(IV) binuclear complex but also to the one-electron-reduced and one-electron-oxidized forms of the complex.

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With the use of electrochemical synthetic techniques, we have established that the bridging oxygens in the bis(μ-oxo) core come from water. This information is important since the incorporation of water oxygens into a manganese complex is desirable for water oxidation via such manganese complexes, and it may have implications for the oxygen-evolving complex (OEC) in photosynthetic plants.

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Registry No. **1**, 123567-56-6; $[(14\text{-aneN}_4)\text{MnO}]_2^{2+}$, 117673-54-8; $[(14\text{-aneN}_4)\text{MnO}]_2^{4+}$, 117673-56-0.

Supplementary Material Available: Tables of positional parameters and isotropic thermal parameters, anisotropic thermal parameters, intramolecular distances, intramolecular angles, torsion angles, and root-mean-square amplitudes of thermal vibrations for **1** and a stereoview of **1** (13 pages). Ordering information is given on any current masthead page.

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Studies of CO Labilization and Intramolecular Hydride Transfer Reactions in Group VI (Cr, Mo, W) Metal–Platinum Heterobimetallic μ-Phosphido Hydrido Carbonyl Complexes

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Oxidative addition of the P–H bond of the secondary phosphine complexes $M(CO)_5(PR_2H)$ (M = Cr, Mo, W; R = Ph, ^{n}Pr) to $Pt(C_2H_4)(PPh_3)_2$ gives $(OC)_5M(\mu\text{-}PR_2)PtH(PPh_3)_2$, which rapidly loses CO (a reversible process) to give $(OC)_4M(\mu\text{-}PR_2)(\mu\text{-}H)Pt(PPh_3)_2$ via a "platinum-assisted mechanism" involving PPh_3 dissociation, formation of a μ-carbonyl intermediate $(OC)_4M(\mu\text{-}PR_2)(\mu\text{-}CO)PtH(PPh_3)$, subsequent rearrangement to $(OC)_4M(\mu\text{-}PR_2)(\mu\text{-}H)Pt(CO)(PPh_3)$, and substitutional loss of CO from Pt (by PPh_3). The complexes $(OC)_4M(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PR_3)_2$ (PR_3 = PEt_3, PMe_2Ph) can be obtained from the reaction of $M(CO)_5(PPh_2Li)$ and *trans*-$PtHCl(PR_3)_2$. Reaction of $M(CO)_5(PPh_2H)$ with $Pt(1,5\text{-}COD)_2$ in the presence of ethylene gives $(OC)_5M(\mu\text{-}PPh_2)PtH(COD)$, which rapidly rearranges, via β-H transfer, to the complex $(OC)_4M(\mu\text{-}PPh_2)(\mu\text{-}CO)Pt(\eta^3\text{-cyclooctenyl})$. Addition of $M(CO)_5(PPh_2H)$ to $Pt(C_2H_4)_2(PCy_3)$ gives the complexes $(OC)_4M(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(CO)(PCy_3)$ while reaction of *cis*-$(OC)_4M(PEt_3)(PPh_2H)$ (M = Mo, W) with $Pt(C_2H_4)_2(PCy_3)$ gives *mer*-$(OC)_3(PEt_3)M(\mu\text{-}PPh_2)(\mu\text{-}CO)PtH(PCy_3)$. For M = Mo this μ-carbonyl terminal-hydrido complex equilibrates with a small amount of the μ-hydrido terminal-carbonyl isomer *fac*-$(OC)_3(PEt_3)Mo(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(CO)(PCy_3)$. The molecular structure of the complexes $(OC)_4Cr(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PEt_3)_2$ and $(OC)_4Cr(\mu\text{-}PPh_2)(\mu\text{-}CO)Pt(\eta^3\text{-cyclooctenyl})$ (contains a semibridging carbonyl ligand) have been determined by single-crystal X-ray diffraction methods. The complex $(OC)_4Cr(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PEt_3)_2$ crystallizes in the space group *Cc* with a = 16.719 (9) Å, b = 11.468 (3) Å, c = 18.275 (6) Å, β = 113.68 (3)°, V = 3209 Å^3, and Z = 4. The structure was refined to R = 0.0346 and R_w = 0.0401 for the 3801 reflections with $I > 3\sigma(I)$. Corresponding data for $(OC)_4Cr(\mu\text{-}PPh_2)(\mu\text{-}CO)Pt(\eta^3\text{-cyclooctenyl})$ are space group $P2_1/a$, a = 25.212 (3) Å, b = 10.172 (2) Å, c = 9.577 (2) Å, β = 90.53 (1)°, V = 2456 Å^3, and Z = 4. R = 0.0329, R_w = 0.0382 for 3384 reflections with $I > 3\sigma(I)$.

Introduction

The recently developed isolobal theory has provided considerable rationalization and proved to be a useful synthetic guide in the field of heterometallic compounds.[1,2] Furthermore the stereochemical "signposting" available in heterometallic systems has considerable potential for the investigation and analysis of cluster assembly and rearrangement processes, for the study of ligand reactivities in multimetallics systems, and for an analysis of the way(s) in which the chemistry of one metal center may be modified by a second metal center in close proximity.[3-13] In this regard systems containing hydrido and phosphine ligands and a platinum atom are particularly amenable to NMR spectroscopic investigation.[14] A suitable entry into heterometallic systems with these features involves oxidative addition of the P–H bond of a secondary phosphine complex to zerovalent complexes of platinum as outlined in Scheme I.[15-17] This reaction has broad potential applicability

Scheme I

$$L_xM(YR_2H) + PtL'_2L'' \longrightarrow L_xM(\mu\text{-}YR_2)\,PtHL'_2 + L''$$

(eg Y=P, As, Si)

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