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(4) The yields of compounds III, IV, and V have not been optimized.
(5) Anal. Calcd for $C_{10}H_6Se_2$: C, 42.28; H, 2.12; Se, 55.59. Found: C, 42.26; H, 2.12; Se, 55.46. IR (KBr): 3060, 1901(w), 1748(w), 1595, 1534, 1481, 1413, 1345, 1188, 1142, 1043, 959, 891, 859, and 751 cm^{-1}. UV λ_{max} (cyclohexane) 212 (ϵ 3.9 × 10^4), 255 (shoulder) (ϵ 1.1 × 10^4), 262 (ϵ 1.5 × 10^4), 367 (shoulder) (ϵ 1.2 × 10^4), and 380 nm (ϵ 1.6 × 10^4). 220-MHz ^1H NMR spectrum: 2 H, d of d; 2 H, d of d; 2 H, t; extending from δ 7.20 to 7.51. ^{13}C NMR: Chemical shift values 121.12, 123.75, 127.62, 137.50, 137.89, 140.91 ppm relative to Me_4Si.
(6) The calculated mass spectra were obtained by use of the MASH computer program, which is a local version of ISOW developed by W. A. G. Graham, University of Alberta, and modified by R. C. Winterton and R. S. Weber, Cornell University. The results are an average of two scans.
(7) Anal. Calcd for $C_{10}H_6Te_2$: C, 31.49; H, 1.59; Te, 66.92. Found: C, 31.31; H, 1.60; Te, 67.12. IR (KBr): 3060, 1925(w), 1777(w), 1531, 1481, 1412, 1343, 1189, 1136, 1040, 959, 890, 794, and 752 cm^{-1}. UV λ_{max} (cyclohexane) 257 (ϵ 7.5 × 10^3), 267 (ϵ 7.7 × 10^3), 383 (shoulder) (ϵ 7.6 × 10^3), and 410 nm (ϵ 1.0 × 10^4). 220-MHz ^1H NMR spectrum: 2 H, d of d; 2 H, d of d; 2 H, t; extending from δ 7.12 to 7.67. ^{13}C NMR: Chemical shift values 127.22, 128.18, 129.41, 132.58, 142.02, 147.83 ppm relative to Me_4Si.
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(11) Compounds VII, VIII, and IX gave satisfactory IR, NMR, and mass spectral data.
(12) This product was found to be identical with 1,8-dimethylnaphthalene prepared by allowing 1,8-dilithionaphthalene to react with methyl iodide.
(13) Perylene was identified by direct comparison with an authentic sample.

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Redox Reactions of Di-μ-oxo Bridged Binuclear Manganese(IV) and -(III) Complexes

Sir:

Although manganese is essential for the oxygen evolution process in photosynthesis,[1] its chemical role in photosystem-II remains uncertain. Furthermore, the chemical environment around the manganese ion is not known, which precludes the rational design of model compounds.

In the mechanism proposed by Kok[2] and supported by flash photolysis data,[3] four discrete one-electron steps lead to oxygen evolution. Because of a multiplicity of oxidation states for manganese and the associated coordination chemistry, most investigators[4] believe its essential role is as a redox catalyst.

Several model ligand systems have been suggested for manganese in photosystem-II, including one with manganese bound to an N_4 macrocyclic ligand.[5] Various di-μ-oxo, di-μ-hydroxo, and μ-oxo-μ-hydroxo binuclear manganese species also have been proposed as photosystem-II models.[6-10] An important test of the merit of model systems is the thermodynamics of their redox reactions.

The di-μ-oxo bridged binuclear manganese complexes, tetrakis(1,10-phenanthroline)di-μ-oxo-dimanganese(IV, IV) perchlorate, $[Mn_2^{IV,IV}O_2(phen)_4](ClO_4)_4$ (**1**), and tetrakis(2,2′-bipyridyl)di-μ-oxodimanganese(III, IV) perchlorate, $[Mn_2^{III,IV}O_2(bpy)_4](ClO_4)_3]$ (**2**), have been prepared and partially characterized.[11-13] Such complexes have proven to be useful starting materials for the present oxidation-reduction investigations. The crystal structure[12] of **2** includes distinct manganese-oxygen bond lengths for the trivalent and tetravalent manganese ions. The magnetic susceptibilities of **1**[13] and **2**[12] are less than expected for the spin-only condition and indicate antiferromagnetic coupling of the manganese ions across the di-μ-oxo bridge. The electrochemical redox reactions and solution magnetic susceptibilities of **1** and **2** are the subject of the present communication.

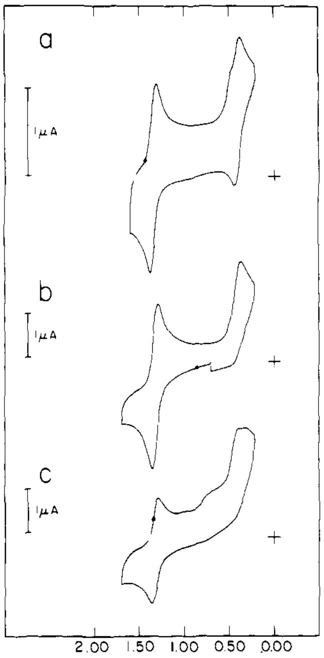


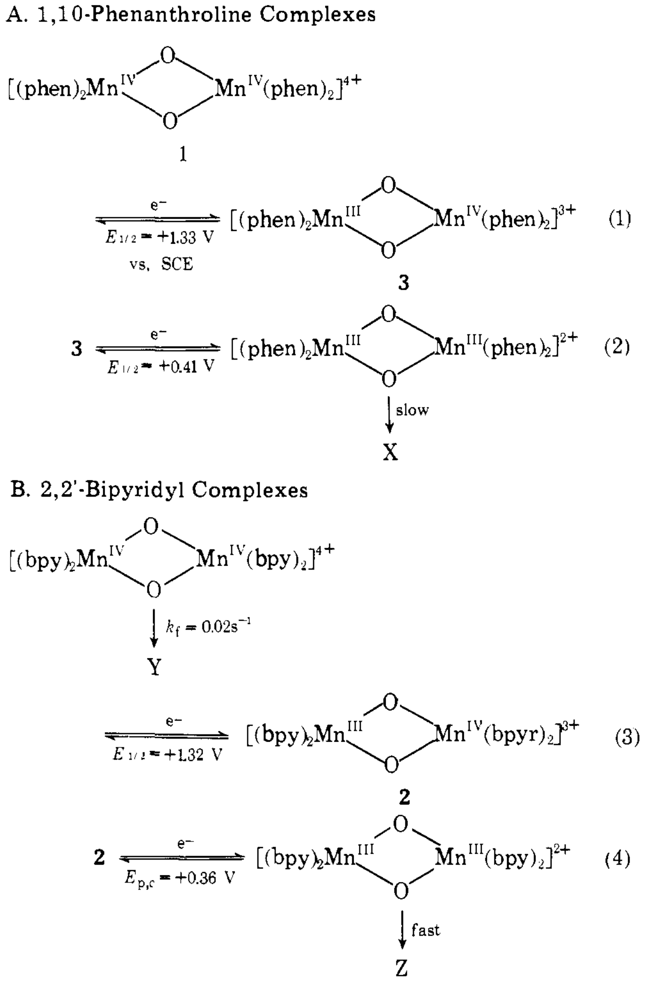
Figure 1. Cyclic voltammograms in 0.1 M TPAP–acetonitrile at a platinum electrode of (a) 0.5 mM $[Mn_2^{IV,IV}O_2(phen)_4](ClO_4)_4$ (**1**), (b) 0.5 mM $[Mn_2^{III,IV}O_2(bpy)_4](ClO_4)_3$ (**2**), and (c) 0.5 mM **2** after electrolysis at +1.45 V vs. SCE. Scan rate, 0.1 V/s.

The cyclic voltammogram of **1** (Figure 1a) exhibits two electrochemically reversible redox reactions. Controlled potential coulometry establishes that each wave is a one-electron process; these reactions are summarized in Scheme I. Electrochemical reduction of $[Mn_2^{III,IV}O_2(phen)_4]^{3+}$ (**3**)[14] to $[Mn_2^{III,III}O_2(phen)_4]^{2+}$ is followed by a coupled chemical reaction. Electrolysis of **1** (a red solution) at +1.00 V vs. SCE yields a green solution that appears identical with a solution of **3**.

The cyclic voltammogram for **2** (Figure 1b) includes a reversible anodic couple; the redox reactions are summarized in Scheme I and are supported by controlled potential coulometric measurements. The coupled chemical reaction that occurs after reduction of **2** is much faster than in the corresponding reaction after the second reduction of **1**. Comparison of anodic and cathodic peak currents confirms that a coupled chemical reaction also follows the oxidation of **2**. The pseudo-first-order rate constant, measured by the method of Nicholson and Shain,[15,16] is 0.02 s^{-1}. Anodic electrolysis of **2** (a green solution) at +1.45 V causes some decomposition, indicated by the cyclic voltammogram of the product solution (Figure 1c), and yields a reddish brown solution.

The solution-phase magnetic susceptibilities of **2** and of **3**[14] have been determined by the NMR method[17,18] at ambient temperature; for **2**, μ_{eff} = 2.56 ± 0.11 μ_B (uncorrected) com-

Scheme I. Redox Reactions for Di-μ-oxo Bridged Binuclear Manganese Complexes in Acetonitrile (0.1 M Tetrapropylammonium Perchlorate) (TPAP) at a Platinum Electrode (Scan Rate, 0.1 V/s)

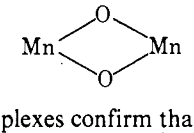


pared to 2.53 μ_B (uncorrected) for the solid by the Guoy method at room temperature[12] and for **3**, $\mu_{eff} = 2.26 \pm 0.08$ μ_B.[19,20] The reduced magnetic moments that are observed relative to those for the spin-only condition support the conclusion that the di-μ-oxo bridged species are stable in solution.

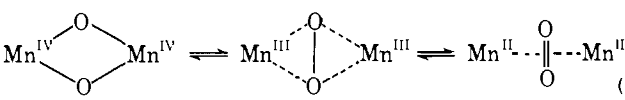
Of the two complexes, the mixed-oxidation state bipyridyl complex (**2**) is slightly easier to oxidize and more difficult to reduce than the corresponding 1,10-phenanthroline derivative. Also, the coupled chemical reactions occur at a faster rate for the bipyridyl complexes. This change in chemical and electrochemical reactivity can be accounted for on the basis of the "floppy" bipyridyl ligand compared to the rigid structure of 1,10-phenanthroline.

A noteworthy feature of the redox chemistry for the di-μ-oxo bridged complexes is the extremely positive potentials for the reversible one-electron (IV-IV)/(IV-III) couples. The 1,10-phenanthroline complex, **1**, appears especially attractive for use as a reagent for one-electron oxidations in nonaqueous media.

The electrochemical data for the



linkage in these complexes confirm that discrete one-electron steps are stabilized. Unfortunately, the stability of this linkage (in association with the bipyridyl and 1,10-phenanthroline ligands) implies that the tautomeric equilibria in this medium must lie far to the left;



(1)

the Mn_2(III, III)-peroxo and Mn_2(II, II)-oxygen species have not been detected. Furthermore, preliminary infrared data indicate, as expected from electrostatics, that the Mn-O bond is stronger for the Mn_2(IV, IV) species than for the Mn_2(III, IV) species. From the data presented, evolution of oxygen from di-μ-oxo bridged binuclear manganese(IV) complexes by reaction 1 must involve a displacement of oxide by some other ligand. This possibility is currently under investigation, as is the use of other ligands to promote a shift of the equilibria to the right in eq 1.

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(20) The magnetic moments are for the dimeric groups. On a per metal basis: for **2**, $\mu_{eff} = 1.81 \pm 0.07$ μ_B per Mn, and for **3**, $\mu_{eff} = 1.56 \pm 0.05$ μ_B per Mn.

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Absolute Configuration of a Ribonucleic Acid Adduct Formed in Vivo by Metabolism of Benzo[*a*]pyrene

Sir:

Incubation of the potent carcinogen benzo[*a*]pyrene (**1**) with bovine bronchial explants followed by extraction and digestion of the cellular RNA led to the isolation of an adduct **4**[1,2] which, by high pressure liquid chromatographic (HPLC) analysis, was shown to correspond to one of the diastereoisomeric in vitro products resulting from reaction of (±)-**3** with poly(G).[3,4] Spectral and chemical data established that the in vivo adduct is represented either by structure **4** or its mirror image at chiral centers C-7 through C-10. The following data now show that the absolute configuration is as shown in **4**. This work, together with our previous studies on the adduct formed between 7,12-dimethylbenz[*a*]anthracene 5,6-oxide and poly(G),[5] constitutes the first full structure determinations of both in vivo and in vitro[5] products derived from the carcinogenic polycyclic aromatic hydrocarbons.