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2,2′-Bipyridine 1,1′-Dioxide and 2,2′,2″-Terpyridine 1,1′,1″-Trioxide Complexes of Manganese(II), -(III), and -(IV)

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Received May 31, 1977

The manganese complexes that are formed by 2,2′-bipyridine 1,1′-dioxide ($bpyO_2$) and 2,2′,2″-terpyridine 1,1′,1″-trioxide ($terpyO_3$) in acetonitrile solution have been studied by electrochemical and spectroscopic methods. Both the $(bpyO_2)_3$ and the $(terpyO_3)_2$ complexes exhibit discrete one-electron reversible oxidation–reduction processes and an irreversible reduction that are consistent with the formation of stable mononuclear manganese(II), -(III), and -(IV) species. Changes in the oxidation state of manganese have been monitored by UV–visible and EPR spectroscopy. Both the $bpyO_2$ and $terpyO_3$ complexes of manganese(IV) react with water, apparently as the result of the highly positive Mn(IV)/Mn(III) redox couple for these complexes.

The possible role of higher valent manganese groups in photosynthetic water oxidation has prompted wide interest in the chemical and electrochemical properties of various manganese complexes as redox models. During a study[1] of the electrochemical oxidation of $Mn(bpy)_3(ClO_4)_2$ to $Mn_2O_2(bpy)_4(ClO_4)_4$, where bpy = 2,2′-bipyridine, investigation of the oxidation–reduction and chemical properties of the *N*-oxides of the ligands became necessary, both to confirm the absence of these species in the electrochemical oxidation process and to examine their ability to stabilize manganese(III) and -(IV).

The coordination properties of pyridine *N*-oxides and poly(pyridine *N*-oxides) have been demonstrated for a variety of transition-metal ions.[2-7] Both divalent[2,5-7] and trivalent[2,7] manganese complexes with 2,2′-bipyridine 1,1′-dioxide ($bpyO_2$) and 2,2′,2″-terpyridine 1,1′,1″-trioxide ($terpyO_3$) have been described. Metal ion complexation by $bpyO_2$ and $terpyO_3$ is novel because of the relatively rare seven-membered chelation ring and the accompanying highly distorted pseudooctahedral ligand field.[7] The present paper summarizes the results of an electrochemical and spectroscopic investigation of $bpyO_2$ and $terpyO_3$ complexes of manganese(II), -(III), and -(IV).

Experimental Section

Spectrophotometric and electrochemical measurements were performed using conventional instrumentation that has been described elsewhere.[8] Electrochemical potentials were measured at 23 ± 1 °C and are vs. the saturated calomel electrode (SCE). Acetonitrile ("Distilled-in-Glass", Burdick & Jackson Labs., Inc.) and tetra-*n*-propylammonium perchlorate[8] were used for the electrochemical measurements. Electron paramagnetic resonance (EPR) spectra (X band) were standardized with potassium nitrosodisulfonate (Alfa) ($g = 2.00550$).

Tris(2,2′-bipyridine 1,1′-dioxide)manganese(III) perchlorate, $Mn(bpyO_2)_3(ClO_4)_3$, was prepared by the method of Nyholm and Turco.[2] An attempt to synthesize the related Mn^{II}–$terpyO_3$ complex, as described by Rieff and Baker,[7] led to the rapid precipitation of bright orange, light-sensitive crystals that analyzed to be $Mn(terpyO_3)_2(ClO_4)_2 \cdot 2H_2O$. Anal. Calcd for $MnC_{30}H_{26}N_6O_{16}Cl_2$: C, 42.27; H, 3.07; N, 9.86. Found:[9] C, 42.91; H, 3.34; N, 9.86.

Results

Electrochemistry. $Mn(terpyO_3)_2(ClO_4)_2$ is oxidized in two reversible one-electron steps in acetonitrile at $E_{1/2} = +1.06$ and +1.77 V vs. SCE, as shown in Figure 1. The peak currents for the peaks at +1.06 and +1.77 V are approximately equal. In addition, an irreversible reduction occurs at a peak potential of −1.28 V. Controlled-potential coulometry of $Mn(terpyO_3)_2^{2+}$ at +1.50 V confirms the one-electron stoichiometry. Further coulometry at +2.00 V yields irreproducible results for the electron stoichiometry, but greater than unity in all cases. Addition of water following exhaustive electrolysis of $Mn(terpyO_3)_2^{2+}$ at +2.00 V causes a gradual negative shift of the rest potential. On the basis of peak currents from cyclic voltammetry the complex remains intact during electrolysis and the addition of water.[10] Attempts to determine the number of electrons transferred for the reduction at −1.35 V have proven unsuccessful, apparently because of electrode filming.

Table I. Spectroscopic Data for the Tris(2,2′-bipyridine 1,1′-dioxide) and Bis(2,2′,2″-terpyridine 1,1′,1″-trioxide) Complexes of Mn(II), -(III), and -(IV) in Acetonitrile (0.1 M TPAP)

	$bpyO_2$ complex	$terpyO_3$ complex
	1. UV–Visible Absorption Maxima of Mn (log ε)[a]	
Mn(II)	220 (4.9), 241 sh (4.8), 275 sh (4.5), 301 sh (4.4), 428 sh (3.5)	220 (4.8), 289 sh (4.5), 338 sh (3.74), 432 sh (3.4)
Mn(III)	214 (5.0), 260 sh (4.7), 280 sh (4.6), 362 sh (4.0), 525 sh (2.9), 605 sh (2.6)	215 (4.9), 286 sh (4.6), 322 sh (4.1), 375 sh (3.9), 550 sh (3.1)
Mn(IV)	213 (4.9), 275 sh (4.6), 375 sh (4.0), 540 sh (3.4)	210 (4.9), 285 sh (4.6), 331 sh (4.1), 385 sh (4.0), 560 sh (3.5)
	2. EPR Spectral Parameters	
Mn(II)	$g = 2.02; A = 92$ G	$g = 1.98; A = 92$ G
Mn(IV)	$g = 2.00; A = 96$ G	$g = 2.01; A = 93$ G

[a] sh = shoulder; log ε calculated for undeconvoluted spectra.

The electrochemistry of $Mn(bpyO_2)_3(ClO_4)_3$ is similar to the related $terpyO_3$ complex, but the redox peaks occur at more negative potentials. Half-wave potentials for the two reversible one-electron steps occur at +0.87 and +1.62 V. An irreversible reduction peak occurs at −1.35 V. The ultraviolet and visible spectra for isovalent manganese $bpyO_2$ and $terpyO_3$ complexes in CH_3CN solution (0.1 M TPAP) are closely related, with the absorption bands for the $bpyO_2$ complexes at slightly higher energy (see Table I).

The electron paramagnetic resonance data for the manganese(II)- and manganese(IV)-*N*-oxide complexes in acetonitrile are given in Table I. For both the $bpyO_2$ and $terpyO_3$ complexes the EPR signals associated with Mn(II) are weak, relative to those for the Mn(IV) signal.

Discussion and Conclusions

The ultraviolet–visible spectra for the manganese 2,2′-bipyridine 1,1′-dioxide and 2,2′,2″-terpyridine 1,1′,1″-trioxide complexes are similar to those observed for the pyridine *N*-oxide complexes. Hexakis(pyridine *N*-oxide)manganese(II) tetrafluoroborate has a charge-transfer band at 378 nm in acetonitrile,[11] and the diffuse reflectance spectrum for hexakis(pyridine *N*-oxide)manganese(II) perchlorate exhibits a charge-transfer band at 411 nm and a shoulder at 443 nm.[12] The $Mn^{II}(bpyO_2)_3^{2+}$ complex has an absorption band at 410 nm.[4] Hence, the bands at 428 and 432 nm for $Mn(bpyO_2)_3^{2+}$ and $Mn(terpyO_3)_2^{2+}$ can reasonably be assigned to a

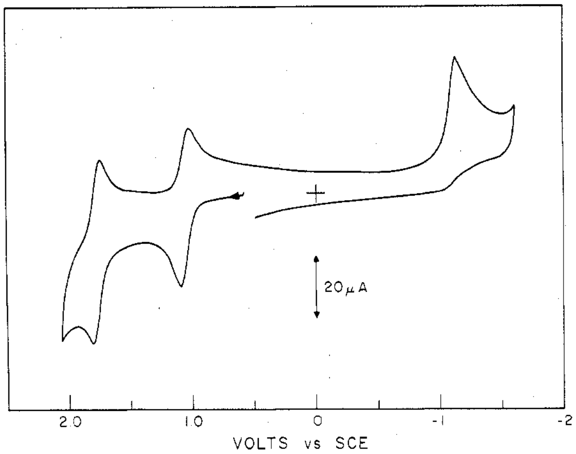

Figure 1. Cyclic voltammogram of 0.495×10^{-3} M Mn$(terpyO_3)_2(ClO_4)_2 \cdot 2H_2O$ in acetonitrile, 0.1 M TPAP: scan rate 0.1 V s^{-1}; Pt working electrode area 0.23 cm^2.

charge-transfer process.[13] Nyholm and Turco[2] described the red color of the $Mn(bpyO_2)_3^{3+}$ complex but did not publish spectral data. The diffuse reflectance spectrum of $Mn(terpyO_3)_2^{3+}$ exhibits bands at 558 nm and several bands at $\lambda > 1000$ nm. The bands at 362 and 375 nm for the Mn(III) $bpyO_2$ and $terpyO_3$ complexes, and at 375 and 385 nm for Mn(IV) complexes (Table I), probably also are due to charge-transfer processes. The other spectral bands in Table I cannot be assigned because of the highly distorted geometry of the complexes that results from the strained seven-membered chelate rings. Furthermore, there is the possibility of partial ligand substitution by CH_3CN.[14]

An interesting feature of these complexes is the shift of their UV-absorption band as the oxidation state of the central metal ion changes. For most first-row transition-metal ion–pyridine *N*-oxide complexes the UV-absorption bands are associated only with the ligand (apparently due to ligand lability).[12]

The EPR spectra for the divalent and tetravalent manganese complexes are similar, with their spectroscopic splitting parameters, A, summarized in Table I. The latter usually are related inversely to the degree of covalent character for the metal–ligand bond.[15] The values for the Mn(II) complexes of the present study are comparable to those for $Mn(pyO)_6^{2+}$ (91–94 G),[14,16] $Mn(CH_3CN)_6^{2+}$ (92 G),[15] and $Mn(H_2O)_6^{2+}$ (95 G)[15] but larger than for $MnCl_6^{4-}$ (79 G),[15] $MnBr_6^{4-}$ (75 G),[15] and $Mn(bpy)_3^{2+}$ (83 G).[1] Because pyridine *N*-oxide is labile, the calculated values of Dq and β, the nephelauxetic parameter, are unreliable.[14] Nevertheless, the A values for $Mn(bpyO_2)_3^{2+}$ and $Mn(terpyO_3)_2^{2+}$ indicate that their metal–ligand bonds have limited covalent character relative to the 2,2′-bipyridine and 2,2′,2″-terpyridine complexes.[1]

The electrochemistry of these complexes indicates that monomeric Mn(II), -(III), and -(IV) can be stabilized by the $bpyO_2$ and $terpyO_3$ ligands. This is in contrast to the dimerization of Mn(III) and -(IV) when coordinated to bipyridine- and phenanthroline-type ligands.[1] The reactivity of monomeric *N*-oxide–manganese(IV) complexes toward water is slow and probably involves reaction with hydroxide ion. Such a reaction is to be expected because of the extremely positive potential for the Mn(IV)/Mn(III) redox couple for both the $bpyO_2$ and $terpyO_3$ complexes. Similar reactivity with water has been observed for transition-metal ion complexes with highly positive III/II redox couples, including Co(III).[17]

Although aromatic amine *N*-oxides are uncommon in nature and are unlikely to be present in photosystem II, the physical and chemical characteristics of these ligands and their ability to stablize mononuclear higher valent manganese ions may not be dissimilar to those of the binding groups for the manganese cofactor of photosystem II. The lack of knowledge of the role and environment of manganese and of its oxidation states in photosystem II continues to preclude development of rational model compounds.

These Mn(IV) complexes possess redox potentials that probably are too positive to be considered realistic models for manganese in photosystem II (if the role of manganese is the active site for water oxidation). However, the Mn(III)/Mn(II) redox couple for the *N*-oxide complexes may be a useful model for the hypothesis that manganese exists in a capacitor protein that stores charge for the four-electron oxidation of water.[18]

Acknowledgment. This work was supported by the U.S. Public Health Service–NIH under Grant No. GM 22761.

Registry No. $Mn(bpyO_2)_3^{2+}$, 64939-12-4; $Mn(bpyO_2)_3^{3+}$, 47839-12-3; $Mn(bpyO_2)_3^{4+}$, 64939-14-6; $Mn(terpyO_3)_2(ClO_4)_2$, 64939-16-8; $Mn(terpyO_3)_2^{3+}$, 64939-18-0; $Mn(terpyO_3)_2^{4+}$, 64939-20-4.

References and Notes

(1) M. M. Morrison and D. T. Sawyer, *Inorg. Chem.*, preceding paper in this issue.
(2) R. S. Nyholm and A. Turco, *J. Chem. Soc.*, 1121 (1962).
(3) R. G. Garvey, J. H. Nelson, and R. O. Ragsdale, *Coord. Chem. Rev.*, **3**, 375 (1968).
(4) S. K. Madan and W. E. Bull, *J. Inorg. Nucl. Chem.*, **26**, 2211 (1964).
(5) A. Vinciguerra, P. G. Simpson, Y. Kakiuti, and J. V. Quagliano, *Inorg. Chem.*, **2**, 286 (1963).
(6) P. G. Simpson, A. Vinciguerra, and J. V. Quagliano, *Inorg. Chem.*, **2**, 282 (1963).
(7) W. M. Reiff and W. A. Baker, *Inorg. Chem.*, **9**, 570 (1970).
(8) M. M. Morrison, E. T. Seo, J. K. Howie, and D. T. Sawyer, *J. Am. Chem. Soc.*, in press.
(9) Galbraith Analytical Laboratories, Knoxville, Tenn.
(10) These Mn(IV) complexes are soluble to about 5×10^{-4} M in acetonitrile, 0.1 M TPAP.
(11) F. Kutek and B. Dusek, *Collect. Czech. Chem. Commun.*, **35**, 13 (1970).
(12) W. Byers, B. Fa-Chun Chou, A. B. P. Lever, and R. V. Parish, *J. Am. Chem. Soc.*, **91**, 1329 (1969).
(13) $Mn(terpyO_3)_2^{2+}$ was not observed to be light sensitive in acetonitrile solution.
(14) G. M. Woltermann and J. R. Wasson, *Inorg. Chem.*, **12**, 2366 (1973).
(15) S. I. Chan, B. M. Fung, and H. Lutje, *J. Chem. Phys.*, **47**, 2121 (1967).
(16) J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, **88**, 499 (1966).
(17) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley-Interscience, New York, N.Y., 1972.
(18) (a) T. Wydrzynski, N. Zumbulyadis, P. G. Schmidt, and Govindjee, *Biochim. Biophys. Acta*, **408**, 349 (1975); (b) T. Wydrzynski, N. Zumbulyadis, P. G. Schmidt, H. S. Gutowsky, and Govindjee, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 1196 (1976).