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Mononuclear Manganese(IV) Complexes of Hydroxyl-Rich Schiff Base Ligands[1]

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Hydroxyl-rich Schiff base ligands react with Mn(II) and Mn(III) salts in basic methanolic solution, generating monomeric Mn(IV) complexes. The general stoichiometry is MnL_2, where L represents a dianionic, tridentate Schiff base ligand that uses one imine nitrogen, one phenolate oxygen, and one alkoxide oxygen atom to form a neutral octahedral complex. The molecular structure of $Mn(SALADHP)_2$ (where $H_2SALADHP$ = 1,3-dihydroxy-2-methyl-2-(salicylideneamino)propane) has been determined by X-ray crystallography. The compound crystallizes from DMF/ether in the monoclinic space group $P2_1/a$ ($Z = 4$, $a = 10.676$ (5) Å, $b = 16.473$ (10) Å, $c = 17.541$ (7) Å, $\beta = 102.82$ (4)°, $V = 3008$ (3) Å^3), and the structure has been refined by using full-matrix least-squares methods to a final $R = 0.076$, $R_w = 0.072$ with 2186 data greater than $3\sigma(I)$. Those complexes that form one five- and one six-membered ring (where L can be $H_2SALAHE$ = 2-(salicylideneamino)-1-ethanol, $H_2SALAPDH$ = 1,3-dihydroxy-3-phenyl-2-(salicylideneamino)propane, $H_2SALATHM$ = tris(hydroxymethyl)(salicylideneamino)methane, and $H_2NO_2SALAPDH$ = 1,3-dihydroxy-3-(4-nitrophenyl)-2-(salicylideneamino)propane) are believed to be isostructural to $Mn(SALADHP)_2$. The X-band EPR spectra, obtained at 90 K in DMF/methanol, show low-field features ranging between $g = 4.32$ and $g = 5.45$. The EPR spectrum for $Mn(SALADHP)_2$ arises from a rhombically distorted $S = {}^3/_2$ spin system with $E/D = 0.22$. The SALAHP ligand also forms mononuclear Mn(IV) complexes; however, it contains two six-membered chelate rings. All complexes exhibit room-temperature solid-state and solution magnetic moments in the range 3.80–4.3 μ_B, further substantiating the Mn(IV) formulation. The E_{p_c} values for the complexes in Me_2SO range between −320 and −480 mV vs. Ag/AgCl. The stabilization of the Mn(IV) oxidation state by alkoxide oxygen ligation is demonstrated by the nearly 1 V more negative reduction potential of these compounds compared to that of another compound, bis(salicylato)(bipyridine)manganese(IV), with an N_2O_4 coordination environment.

Introduction

In biological systems the catalytic role of many first-row transition elements, notably iron and copper, has been established for many years. Only recently, however, have functions been enumerated for manganese. A mononuclear Mn(III) center has been established at the active site of some enzymes that display superoxide dismutase activity.[4] The possibility of a binuclear center in the catalase isolated from *Lactobacillus plantarum* has been proposed.[5] In addition, manganese plays an integral role in the thylakoid-membrane-associated oxygen-evolving complex (OEC) of photosystem II[6,7] catalyzing the reaction

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+$$

In the photosynthetic process, four manganese ions are essential to catalysis,[8] with the possibility that some or all of the manganese ions may interact during turnover.[8,9] As well as containing a multinuclear center, the active site in this enzyme may contain manganese in the +4 oxidation state.[9,10] While EXAFS data[11] indicate that only N or O donor atoms are bound to manganese, there is no evidence for a manganoporphyrin center in the OEC. Given these observations, manganese centers in metalloenzymes represent a fertile area for coordination chemists to direct their attention.

In the last 10 years, a number of biologically relevant coordination complexes of manganese have been reported;[21–26] however, few of these have been mononuclear Mn(IV) compounds. Of these, structurally defined mononuclear Mn(IV) complexes[1,12b,16b,19a,26] are rarely documented. Herein, we report the general synthetic approach to a series of Mn(IV) complexes containing hydroxyl-rich Schiff base ligands. Due to the strong Lewis basicity

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Table I. Physical Properties of Mn(IV) Complexes

		anal. %			UV/vis λ, nm (ϵ, M^{-1} cm^{-1})			μ_{eff}, μ_B	
complex		obsd	calcd	yield, %	Me_2SO	CH_2Cl_2	*g* values[a]	solid	sol[b]
$Mn(SALAHE)_2 \cdot 2H_2O$	C	52.20	51.81	75	396 (4846)	473 (3140)	5.45 (0.32)	4.0	4.0
	H	5.10	5.31		472 (1731)	396 (6250)			
	N	7.00	6.71		554 (1710)				
	Mn	12.44	13.16						
$Mn(SALAHP)_2 \cdot 3H_2O$	C	52.59	51.83	60	398 (6844)	393 (8200)	1.96	3.8	4.3
	H	5.53	6.09		467 (3590)	471 (4520)	4.38 (0.07)		
	N	5.98	6.04		553 (2202)	562 (2380)	5.91		
	Mn	12.03	12.57						
$Mn(SALADHP)_2 \cdot 2DMF$	C	53.43	54.63	70	400 (6733)	392 (6512)	5.15 (0.22)	3.9	3.9
	H	6.55	6.55		467 (4011)	472 (3637)			
	N	8.98	9.10		554 (1863)	568 (1762)			
	Mn	9.15	8.92						
$Mn(SALATHM)_2 \cdot 3H_2O$	C	48.06	47.56	50	398 (6520)	insol	insol	3.9	insol
	H	5.82	5.76		470 (4040)				
	N	5.07	5.04		562 (1850)				
	Mn	10.05	10.00						
$Mn(SALAPDH)_2 \cdot H_2O$	C	62.45	62.84	47	386 (8040)	402 (6908)	4.32 (0.06)	3.9	
	H	5.54	5.54		487 (2160)	478 (3314)			
	N	4.35	4.58		569 (1508)	562 (1724)			
	Mn	8.94	9.00						
$Mn(NO_2SALAPDH)_2 \cdot DMF$	C	55.39	55.56	53	382 (8313)	377 (8985)	4.98 (0.19)	4.0	
	H	4.42	4.63		447 (4635)	481 (3822)			
	N	9.52	9.26		560 (1860)	...			
	Mn	7.53	7.28						

[a] In DMF/MeOH at X-band (9.3 GHz) frequency. *E*/*D* ratios in parentheses are from the calculations in ref 42. [b] Obtained in MeOH with *tert*-butyl alcohol as standard.

of the alkoxide residue, these Mn(IV) complexes are stable and amenable to physical characterization by X-ray crystallography, electrochemistry, and EPR and UV/vis spectroscopies.

Materials and Methods

The following abbreviations are used throughout the text: $H_2SALAHE$ = 1-hydroxy-2-(salicylideneamino)ethane, $H_2SALAHP$ = 1-hydroxy-3-(salicylideneamino)propane, $H_2SALADHP$ = 1,3-dihydroxy-2-methyl-2-(salicylideneamino)propane, $H_2SALATHM$ = tris(hydroxymethyl)(salicylideneamino)methane, $H_2SALAPDH$ = 1,3-dihydroxy-3-phenyl-2-(salicylideneamino)propane, $H_2NO_2SALAPDH$ = 1,3-dihydroxy-3-(4-nitrophenyl)-2-(salicylideneamino)propane, H_2SALPS = bis[2-(salicylideneamino)phenyl]disulfide.

Materials. Salicylaldehyde (sal), (1*R*,2*S*)-2-amino-1-phenyl-1,3-propanediol, and *threo*-2-amino-1-(4-nitrophenyl)-1,3-propanediol were obtained from Aldrich Chemical Co. 2-Amino-2-methyl-1,3-propanediol $Mn(CH_3CO_2)_3 \cdot 2H_2O$, and $Mn(CH_3CO_2)_2 \cdot 4H_2O$ were obtained from Fluka Co. Tris(hydroxymethyl)aminomethane and tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) were obtained from Sigma Chemical Co. and Alfa Products, respectively. TBAHFP was recrystallized from hot methanol prior to electrochemical studies. High-purity solvents (methylene chloride, dimethylformamide (DMF), dimethyl sulfoxide (Me_2SO), and methanol) were purchased from American Burdick and Jackson Co. and used as received in electrochemical studies. These solvents were stored under nitrogen. High-purity argon gas was used to deaerate solutions. All other chemicals and solvents were reagent grade. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of Compounds. Mononuclear manganese(IV) complexes of SALAHE, SALAHP, SALADHP, SALAPDH, 5-NO_2SALAPDH, and SALATHM can be obtained by identical synthetic procedures. The general preparation of these materials is presented for $Mn(SALAHE)_2 \cdot 2H_2O$ and $Mn(SALADHP)_2 \cdot 2DMF$ below. Unless otherwise specified, all manipulations were performed under nitrogen with use of standard inert-atmosphere procedures. Elemental analysis yields and physical parameters are reported in Table I.

$Mn(SALAHE)_2 \cdot 2H_2O$. To a solution of salicylaldehyde (2 mL, 18.8 mmol) and 2-amino-1-ethanol (1.15 g, 18.8 mmol) in 150 mL of methanol was added $MnCl_2 \cdot 4H_2O$ (1.86 g, 9.4 mmol). The mixture was refluxed for 2 h, resulting in a yellow solution. Then, 0.76 g of NaOH (18.8 mmol) was added and the deep yellow solution was refluxed for an additional 4 h. After it was cooled, the solution was exposed to air through vigorous stirring overnight. After 12 h, 15 mL of anhydrous diethyl ether was added to the deep red solution to precipitate NaCl. The solution was filtered and the volume reduced to half under vacuum. $Mn(SALAHE)_2 \cdot 2H_2O$ was recovered by filtration as a black microcrystalline solid.

$Mn(SALADHP)_2 \cdot 2DMF$. Twenty millimoles (2.16 mL) of salicylaldehyde was added to a solution of 20 mmol (2.10 g) of 2-amino-2-methyl-1,3-propanediol in 50 mL of DMF. The resulting mixture was refluxed for 1 h, generating a pale yellow solution. When the solution was cooled to room temperature, 60 mmol (2.4 g) of NaOH was added with stirring, generating a more intense yellow solution. At this point, 10 mmol (2.68 g) of $Mn(CH_3CO_2)_3 \cdot 2H_2O$ was added with stirring. This deep brown reaction mixture was refluxed for 4 h. After the reaction mixture was cooled to room temperature (23 °C), it was exposed to air and stirred overnight. A white solid (sodium acetate) was removed by filtration, leaving a dark red filtrate. Anhydrous diethyl ether (100 mL) was layered onto the filtrate and the mixture placed in the refrigerator overnight. The black crystals that deposited were collected by filtration and used in subsequent crystal structure analysis. An identical material was recovered if manganese(II) acetate was used as the source of metal.

An alternative synthesis of $Mn(SALADHP)_2$ was achieved with $KMnO_4$ as the source of metal. To 20 mmol (2.16 mL) of salicylaldehyde in 50 mL of methanol was added 20 mmol (2.10 g) of 2-amino-2-methyl-1,3-propanediol. This solution was refluxed for 1 h. When the solution was cooled to room temperature, 40 mmol (1.6 g) of NaOH was added to it. With no precautions to exclude air, 10 mmol (1.6 g) of $KMnO_4$ was added and the reaction mixture was stirred for 12 h. The volume was reduced under vacuum to half and placed in the refrigerator overnight. A dark purple solid that had UV/vis, EPR, electrochemical, and magnetic behavior identical with that of $Mn(SALADHP)_2$ prepared above was obtained. The yield for this reaction was 40%.

Collection and Reduction of X-ray Data. Suitable crystals of $Mn(SALADHP)_2 \cdot 2DMF$ were obtained as described above. The crystal was mounted in a glass capillary and sealed under nitrogen. Data were collected at room temperature on a Syntex $P2_1$ diffractometer. Intensity data were obtained with Mo Kα (0.7107 Å) radiation monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. Three standard reflections were measured every 50 reflections. The crystal and machine parameters are given in Table I. Intensity data were collected with use of $\theta/2\theta$ scans. An empirical absorption correction was applied to the data set. The data were reduced by using the SHELX program package,[27] and the structure was solved by using the direct-methods program MULTAN.[27] Atomic

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(27) Computations were carried out on an Amdahl 5860 computer. Computer programs used during structural analysis were from the SHELX program package by George Sheldrick, Institute für Anorganische Chemie der Universität Göttingen, Federal Republic of Germany. Other programs used include ORTEP, a thermal ellipsoidal drawing program by C. K. Johnson, and the direct-methods program MULTAN78 by Peter Main.

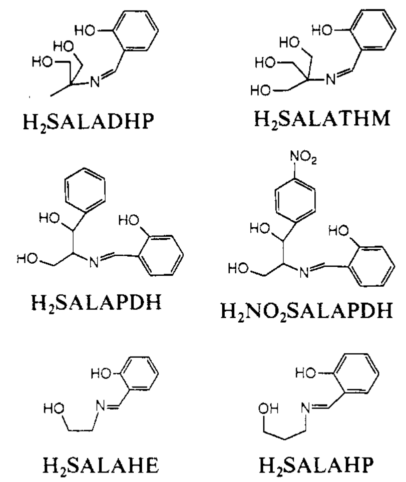

Figure 1. Hydroxyl-rich Schiff base ligands used in this study.

scattering factors were from ref 28. Hydrogen atoms were located, but not refined, and placed at fixed distances from bonded carbon atoms of 0.95 Å in the final least-squares refinement. Both DMF solvent molecules are disordered. The disorder of the first DMF is primarily in the amide carbon atom, while the second DMF occupies a hole in the lattice that allows for a small degree of rotation of the solvent molecule. Neither DMF molecule is involved in hydrogen bonding with atoms of the Mn-$(SALADHP)_2$ complex. The structure was refined by using a model with DMF molecules being assigned 0.9 and 0.1 occupancy factors in the two positions, respectively. Unique data used and final *R* indices are reported in Table I.

Electrochemical Measurements. Electrochemical measurements were performed with a BAS-100 electrochemical analyzer. Cyclic voltammetric measurements were performed under argon at 23 ± 2 °C in the designated high-purity solvent. The electroactive component was at 10^{-3} M concentration with TBAHFP (0.1 M) used as the supporting electrolyte. A three-electrode configuration was employed, with a Ag/AgCl reference and platinum working and auxiliary electrodes. The ferrocene/ferrocenium couple (+400 mV vs. Ag/AgCl) was used as an external reference.

Spectroscopic and Magnetic Measurements. UV/vis spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer equipped with a Perkin-Elmer 3600 data station. Infrared spectra were recorded on a Nicolet 60 SX Fourier transform infrared spectrophotometer with samples prepared as KBr pellets. Solution and solid-state EPR spectra were recorded on a Bruker ER200 E-SRC spectrometer equipped with a Varian variable-temperature controller. DPPH ($g = 2.0037$) was used as an external standard. Room-temperature magnetic moments were calculated from data obtained with a Faraday balance composed of a Cahn/Ventron R-100 electronic balance and a Varian Fieldial Mark I field-regulated magnetic power supply. The standard used was $Hg[Co(SCN)_4]$. Solution magnetic moments were calculated by the Evans NMR method[29,30] with a Bruker 360-MHz NMR spectrometer.

Results and Discussion

Synthesis of Mn(IV) Complexes. In this paper we report the synthesis of Mn(IV) complexes of hydroxyl-rich Schiff base ligands. The ligands illustrated in Figure 1 were chosen for this study since they could donate alkoxide oxygen atoms to the metal atom. We felt that this strong Lewis base would stabilize the Mn(IV) oxidation state, making it amenable to physical characterization. In every case, materials that have a 2:1 ligand to metal stoichiometry are isolated. The general unbalanced reaction scheme, which is applicable in methanol or DMF, is

$$Mn(CH_3CO_2)_n + \text{ligand} + NaOH \rightarrow MnL_2 + \text{sodium acetate}$$

The initial source of metal ion apparently does not dictate the final product composition as both Mn(II) and Mn(III) salts are aerially oxidized to the same material. In addition, $KMnO_4$ can be used to generate $Mn(SALADHP)_2$ although in lower yield than with a manganese acetate or chloride salt. The most likely pathway for the permanganate reaction is first ligand hydroxyl oxidation, generating free Mn(II) or Mn(III) in solution. The metal is chelated by unoxidized ligand and then aerially oxidized to the Mn(IV) complex. This would explain the relatively low yield of $Mn(SALADHP)_2$ by this synthetic route and also the observation that when potassium permanganate is reacted with $H_2SALAHP$ under the same conditions as for $H_2SALADHP$, no $Mn(SALAHP)_2$ is recovered. $H_2SALADHP$ presents excess hydroxyl groups allowing for both metal reduction and chelation, while stoichiometric amounts of $H_2SALAHP$ provide hydroxyls to reduce the MnO_4^- but an insufficient level of unoxidized ligand to form a high yield of $Mn(SALAHP)_2$. Recently, Christou and co-workers have reported the use of alkylammonium permanganates as useful reagents for the synthesis of Mn(III) dimers.[19b] Our results further substantiate the generality of this approach for the synthesis of biologically relevant high-oxidation-state manganese complexes. The one requirement we have found for the synthesis of mononuclear Mn(IV) complexes is the presence of a strong base such as sodium hydroxide. Presumably, the base is required to deprotonate the hydroxyl oxygen atom. Dimeric and trimeric materials, which are the subject of a separate report,[31] can be isolated when the reaction is carried out in the absence of base.

Table II. Summary of Crystallographic Data for $Mn(SALADHP)_2 \cdot 2DMF$

formula	$C_{28}H_{40}MnN_4O_8$
mol wt	615.6
a, Å	10.676 (5)
b, Å	16.473 (10)
c, Å	17.541 (7)
β, Å	102.82 (4)
V, $Å^3$	3008 (3)
cryst syst	monoclinic
space group	$P2_1/a$
d_{calcd}, g cm^{-3}	1.359
d_{obsd},[a] g cm^{-3}	1.35
Z	4
radiation	Mo Kα
abs coeff, μ, cm^{-1}	4.72
temp, K	298
cryst size, mm	0.090 × 0.310 × 0.520
scan speed, deg min^{-1}	2.5–12
scan range, deg	$0 < 2\theta < 45$
bkgd/scan time ratio	0.8
data collected	4657
unique data ($I > 3\sigma(I)$)	2186
largest nonsolv residual, e $Å^{-3}$	0.34
R, %	7.6
R_w, %	7.2

[a] Determined by flotation in hexane/CCl_4.

The compounds are neutral both in the solid state and in solution. This is demonstrated by the X-ray crystal structure discussed below and the lack of conductivity in all solvents that were tested (water, methanol, DMF, and methylene chloride). Thus, the ligands are dianionic in the complexes and, as shown below, act as tridentate chelating agents using an imine nitrogen and phenolate and alkoxide oxygen atoms to bind the metal. The materials, with the exception of $Mn(SALATHM)_2$, are soluble in alcohols, methylene chloride, DMF, and Me_2SO. $Mn(SALATHM)_2$ is soluble only in Me_2SO. The complexes do not react with water and appear stable in solution for long time periods. In addition, they do not react with water to form O_2 when irradiated with tungsten light under conditions where Mn(III) Schiff base complexes have been shown to oxidize water.[20] We believe that all the materials are isostructural with the $Mn(SALADHP)_2$ described below.

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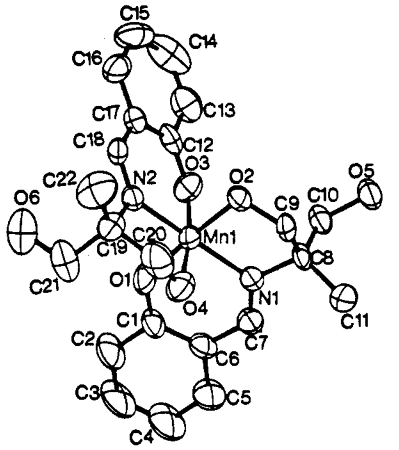

Figure 2. ORTEP diagram of Mn(SALADHP)$_2$ (showing numbering scheme) with thermal ellipsoids at 50% probability. Important bond lengths and angles are reported in Table IV.

Table III. Fractional Atomic Coordinates

atom	x	y	z	U_{eq},[a] Å^2
Mn1	0.5218 (2)	0.0105 (1)	0.3033 (1)	0.0454
O1	0.5073 (6)	−0.0280 (5)	0.1994 (4)	0.0642
O2	0.5200 (6)	0.0404 (4)	0.4049 (4)	0.0495
O3	0.5767 (7)	−0.0965 (5)	0.3372 (4)	0.0593
O4	0.4882 (7)	0.1186 (5)	0.2625 (4)	0.0618
O5	0.2644 (7)	−0.0676 (4)	0.4826 (4)	0.0579
O6	0.8457 (9)	0.0843 (7)	0.1985 (6)	0.1349
N1	0.3332 (7)	−0.0037 (5)	0.2939 (4)	0.0432
N2	0.7060 (8)	0.0468 (5)	0.3210 (5)	0.0417
C1	0.4061 (10)	−0.0374 (6)	0.1442 (6)	0.0534
C2	0.4214 (11)	−0.0528 (8)	0.0684 (7)	0.0770
C3	0.3169 (13)	−0.0642 (9)	0.0077 (7)	0.0942
C4	0.1931 (13)	−0.0604 (10)	0.0179 (7)	0.1129
C5	0.1761 (11)	−0.0468 (8)	0.0918 (7)	0.0757
C6	0.2804 (10)	−0.0349 (6)	0.1554 (6)	0.0529
C7	0.2507 (9)	−0.0207 (6)	0.2306 (6)	0.0480
C8	0.2944 (9)	0.0113 (6)	0.3687 (5)	0.0420
C9	0.3972 (9)	0.0686 (6)	0.4124 (6)	0.0463
C10	0.2996 (10)	−0.0713 (7)	0.4080 (6)	0.0491
C11	0.1626 (10)	0.0504 (7)	0.3588 (6)	0.0594
C12	0.6867 (11)	−0.1182 (6)	0.3807 (6)	0.0503
C13	0.6953 (12)	−0.1935 (8)	0.4174 (7)	0.0743
C14	0.8079 (15)	−0.2233 (7)	0.4610 (7)	0.0959
C15	0.9190 (12)	−0.1769 (8)	0.4719 (7)	0.0787
C16	0.9163 (10)	−0.1022 (8)	0.4369 (6)	0.0621
C17	0.8014 (10)	−0.0707 (7)	0.3921 (6)	0.0473
C18	0.8033 (9)	0.0070 (7)	0.3597 (5)	0.0487
C19	0.7209 (10)	0.1295 (7)	0.2903 (7)	0.0575
C20	0.5961 (13)	0.1698 (7)	0.2951 (7)	0.0877
C21	0.7343 (12)	0.1237 (8)	0.2055 (7)	0.0926
C22	0.8318 (12)	0.1788 (8)	0.3425 (8)	0.0904
C51	0.3456 (15)	0.1774 (10)	0.0778 (10)	0.1423
C52	0.1150 (16)	0.1924 (11)	−0.0036 (11)	0.1659
N53	0.2027 (12)	0.1778 (7)	0.0717 (8)	0.1159
C54	0.1976 (18)	0.1598 (14)	0.1547 (14)	0.1878
O55	0.0507 (13)	0.1553 (9)	0.1433 (8)	0.1495
C61	0.1238 (20)	0.2569 (17)	0.7518 (16)	0.2098
C62	0.3108 (19)	0.2098 (15)	0.8130 (14)	0.1834
N63	0.1696 (9)	0.1881 (6)	0.7858 (6)	0.0810
C64	0.1315 (17)	0.0979 (13)	0.7956 (12)	0.1860
O65	0.0007 (17)	0.1347 (13)	0.7581 (12)	0.2279
O65′	0.0686 (18)	0.0609 (14)	0.7907 (14)	0.0733
O64′	0.2338 (21)	0.1319 (19)	0.8151 (18)	0.1668
N53′	0.1217 (24)	0.2580 (24)	0.7600 (23)	0.1119
C54′	0.1483 (19)	0.1639 (16)	0.1306 (15)	0.0261

[a] U_{eq} is defined as one-third of the trace of the U_{ij} tensor.

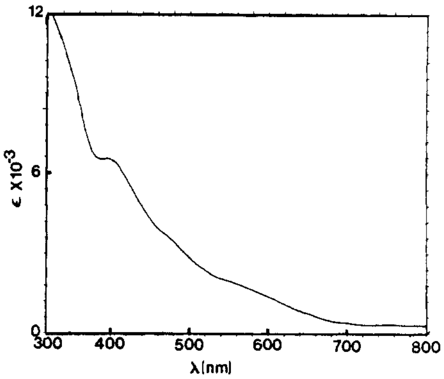

Figure 3. UV/vis spectrum of Mn(SALADHP)$_2$ in Me$_2$SO. The approximate concentration is 1 × 10^{-3} M.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Mn(SALADHP)$_2$

Mn1–O1	1.903 (6)	Mn1–O2	1.854 (6)
Mn1–O3	1.909 (7)	Mn1–O4	1.923 (7)
Mn1–N1	1.997 (7)	Mn1–N2	2.013 (7)
O1–Mn1–O2	173.5 (3)	O1–Mn1–O3	86.8 (3)
O1–Mn1–O4	89.1 (3)	O1–Mn1–N1	90.9 (3)
O1–Mn1–N2	96.6 (3)	O2–Mn1–O3	90.8 (3)
O2–Mn1–O4	94.0 (3)	O2–Mn1–N1	83.4 (3)
O2–Mn1–N2	89.5 (3)	O3–Mn1–O4	171.6 (3)
O3–Mn1–N1	98.7 (3)	O3–Mn1–N2	90.2 (3)
O4–Mn1–N1	88.6 (3)	O4–Mn1–N2	82.9 (3)
N1–Mn1–N2	168.6 (3)		

Structural Description of Mn(SALADHP)$_2$. Parameters for data collection are given in Table I. Fractional atomic coordinates for the non-hydrogen atoms are listed in Table II. The nearly octahedral geometry of the Mn(IV) ion in Mn(SALADHP)$_2$ is illustrated in Figure 2. Each ligand acts as a tridentate chelating agent in forming a meridional isomer. That this isomer is prepared relative to the facial orientation most likely results from the rigidity of the salicylideneamine group, which conformationally restricts the five-membered ring formed by the hydroxyethyl moiety to the meridional position.

Bond lengths and angles associated with the Mn(IV) coordination sphere are reported in Table III. The lengths for Mn–N and Mn–O bonds are in good agreement with the corresponding bonds in the complex bis(salicylato)(bipyridine)manganese(IV), which has appeared recently.[19a] Although there is a marked decrease in metal–ligand bond lengths when Mn(II) Schiff base complexes are compared to those of Mn(IV) (Mn(IV)–O(phenolate)$_{av}$ = 1.906 Å, Mn(II)–O(phenolate)$_{av}$ = 2.054 Å, Mn(IV)–N(imine)$_{av}$ = 2.005 Å, Mn(II)–N(imine)$_{av}$ = 2.258 Å, Mn(II) bond lengths from Mn^{II}SALPS·CH$_3$OH),[32] there is little difference between metal–ligand bond lengths in Mn^{III}(SALEN)Cl[23a] and Mn^{IV}(SALADHP)$_2$ (Mn(III)–O(phenolate)$_{av}$ = 1.892 Å, Mn(III)–N(imine)$_{av}$ = 1.987 Å). Manganese(II) and especially manganese(IV) complexes (high-spin d^5 and d^3, respectively) adopt octahedral coordination geometries in most complexes.[12b,16b,18b,19a,21a,23b,26,33] In contrast, Mn(III) (usually high-spin d^4) is much less selective and has been reported in distorted octahedral,[22c,d,34] trigonal-bipyramidal,[35] and square-pyramidal[12c,14b,23a,34] coordination environments.

UV/Visible Spectra. The UV/vis spectra of the complexes in Me$_2$SO are illustrated in Figure 3 and tabulated in both Me$_2$SO and methylene chloride solutions in Table IV. The spectra are essentially featureless in the visible region with strong absorbance in the ultraviolet region. Mn(IV) is isoelectronic with Cr(III) and, as such, is expected to exhibit two absorption bands due to d–d electronic transitions (from the octahedral approximation $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$). Usually these transitions are of low

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(33) The following reports illustrate examples of Mn^{2+} chelate complexes with coordination numbers other than 6: Watson, A. D.; Pulla Rao, C. H.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 2820. Meyer, E. M.; Floriani, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 356. Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 457.

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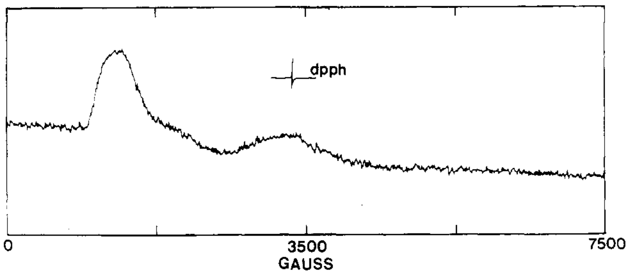

Figure 4. X-Band (9.31-GHz) EPR spectrum of $Mn(SALADHP)_2$ in DMF/methanol (3:2) at 100 K (power 20 mW time constant 50 s, gain 2.5×10^5).

intensity ($\epsilon \leq 200\ M^{-1}$) and, in this case, may be dominated by the strong UV tail in the visible region. However, there are shoulders at 450–490 and 550–570 nm for the complexes in Me_2SO solution (Table IV), which probably are due to d–d transitions. The abnormally large extinction coefficients for these transitions are, once again, a consequence of the intense tail from the UV absorption. The visible spectra of the hydroxyl-rich mononuclear Mn(IV) Schiff base complexes are in excellent agreement with those reported for tris(thiohydroxamato)manganese(IV)[36] and the mononuclear tris(glucarato)-, tris(gluconato)-, and tris(sorbitolato)manganese(IV) complexes[18b,c] (two shoulders are observed at 475–480 and 545–575 nm).

EPR Spectroscopy and Magnetic Data. The EPR spectrum of $Mn(SALADHP)_2$ in methanol/DMF (2:3) is given as Figure 4 to illustrate the signal observed for these Mn(IV) complexes. Values for g are reported for all of the complexes in Table IV. The Mn(IV) ion is a d^3 system and can be treated theoretically by using the literature developed for Cr(III) compounds.[37–39]

As has been discussed previously,[36–38] the complexity of an EPR spectrum of a d^3 ion in an axial field ($E/D = 0$) is dependent on the magnitude of the zero-field splitting parameters. Two limiting cases are when the value of the axial zero-field splitting parameter, $2D$, is either much larger than or much smaller than $h\nu$ (0.31 cm^{-1} at X-band frequencies). In the first case, the feature at low field is predicted to be strong while the $g = 2$ component is weak. This is the observation for tris(catecholato)manganese(IV)[18a] and the tris(sorbitolato)manganese(IV)[40] complexes. When D is small, the $g = 2$ component should dominate with relatively weak signals in the low-field region. This is observed for tris(thiohydroxamato)manganese(IV)[36] and tris(dithiocarbamato)manganese(IV)[41] complexes. The EPR spectra of the hydroxyl-rich Schiff base Mn(IV) complexes presented herein do not fit either axial limit. Instead, they exhibit marked rhombic electronic distortions.

The $g_{eff} = 4.1$ component arising from an axial $S = {}^3/_2$ spin system shifts to lower field as E/D deviates from zero.[42] For our complexes g_{eff} ranges between 4.32 ($Mn(SALAPDH)_2$) and 5.45 ($Mn(SALAHE)_2$). These resonances are broad, showing no evidence for ^{55}Mn hyperfine coupling. In addition to the g_{eff} range, the spectra also vary with the intensity of the low-field component (those complexes with larger g_{eff} values tend to have smaller intensities for the component). $E/D = 0.22$ is obtained for $Mn(SALADHP)_2$ ($g_{eff} = g_y = 5.15$). The minor features at higher field arise from the predicted g_x (2.55) and g_z (1.71) components of the rhombic system. A complete listing of E/D ratios is given in Table I.

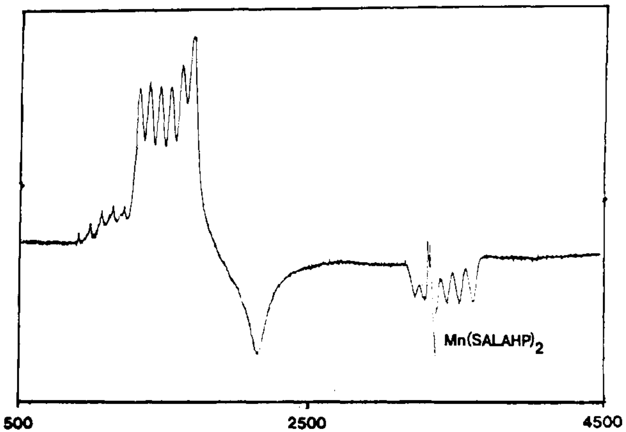

Figure 5. X-Band (9.31-GHz) EPR spectrum of $Mn(SALAHP)_2$ in DMF/MeOH (3:2) at 100 K. Conditions are as in Figure 4. The Mn nuclear hyperfine coupling is 77 G.

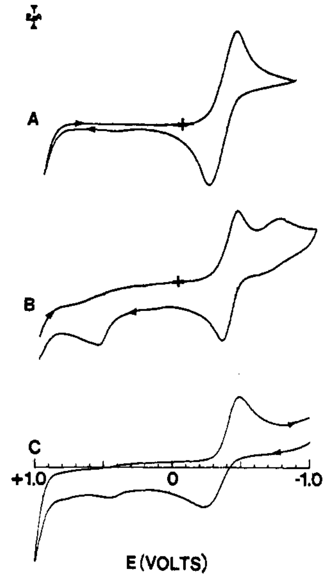

Figure 6. Cyclic voltammetric traces for $Mn(SALAHP)_2$ (A), $Mn(SALADHP)_2$ (B), and $Mn(SALATHM)_2$ (C) in Me_2SO at 25 °C with TBAHFP (0.1 M) as supporting electrolyte. Potentials are vs. the Ag/AgCl reference electrode (scan rate 50 mV/s).

Table V. Electrochemical Data for the Redox Couple $MnL_2^{0/-}$ in Me_2SO with 0.1 M TBAHFP at 25 °C[a]

compd	E_a, mV	E_c, mV	i_a/i_c
$Mn(SALAHE)_2$		−542	
	+629		
$Mn(SALAHP)_2$	−226	−320	0.70
$Mn(SALADHP)_2$	−256	−460	0.59
		−750	
	+485		
$Mn(SALATHM)_2$	−253	−476	0.49
	+465		
$Mn(SALAPDH)_2$	−256	−419	0.62
$Mn(NO_2SALAPDH)_2$	−880	−1148	0.31
		−430	
	+378		
$H_2NO_2SALAPDH$	−976	−1051	0.94

[a] All potentials are reported vs. the Ag/AgCl reference electrode. Cyclic voltammograms were recorded at 50 mV/s.

The majority of the manganese(IV) complexes formed by the SALA series of ligands have EPR spectra similar to that of $Mn(SALADHP)_2$, shown in Figure 4. In contrast, $Mn(SALAHP)_2$ displays well-resolved ^{55}Mn hyperfine structure on each of the observed resonances as illustrated in Figure 5 and reported in Table I. The magnitude of the ^{55}Mn hyperfine coupling (77 G) is consistent with previous reports for the Mn(IV) oxidation state.[43] The $Mn(SALAHP)_2$ spectra follow a Curie law de-

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pendence between 100 and 20 K.[44] A detailed analysis of the EPR spectra of these mononuclear Mn(IV) complexes, as well as of mixed-valence trinuclear species, will be reported separately.[45]

Electrochemistry of Complexes. A summary of the electrochemical potentials of the Mn(IV) Schiff base complexes is reported in Table V. The cyclic voltammograms of selected complexes are illustrated in Figure 6. The simplest electrochemical response is observed for Mn(SALAHP)$_2$. In this case a quasi-reversible, one-electron reduction of the Mn(IV) complex occurs at $E_{p_c} = -320$ mV (all potentials vs. the Ag/AgCl reference electrode). The electrochemistry of Mn(SALADHP)$_2$ and Mn(NO$_2$SALAPDH)$_2$ is complicated by ligand-centered redox reactions. In addition to the quasi-reversible, one-electron, metal-based reductive wave at $E_{p_c} = -460$ mV, an oxidative feature at +470 mV is also observed for Mn(SALADHP)$_2$. This wave is also present in a solution of SALADHP that does not contain manganese, thus demonstrating that this is a ligand-centered oxidation. Ligand-based electrochemistry is also apparent in the cyclic voltammetry of Mn(NO$_2$SALAPDH)$_2$. The irreversible one-electron process seen at −1148 mV is associated with the nitrophenyl group. This assignment is supported by two observations. First, a reversible one-electron wave ($E_{p_c} = -1051$ mV, Table V) is apparent in the electrochemistry of H$_2$NO$_2$SALAPDH in the absence of manganese. Second, the cyclic voltammetry of Mn(SALAPDH)$_2$, which lacks the nitro group, is nearly identical with that of Mn(SALADHP)$_2$. As shown in Table V, all of the complexes exhibit a manganese reductive wave in the range −300 to −480 mV. There is no evidence for the Mn(III)/Mn(II) couple for any of the complexes.

The negative reduction potential exhibited by all of the hydroxyl-rich Schiff base complexes demonstrates the ability of these ligands to stabilize the Mn(IV) oxidation state. Another mononuclear Mn(IV) complex, Mn^{IV}(SAL)$_2$(bpy) (H$_2$SAL = salicylic acid; bpy = 2,2′-bipyridine), also contains an N$_2$O$_4$ coordination geometry. In this case, the reduction potential is +440 mV (vs. the standard calomel electrode (SCE) in DMF). When the reduction potential of Mn(SALADHP)$_2$ is determined in DMF relative to the SCE, a value of −520 mV is obtained. Even though both Mn^{IV}(SAL)$_2$(bpy) and Mn(SALADHP)$_2$ couples correspond to reduction of the neutral complex to the monoanion and both complexes contain an N$_2$O$_4$ coordination environment, the Mn(IV) ion is stabilized by nearly 1 V by the SALADHP ligand. This effect results from the coordination of the alkoxide oxygen atom, which is a much stronger Lewis base as compared to the carboxylate oxygen atom of salicylic acid.[46]

The properties of Mn(SALAHP)$_2$ seem to differ most markedly from those of the other complexes reported herein. For example, this complex has the least negative reduction potential and is the most difficult to synthesize of the hydroxyl-rich Schiff base compounds. The synthetic complexity arises due to the facile formation of an acetate-bridged Mn(III) dimer when manganese acetate is the source of metal. This dimer is obtained even when 2 equiv of ligand is added. Mn(SALAHP)$_2$ is most conveniently prepared when manganese chloride is used in the synthesis. In contrast, the corresponding Mn(III) SALADHP dimer has not been prepared and a mixed-valence trinuclear compound[29] is isolated in high yield only when (1) manganese acetate is the source of metal, (2) 1 equiv of ligand is used, and (3) strong base, such as potassium hydroxide, is omitted from the procedure. Thus, it would appear that the SALAHP ligand generally stabilizes Mn(IV) complexes more poorly than the other ligands we have discussed. This relative instability probably results from the additional methylene group, which requires the formation of a six-membered chelate ring rather than the five-membered ring formed by the other ligands of this series.

Conclusions

Many mechanistic proposals for photosynthetic oxygen evolution include manganese species at the +4 oxidation level. Indeed, the S$_4$ state (from which oxygen is ultimately released) may contain four Mn(IV) ions. Although the S$_4$ state must be highly oxidizing, the precursor enzymatic forms that may contain Mn(IV) (such as S$_3$ and S$_2$) should not have reduction potentials that are too positive, else protein or other membrane components could be attacked prior to water oxidation. Indeed, the most fascinating aspect of biological water oxidation may not be the generation of species capable of forming O$_2$ directly from water but rather the elegant fine tuning of intermediate enzymatic oxidation states at potentials incapable of participating in damaging side reactions. Often, Mn(IV) is solely discussed in the biological literature as a moderate or strong oxidant without consideration for the ligand donor set. The data presented in this paper illustrate that Mn(IV) has a wide redox potential range (nearly 900 mV) within a similar heteroatom donor set (N$_2$O$_4$) and demonstrate the degree of stabilization of the Mn(IV) oxidation state imparted by alkoxide oxygen donors. Within the framework of the oxygen-evolving complex, alkoxide or oxo groups could moderate the oxidizing power of the manganese center(s) in the enzyme until oxidizing equivalents become essential for catalysis. In so doing, membrane components would be protected and dissipative energy losses minimized.

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Supplementary Material Available: Table VI (anisotropic thermal parameters for Mn(SALADHP)$_2$), Table VII (isotropic thermal parameters for solvent molecules), Table VIII (bond distances in angstroms), and Table IX (bond angles in degrees) and Figure 7 (numbering diagram for Mn^{IV}(SALADHP)$_2$) (6 pages); Table X (observed and calculated structure factors) (10 pages). Ordering information is given on any current masthead page.

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[43] Rasmussen, P. G.; Been, K. M.; Hornyak, E. J. *J. Chem. Phys.* **1969**, *50*, 3647.

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[46] A reviewer has suggested a reasonable explanation for the trend in redox potentials with the Mn(IV) hydroxyl-rich Schiff base complex series. Although Mn(IV) prefers octahedral coordination, a high-spin Mn(III), with a d^4 electronic environment, might exhibit a tetragonal distortion. In this case, the ligands with one five- and one six-membered chelate ring would more severely constrain the Mn(III) to octahedral coordination, making these complexes more difficult to reduce. In contrast, Mn(SALAHP)$_2$ has two six-membered rings, imparting more flexibility to the Mn(III) coordination environment, which allows easier reduction. Although this explanation rationalizes the trends in potentials within these complexes, we believe that the primary factor stabilizing the Mn(IV) oxidation state is the base strength of the alkoxide oxygen (pK > 13) relative to that of the carboxylate of salicylic acid (pK = 2.8: *Critical Stability Constants*; Martell, A. E., Smith, R. M., Eds.; Plenum: New York, 1977; Vol. 3).