

# Synthesis, Crystal Structure, and Electrochemical and Spectroelectrochemical Properties of the New Manganese(III) Complex $[\text{Mn}^{\text{III}}(\text{BBPEN})][\text{PF}_6]$ $[\text{H}_2\text{BBPEN} = \text{N,N}'\text{-Bis}(2\text{-hydroxybenzyl})\text{-N,N}'\text{-bis}(2\text{-methylpyridyl})\text{ethylenediamine}]$

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Two new hexadentate ligands ( $\text{H}_2\text{L}$ ) derived from alkyldiamines containing phenolate-type and  $\alpha$ -pyridyl pendant arms have been prepared:  $\text{N,N}'\text{-bis}(2\text{-hydroxybenzyl})\text{-N,N}'\text{-bis}(2\text{-methylpyridyl})\text{ethylenediamine}$  ( $\text{H}_2\text{BBPEN}$ ;  $\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_2$ ) and  $\text{N,N}'\text{-bis}(2\text{-hydroxybenzyl})\text{-N,N}'\text{-bis}(2\text{-methylpyridyl})\text{-1,3-propanediamine}$  ( $\text{H}_2\text{BBPPN}$ ;  $\text{C}_{29}\text{H}_{32}\text{N}_4\text{O}_2$ ). The reaction of  $\text{H}_2\text{L}$  with  $\text{Mn}(\text{CH}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$  in methanolic solution affords upon addition of  $\text{NH}_4\text{PF}_6$  monomeric Mn(III) complexes ( $[\text{MnL}][\text{PF}_6]$ ) in high yields. The crystal structure of  $[\text{Mn}(\text{BBPEN})][\text{PF}_6]$  (**1**) has been determined by X-ray crystallography. Crystal data: monoclinic, space group  $P2_1/n$ ,  $a = 11.310$  (2) Å,  $b = 21.266$  (3) Å,  $c = 11.791$  (4) Å,  $\beta = 106.7$  (2)°,  $V = 2716$  (1) Å<sup>3</sup>,  $Z = 4$ . The structure has been refined to an  $R$  factor of 6.3% based on 3023 observed reflections. In the complex cation of **1**, the manganese is coordinated by the hexadentate  $\text{BBPEN}^{2-}$  ligand producing a distorted octahedral  $\text{MnN}_4\text{O}_2$  geometry, with two pyridyl groups, bound in the trans position. Average Mn–O and Mn–N (two types) bond lengths are 1.867 (4), 2.101 (4), and 2.244 (5) Å. The presence of four short Mn–O and Mn–N bonds and two long Mn–N bonds are consistent with Jahn–Teller effects. The magnetic moments (4.85–4.90  $\mu_B$ ) of the  $[\text{MnL}][\text{PF}_6]$  complexes correspond to the  $d^4$  configuration. Cyclic voltammograms of (**1**) and  $[\text{Mn}(\text{BBPPN})][\text{PF}_6]$  (**2**) in acetonitrile show two quasi-reversible one-electron-transfer processes corresponding to Mn(IV)/Mn(III) at 0.49 and 0.61 V and Mn(III)/Mn(II) at –0.37 and –0.44 V vs.  $\text{Fc}^+/\text{Fc}$ . Spectroelectrochemistry in the UV–vis spectral region has been used to characterize the Mn(IV) analogues of these complexes.  $E^\circ$  values obtained from these spectropotentiostatic data are consistent with values determined from cyclic voltammograms. The electronic spectra of the oxidized species show two intense LMCT transitions in the 400–800-nm range, and solutions of  $[\text{Mn}^{\text{IV}}(\text{BBPEN})]^{2+}$  are stable for at least 24 h under argon. The X-band EPR spectra of this solution obtained at 110 K shows prominent features at  $g_1 = 5.84$ ,  $g_2 = 4.77$ , and  $g_3 = 1.99$  and is consistent with a rhombically distorted  $S = 3/2$  spin system.

## Introduction

It is well established that manganese plays an important role in many biological redox processes including disproportionation of hydrogen peroxide (catalase activity) in microorganisms,<sup>1</sup> decomposition of  $\text{O}_2^-$  radicals catalyzed by superoxide dismutases (SODs),<sup>2</sup> and water oxidation by photosynthetic enzymes (photosystem II; PSII).<sup>3</sup> In view of the importance of these metalloenzymes containing manganese as active sites, the chemistry and biochemistry of these systems has been the subject of a number of recent reviews.<sup>4</sup> All three enzymes probably contain

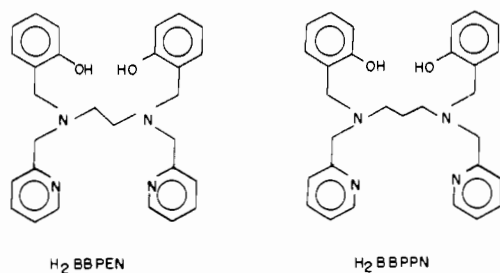
Mn(III) in at least one of their catalytic forms. The SODs are red and contain mononuclear Mn(III) sites surrounded by nitrogen and oxygen donor atoms,<sup>5</sup> whereas in the PSII system it appears that four manganese centers make up the active site.<sup>6a</sup> A mononuclear and trinuclear arrangement for the organization of

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the manganese ions in this enzyme has been proposed on the basis of the low-field EPR signal ( $g \approx 4.1$ ).<sup>6b,c</sup> While the preparation and structural characterization of polynuclear complexes containing N,O-donor ligands have been studied extensively<sup>7</sup> as simple active-site models for the photosynthetic enzymes PSII, those of mononuclear Mn(III)<sup>8</sup> and Mn(IV)<sup>9</sup> complexes have received much less attention in the last few years. A mononuclear Mn(V) complex has been reported recently.<sup>10</sup> Therefore, the syntheses and characterization of new mononuclear manganese complexes in high oxidation states with relevant heteroatom donor ligands is an important area of investigation.

In this paper we describe the preparation of two hexadentate ligands (H<sub>2</sub>BBPEN and H<sub>2</sub>BBPPN) derived from alkyldiamines containing phenolate-type and  $\alpha$ -pyridyl pendant arms. The Mn(III) complexes formed with these ligands have been examined using spectral, solution electrical conductivity, magnetic, and spectroelectrochemical techniques. The structure of the [Mn<sup>III</sup>(BBPEN)][PF<sub>6</sub>]<sup>-</sup> complex has been determined by X-ray crystallography. Interestingly, this complex shows unusual short axial Mn(III)-N(pyridine) bond distances and a relatively high redox potential for the Mn(IV)/Mn(III) couple which is required for water splitting in the active site of PSII.



## Experimental Section

**Abbreviations.** H<sub>2</sub>SALEN = *N,N'*-disalicylideneethylenediamine; H<sub>2</sub>BBEN = *N,N'*-bis(2-hydroxybenzyl)ethylenediamine; H<sub>2</sub>BBPPN = *N,N'*-bis(2-hydroxybenzyl)propanediamine.

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bis(2-hydroxybenzyl)-1,3-propanediamine; EHPG = ethylenebis[(*o*-hydroxyphenyl)glycine]; BHBB = 1,2-bis(2-hydroxybenzamido)benzene anion; py = pyridine; H<sub>2</sub>als = *N*-(2-carboxyethyl)salicylideneamine.

**Materials.** Salicylaldehyde, 2-picoyl chloride hydrochloride, NH<sub>4</sub>PF<sub>6</sub>, and tetra-*n*-butylammonium hexafluorophosphate [(TBA)PF<sub>6</sub>]<sup>-</sup> were obtained from Aldrich Chemical Co. Ethylenediamine and 1,3-propanediamine were obtained from Merck. For the electrochemical, spectroelectrochemical, and spectroscopic studies, high purity solvents were used as received from Merck. High-purity argon was used to deoxygenate solutions. All other chemicals and solvents were reagent grade.

**Syntheses.** H<sub>2</sub>SALEN. This compound was prepared by the method of Diehl and Hach.<sup>11</sup>

H<sub>2</sub>BBEN. This compound was prepared in high yield by a modified method described in the literature.<sup>12</sup> To a solution of H<sub>2</sub>SALEN (35.0 g, 130 mmol) in methanol (150 mL) was slowly added NaBH<sub>4</sub> (5.0 g, 130 mmol) with stirring. The precipitate was filtered off, washed with water (1300 mL), and dried in vacuum under P<sub>2</sub>O<sub>5</sub>. Yield: 31.0 g; 87%. Mp = 124 °C (lit.<sup>12</sup> value: 124 °C).

H<sub>2</sub>BBPEN. To a solution of 2-(chloromethyl)pyridine hydrochloride (19.9 g, 120 mmol) in water (40 mL) previously neutralized with NaOH, was added the diamine H<sub>2</sub>BBEN (16.5 g; 60 mmol) with stirring. The reaction mixture was heated (65 °C) and more NaOH (30 mL 4 M; 120 mmol) was added over a period of 1 h in small portions so that the pH never exceeded 10. The red solution was cooled and extracted with chloroform (10 × 60 mL). The combined organic phases were dried over MgSO<sub>4</sub>. After removal of the solvent by rotatory evaporation, a red residue was obtained which was dissolved in hot methanol (120 mL) and then cooled to 5 °C. After 4 h a white precipitate of the desired ligand (H<sub>2</sub>BBPEN) had formed, which was filtered off, washed with cold methanol and ether, and dried under vacuum. Yield: 16 g; 58% with respect to H<sub>2</sub>BBEN. Mp = 115 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>);  $\delta$ : 10.6 (s, two phenolic protons), 6.7–8.5 (m, 16 H, phenyl and py), 3.6–3.8 (d, 8H, N-CH<sub>2</sub>-R), 2.7–2.8 (s, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>-N). MS: *m/z* 455. Anal. Calcd for C<sub>28</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>: C, 74.0; H, 6.7; N, 12.3. Found: C, 74.5; H, 7.2; N, 12.4.

H<sub>2</sub>BBPPN. The same procedure as described for H<sub>2</sub>BBPEN was employed with 1,3-propanediamine as the starting material instead of ethylenediamine. Yield: 55%. Mp = 98 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>);  $\delta$ : 8.4–8.6 (d, 2H, py), 6.6–7.8 (m, 14H, phenyl and py), 3.6–3.9 (d, 8H, N-CH<sub>2</sub>-R), 2.3–2.7 (t, 4H, N-C<sub>2</sub>H<sub>2</sub>), 1.6–2.0 (m, 2H, C-CH<sub>2</sub>-C). The phenolic protons were not observed. MS: *m/z* 468.

[Mn<sup>III</sup>(BBPEN)][PF<sub>6</sub>]<sup>-</sup>·1/2C<sub>2</sub>H<sub>5</sub>OH (1). To a solution of H<sub>2</sub>BBPEN (1.36 g, 3 mmol) in methanol/ethanol (10 mL/40 mL) was added Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (0.80 g, 3 mmol). The deep red solution was heated to 60 °C, and NH<sub>4</sub>PF<sub>6</sub> (0.57 g, 3.5 mmol) was added. After the solution was cooled to room temperature, a microcrystalline precipitate was obtained to have formed, which was collected by filtration, washed with cold ethanol and ether, and air dried. Yield: 70%. Anal. Calcd for MnC<sub>28</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub>PF<sub>6</sub>·1/2C<sub>2</sub>H<sub>5</sub>OH: C, 51.56; H, 4.62; N, 8.30; Mn, 8.13. Found: C, 51.9; H, 4.8; N, 8.2; Mn, 7.9. Molar conductivity = 124  $\Omega^{-1}$  cm<sup>2</sup> M<sup>-1</sup>.

Crystals of [Mn<sup>III</sup>(BBPEN)][PF<sub>6</sub>]<sup>-</sup> suitable for X-ray crystallography were obtained by slow evaporation of an acetonitrile-propanol-2 (2:1) solution of the complex.

[Mn<sup>III</sup>(BBPPN)][PF<sub>6</sub>]<sup>-</sup> (2). A mixture of H<sub>2</sub>BBPPN (1.41 g, 3 mmol) and Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (0.8 g, 3 mmol) in methanol (50 mL) was heated to 50 °C for 30 min. To the deep green solution was added NH<sub>4</sub>PF<sub>6</sub> (0.6 g, 3.7 mmol), which initiated the precipitation of a green microcrystalline solid, which was filtered off, washed with cold methanol and ether, and air dried. This complex was recrystallized from a methanol-water (5:1) mixture. Anal. Calcd for MnC<sub>29</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>PF<sub>6</sub>: C, 52.26; H, 4.54; N, 8.41. Found: C, 52.36; H, 4.57; N, 8.40. Molar conductivity = 134  $\Omega^{-1}$  cm<sup>2</sup> M<sup>-1</sup>.

**Physical Measurements.** Electronic absorption spectra in the 200–800-nm range were recorded with a Hewlett-Packard HP-8450A spectrophotometer, and infrared spectra (KBr disk) with a Perkin-Elmer Model 781 IR spectrophotometer. The solution electrical conductivity was measured with an Digimed conductivity bridge, Type CD-21, with solute concentrations of ca. 10<sup>-3</sup> M. The 200-MHz <sup>1</sup>H NMR spectra were recorded on a Bruker 200 FT spectrometer. The magnetic susceptibility of powdered samples of the manganese(III) complexes was

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**Table I.** Crystallographic Parameters for [Mn(BBPEN)]PF<sub>6</sub>

chem formula	C <sub>28</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> MnPF <sub>6</sub>	Z	4
fw	652.42	T, °C	25
space group	P2 <sub>1</sub> /n (No. 14)	λ, Å	0.710 73
a, Å	11.310 (2)	ρ <sub>calcd</sub> , g cm <sup>-3</sup>	1.60
b, Å	21.266 (3)	μ, cm <sup>-1</sup>	5.74
c, Å	11.791 (4)	R, %	6.3
β, deg	106.72 (2)	R <sub>w</sub> , %	7.2
V, Å <sup>3</sup>	2716 (1)		

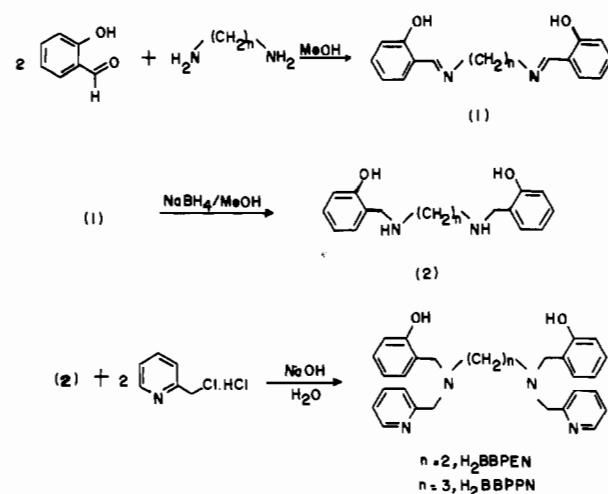
$$^a R = \sum |k|F_o| - |F_c|| / \sum |k|F_o| \quad ^b R_w = [\sum w(k|F_o| - |F_c|)^2 / \sum w k^2 F_o^2]^{1/2}; w^{-1} = \sigma^2(|F_o| + g|F_o|^2); g = 0.007 794.$$

measured by the Faraday method (Sartorius microbalance, Bruker B-E 1008 research magnet, and Bruker B-VT 1000 automatic temperature control) in the temperature range 81–293 K. Diamagnetic corrections were applied in the usual manner with use of tabulated Pascal constants. X-Band EPR spectra were obtained in frozen acetonitrile solutions with a Varian spectrometer, Model E-109, equipped with a Variable-temperature controller. The samples were prepared by exhaustive electrolysis of the [Mn<sup>III</sup>(BBPEN)]<sup>+</sup> species and transferred to the quartz tube under nitrogen atmosphere.

**Electrochemical Measurements.** Electrochemical experiments were performed with a Princeton Applied Research (PARC) Model 273 potentiostat/galvanostat equipped with an X-Y-T recorder (ECB Equipamentos Científicos do Brasil). Cyclic voltammograms (CVs) were performed in acetonitrile solutions containing 0.1 M [TBA(PF<sub>6</sub>)] as supporting electrolyte and were conducted at 25 °C under an argon atmosphere. The electrochemical cell employed was of a standard three-electrode configuration: a platinum or glassy-carbon working electrode, a platinum-wire auxiliary electrode, and a SCE reference electrode. Electrode performance was monitored by observing the ferrocene (Fc<sup>+</sup>/Fc) couple. The half-wave potentials were taken as the average of the anodic and cathodic peak potentials of reversible or quasi-reversible cyclic voltammograms. Diagnostic criteria for reversibility of electron-transfer processes were employed in the usual manner.<sup>14</sup>

**Spectroelectrochemical Measurements.** The optically transparent thin-layer cell was constructed according to a procedure described as follows: the transparent electrode was a 500 wires per inch (60% transmittance) Buckbee Mears Co. gold minigrd, sandwiched between two microscope slides by a Teflon tape spacer. The minigrd acts as a working electrode and extended outside of the slides for electrical contact. The solutions were prepared and degassed under an inert atmosphere (argon) and introduced into the cell through a capillary. The minigrd was located within 4–6 mm of the cell bottom to minimize *iR* drop. All potentials were measured vs a saturated calomel electrode. Potentials were applied to the cell by a Bioanalytical SP-2 potentiostat/galvanostat, and the spectra were collected with a HP-8450 diode-array apparatus.

**X-ray Crystallography.** A brown prismatic shaped crystal (1.62 × 0.60 × 0.38 mm<sup>3</sup>) of **1** was mounted on a CAD-4 Enraf-Nonius diffractometer. The cell parameters were obtained by a least-square fit of 25 reflections (8.1° < 2θ < 27.6°). Crystal parameters are given in Table I. Data were collected by the θ–2θ scan with graphite-monochromated Mo Kα radiation, scan speed of 4–20 deg/min and scan range of (0.80 + 0.35 tan θ) deg. No significant decline in intensities of one standard reflection (0–18, 0) was observed. Intensity data were corrected for Lorentz and polarization effects, but no absorption or extinction corrections were applied. The number of measured reflections was 5184 in the range –13/13, 0/25, 0/14 with 4761 unique reflections. The systematic absences were *h*0*l*, *h* + *l* = 2*n*, and 0*k*0, *k* = 2*n*, consistent with the space group P2<sub>1</sub>/n. Equivalent reflections were merged with R<sub>int</sub> = 8.1%. The structure was solved with MULTAN-80<sup>15</sup> and successive Fourier syntheses. The structure was refined by a least-square procedure that utilized a “blocked cascade” algorithm. The function minimized during least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$  with  $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$  where  $\sigma(F_o)$  is the esd for the observed amplitude based on counting statistics. The positions of H atoms were calculated and included in the final refinement cycle, using the SHELX-76<sup>16</sup> program. All non-hydrogen atoms were refined with the use of anisotropic thermal parameters. The number of

**Scheme I**

refined parameters was 378. In the final refinement cycle a maximum ( $\Delta/\sigma$ ) = 0.60 and a maximum height in the final  $\Delta F$  map of 0.9 e/Å<sup>3</sup> near to Mn atom were observed. During all calculations the analytical scattering factors for neutral atoms were corrected for both  $\Delta f'$  and  $i(\Delta f'')$  terms. The calculations were carried out on an IBM/3090 computer using the SHELX-76 program package and the scattering factors were taken from ref 17.

## Results and Discussion

**Syntheses.** The ligands H<sub>2</sub>BBPEN and H<sub>2</sub>BBPPN are produced in good yields by the reaction of 2-(chloromethyl)pyridine and the corresponding diamine (H<sub>2</sub>BBEN or H<sub>2</sub>BBPN). The diamines were prepared in excellent yields (≈90%) and purity by using a modified method described in the literature.<sup>12</sup> The general route is given in Scheme I. The characterization of H<sub>2</sub>BBPEN and H<sub>2</sub>BBPPN was established unambiguously by mass spectrometry and <sup>1</sup>H NMR spectroscopy. The ligands H<sub>2</sub>BBPEN and H<sub>2</sub>BBPPN react in methanol with manganese(III) acetate dihydrate to form the stable monocationic [Mn<sup>III</sup>(BBPEN)]<sup>+</sup> and [Mn<sup>III</sup>(BBPPN)]<sup>+</sup> complexes. These were isolated in high yields as hexafluorophosphate salts. The complexes can be obtained as adequate crystals for X-ray crystallography, without solvate molecules when recrystallized from acetonitrile:propanol-2 (2:1) mixtures. Complexes **1** and **2** are soluble in water and in a variety of organic solvents (CH<sub>3</sub>CN, CH<sub>3</sub>OH, DMF, CH<sub>2</sub>Cl<sub>2</sub>, THF) and are exceedingly stable, since no spectral change was observed in these solvents. In the solid state, **1** and **2** seem indefinitely stable in air. Conductivity measurements in acetonitrile solution at ca. 10<sup>-3</sup> M, determined at 25 °C, are in the range 120–160 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, indicating their 1:1 electrolyte behavior,<sup>18</sup> consistent with the formula from elemental analyses.

**Crystal and Molecular Structure of [Mn<sup>III</sup>(BBPEN)]PF<sub>6</sub> (1).** The structure of complex **1** consists of discrete mononuclear [Mn<sup>III</sup>(BBPEN)]<sup>+</sup> cations and uncoordinated hexafluorophosphate anions on general positions. An ORTEP drawing of the complex with atom-labeling scheme is shown in Figure 1. The atomic parameters and selected bond distances and angles are given in Tables II and III, respectively. The manganese(III) ion is coordinated to BBPEN<sup>2-</sup> in a pseudooctahedral environment, in which the two halves of the hexadentate ligand are in a facial arrangement (*fac*-N<sub>2</sub>O set): two phenolato oxygen and two aliphatic nitrogen atoms of the ethylenediamine “backbone” form the equatorial plane, where atoms of the same type occupy the *cis* positions with respect to each other. The remaining pyridine nitrogen atoms, mutually *trans*, complete the coordination sphere. The preference of six-membered chelate rings, which have longer

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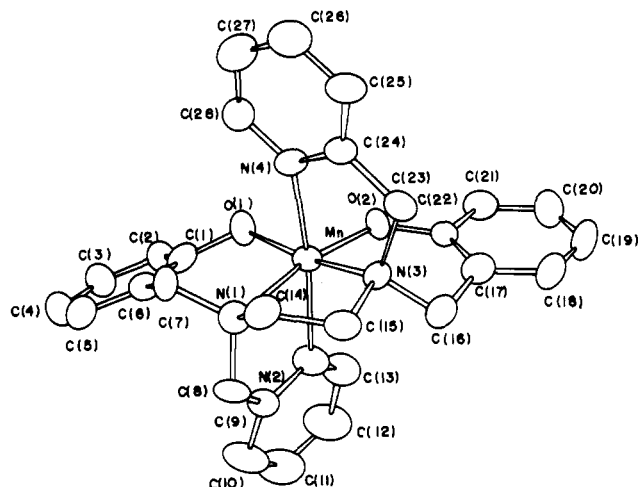


Figure 1. Structure of the cation of 1, showing the atom-labeling scheme.

Table II. Atomic Parameters for  $[\text{Mn}(\text{BBPEN})][\text{PF}_6]$ 

atom	x	y	z	$B_{\text{eq}}^a \text{ \AA}^2$
Mn	0.2824 (1)	0.2586 (0)	0.2787 (1)	2.27 (2)
O(1)	0.2718 (3)	0.3221 (2)	0.1692 (4)	3.0 (1)
O(2)	0.1093 (3)	0.2487 (2)	0.2365 (3)	2.9 (1)
N(1)	0.4753 (4)	0.2715 (2)	0.3565 (4)	2.7 (1)
N(2)	0.2881 (5)	0.3271 (2)	0.4247 (5)	3.2 (1)
N(3)	0.3069 (4)	0.1752 (2)	0.3747 (4)	2.6 (1)
N(4)	0.3173 (4)	0.1896 (2)	0.1475 (4)	2.7 (1)
C(1)	0.3501 (5)	0.3706 (3)	0.1792 (5)	2.7 (2)
C(2)	0.3036 (6)	0.4290 (3)	0.1349 (6)	3.2 (2)
C(3)	0.3815 (7)	0.4790 (3)	0.1344 (6)	4.1 (2)
C(4)	0.5088 (7)	0.4719 (3)	0.1825 (6)	3.8 (2)
C(5)	0.5558 (6)	0.4129 (3)	0.2293 (6)	3.5 (2)
C(6)	0.4786 (5)	0.3624 (3)	0.2278 (5)	3.0 (2)
C(7)	0.5301 (5)	0.2983 (3)	0.2667 (5)	2.8 (2)
C(8)	0.5062 (5)	0.3125 (3)	0.4643 (5)	3.0 (2)
C(9)	0.3991 (6)	0.3506 (3)	0.4768 (5)	3.1 (2)
C(10)	0.4162 (7)	0.4049 (3)	0.5462 (6)	4.3 (2)
C(11)	0.3130 (8)	0.4335 (3)	0.5603 (7)	5.6 (3)
C(12)	0.1959 (8)	0.4100 (4)	0.5052 (7)	5.3 (3)
C(13)	0.1880 (6)	0.3581 (3)	0.4362 (7)	4.4 (2)
C(14)	0.5242 (6)	0.2054 (3)	0.3920 (5)	3.1 (2)
C(15)	0.4397 (6)	0.1730 (3)	0.4518 (5)	3.2 (2)
C(16)	0.2231 (6)	0.1743 (3)	0.4547 (5)	3.1 (2)
C(17)	0.0870 (6)	0.1763 (3)	0.3877 (5)	2.8 (2)
C(18)	0.0061 (6)	0.1395 (3)	0.4299 (6)	3.5 (2)
C(19)	-0.1193 (7)	0.1440 (3)	0.3793 (7)	4.6 (2)
C(20)	-0.1682 (6)	0.1849 (4)	0.2874 (7)	4.4 (2)
C(21)	-0.0902 (6)	0.2211 (3)	0.2437 (6)	3.5 (2)
C(22)	0.0389 (5)	0.2158 (3)	0.2896 (5)	2.8 (2)
C(23)	0.2781 (6)	0.1194 (3)	0.2936 (5)	3.0 (2)
C(24)	0.3067 (5)	0.1308 (3)	0.1777 (5)	2.7 (2)
C(25)	0.3171 (6)	0.0796 (3)	0.1067 (6)	3.5 (2)
C(26)	0.3397 (6)	0.0928 (3)	0.0002 (6)	3.9 (2)
C(27)	0.3525 (6)	0.1536 (4)	-0.0318 (6)	4.1 (2)
C(28)	0.3404 (5)	0.2018 (3)	0.0440 (5)	3.3 (2)
P	0.5867 (2)	-0.0199 (1)	0.3083 (2)	3.64 (5)
F(1)	0.5639 (5)	0.0514 (2)	0.3333 (4)	7.2 (2)
F(2)	0.6107 (6)	-0.0907 (2)	0.2832 (5)	8.0 (2)
F(3)	0.5493 (6)	-0.0056 (3)	0.1715 (4)	8.4 (2)
F(4)	0.6221 (6)	-0.0353 (2)	0.4447 (4)	7.7 (2)
F(5)	0.7224 (5)	-0.0056 (3)	0.3175 (8)	11.3 (3)
F(6)	0.4494 (5)	-0.0332 (3)	0.2966 (6)	9.3 (3)

$$^a B_{\text{eq}} = \frac{1}{3} \sum_{ij} \beta_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j).$$

bite angles, for the equatorial configuration has been observed previously.<sup>19</sup> Since  $[\text{Mn}^{\text{III}}(\text{BBPEN})]\text{PF}_6$  crystallizes in the centrosymmetric space group  $P2_1/n$ , two enantiomers,  $\Delta$  or  $\Lambda$ , are present in the unit cell. The molecule has a pseudo-2-fold axis running through manganese and the middle point of the C(14)–C(15) bond. The four coordinating atoms in the equatorial

Table III. Bond Distances ( $\text{\AA}$ ) and Angles (deg) for  $[\text{Mn}(\text{BBPEN})]\text{PF}_6$ 

Mn–O(1)	1.846 (4)	C(4)–C(5)	1.405 (8)
Mn–O(2)	1.888 (4)	C(5)–C(6)	1.379 (8)
Mn–N(1)	2.124 (4)	C(6)–C(1)	1.405 (7)
Mn–N(2)	2.237 (5)	C(6)–C(7)	1.494 (7)
Mn–N(3)	2.078 (4)	C(8)–C(9)	1.499 (8)
Mn–N(4)	2.252 (5)	C(9)–C(10)	1.390 (8)
O(1)–C(1)	1.350 (6)	C(10)–C(11)	1.372 (11)
O(2)–C(22)	1.340 (7)	C(11)–C(12)	1.376 (10)
N(1)–C(7)	1.490 (8)	C(12)–C(13)	1.367 (10)
N(1)–C(8)	1.504 (7)	C(14)–C(15)	1.525 (6)
N(1)–C(14)	1.521 (4)	C(16)–C(17)	1.512 (7)
N(2)–C(9)	1.322 (7)	C(17)–C(18)	1.402 (9)
N(2)–C(13)	1.344 (8)	C(17)–C(22)	1.405 (7)
N(3)–C(15)	1.510 (8)	C(18)–C(19)	1.382 (9)
N(3)–C(16)	1.508 (8)	C(19)–C(20)	1.371 (9)
N(3)–C(23)	1.498 (7)	C(20)–C(21)	1.380 (10)
N(4)–C(24)	1.310 (7)	C(21)–C(22)	1.395 (8)
N(4)–C(28)	1.351 (7)	C(23)–C(24)	1.511 (8)
C(1)–C(2)	1.390 (7)	C(24)–C(25)	1.403 (8)
C(2)–C(3)	1.370 (9)	C(25)–C(26)	1.377 (9)
C(3)–C(4)	1.383 (9)	C(26)–C(27)	1.370 (9)
		C(27)–C(28)	1.380 (9)
P–F(1)	1.575 (5)	P–F(4)	1.576 (4)
P–F(2)	1.584 (5)	P–F(5)	1.543 (6)
P–F(3)	1.582 (5)	P–F(6)	1.544 (5)
O(1)–Mn–O(2)	92.4 (2)	N(2)–C(9)–C(8)	116.0 (5)
O(1)–Mn–N(1)	93.6 (2)	N(2)–C(9)–C(10)	122.5 (6)
O(1)–Mn–N(2)	92.2 (2)	N(2)–C(13)–C(12)	122.9 (6)
O(1)–Mn–N(3)	167.5 (2)	N(3)–C(15)–C(14)	111.1 (4)
O(1)–Mn–N(4)	89.5 (2)	N(3)–C(16)–C(17)	113.7 (4)
O(2)–Mn–N(1)	169.9 (2)	N(3)–C(23)–C(24)	112.7 (4)
O(2)–Mn–N(2)	94.1 (2)	N(4)–C(24)–C(23)	117.2 (5)
O(2)–Mn–N(3)	90.7 (2)	N(4)–C(24)–C(25)	122.9 (5)
O(2)–Mn–N(4)	97.0 (2)	N(4)–C(28)–C(27)	121.2 (5)
N(1)–Mn–N(2)	77.6 (2)	C(1)–C(2)–C(3)	120.3 (5)
N(1)–Mn–N(3)	85.1 (2)	C(1)–C(6)–C(5)	119.0 (5)
N(1)–Mn–N(4)	91.2 (2)	C(1)–C(6)–C(7)	119.9 (5)
N(2)–Mn–N(3)	99.7 (2)	C(2)–C(3)–C(4)	121.1 (5)
N(2)–Mn–N(4)	168.8 (2)	C(3)–C(4)–C(5)	118.6 (6)
N(3)–Mn–N(4)	78.1 (2)	C(4)–C(5)–C(6)	121.2 (5)
Mn–O(1)–C(1)	126.4 (3)	C(5)–C(6)–C(7)	121.0 (5)
Mn–O(2)–C(22)	130.3 (3)	C(8)–C(9)–C(10)	121.3 (5)
Mn–N(1)–C(7)	108.9 (3)	C(9)–C(10)–C(11)	117.7 (6)
Mn–N(1)–C(8)	118.7 (3)	C(10)–C(11)–C(12)	120.4 (7)
Mn–N(1)–C(14)	104.7 (2)	C(11)–C(12)–C(13)	117.8 (7)
Mn–N(2)–C(9)	114.7 (4)	C(16)–C(17)–C(18)	117.9 (4)
Mn–N(2)–C(13)	123.8 (3)	C(17)–C(18)–C(19)	120.2 (5)
Mn–N(3)–C(15)	107.9 (3)	C(18)–C(19)–C(20)	120.9 (7)
Mn–N(3)–C(16)	109.9 (3)	C(19)–C(20)–C(21)	119.5 (6)
Mn–N(3)–C(23)	110.9 (3)	C(20)–C(21)–C(22)	121.4 (5)
Mn–N(4)–C(24)	112.7 (4)	C(21)–C(22)–C(17)	118.6 (5)
Mn–N(4)–C(28)	128.0 (4)	C(23)–C(24)–C(25)	119.8 (5)
O(1)–C(1)–C(2)	118.8 (4)	C(24)–C(25)–C(26)	117.3 (5)
O(1)–C(1)–C(6)	121.3 (5)	C(25)–C(26)–C(27)	120.0 (6)
O(2)–C(22)–C(17)	123.4 (5)	C(26)–C(27)–C(28)	119.3 (6)
O(2)–C(22)–C(21)	118.0 (4)	C(16)–C(17)–C(22)	122.8 (5)
N(1)–C(7)–C(6)	112.0 (5)	C(18)–C(17)–C(22)	119.2 (5)
N(1)–C(14)–C(15)	107.8 (3)		
N(1)–C(8)–C(9)	113.2 (4)	F(2)–P–F(6)	92.1 (3)
F(1)–P–F(2)	178.9 (3)	F(3)–P–F(4)	179.1 (3)
F(1)–P–F(3)	90.1 (3)	F(3)–P–F(5)	90.1 (4)
F(1)–P–F(4)	90.4 (3)	F(3)–P–F(6)	88.8 (3)
F(1)–P–F(5)	89.7 (3)	F(4)–P–F(5)	90.6 (4)
F(1)–P–F(6)	89.0 (3)	F(4)–P–F(6)	90.5 (3)
F(2)–P–F(3)	89.9 (3)	F(5)–P–F(6)	178.3 (4)
F(2)–P–F(4)	89.6 (3)		
F(2)–P–F(5)	89.2 (3)		

positions are tetrahedrally displaced from the mean coordination plane [O(1), 0.17  $\text{\AA}$ ; O(2), -0.15  $\text{\AA}$ ; N(1), -0.20  $\text{\AA}$ ; N(3), 0.21  $\text{\AA}$ ; Mn, -0.02  $\text{\AA}$ ]. The five-membered ring formed by the ethylenediamine "backbone" ( $\text{MnN}_2\text{C}_2$ ) has the usual skew conformation with the torsion angle N(1)–C(14)–C(15)–N(3) = 53.2°; the two atoms of the ethylene bridge [C(14) and C(15)] are displaced by 0.56 and -0.13  $\text{\AA}$  on opposite sides of the MnNN

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Table IV. Electronic Spectral Data<sup>a</sup> and Magnetic Properties

compound	$\lambda_{\text{max}}$ , nm ( $\epsilon$ , L mol <sup>-1</sup> cm <sup>-1</sup> )	$\mu_{\text{eff}}$ , $\mu_B$
H <sub>2</sub> BBPEN	211 (35 000), 229 (sh), 225 (sh)	
H <sub>2</sub> BBPPN	261 (19 000), 269 (sh), 280 (sh)	
[Mn <sup>III</sup> (BBPEN)][PF <sub>6</sub> ]	210 (29 000)	
[Mn <sup>III</sup> (BBPPN)][PF <sub>6</sub> ]	261 (10 200), 268 (sh), 282 (sh)	4.85
[Mn <sup>III</sup> (BBPPN)][PF <sub>6</sub> ]	203 (58 000), 258 (29 000), 369 (4200), 506 (2100)	4.90
[Mn <sup>IV</sup> (BBPEN)] <sup>2+</sup> <sup>b</sup>	369 (15 000), 353 (5900), 356 (3800), 402 (sh), 663 (1300)	
[Mn <sup>IV</sup> (BBPPN)] <sup>2+</sup> <sup>b</sup>	506 (2700), 790 (3700)	
[Mn <sup>III</sup> (EHPG)] <sup>-c</sup>	405 (3700), 667 (1400)	5.1
[Mn <sup>III</sup> (EHPG)] <sup>-c</sup>	350 (3000), 427 (1175) <sup>b</sup>	

<sup>a</sup> Measured in CH<sub>3</sub>CN except as indicated otherwise. <sup>b</sup> Data obtained from spectroelectrochemical and coulometric measurements. <sup>c</sup> From ref 8g.

plane. The two six-membered chelate rings (MnONC<sub>3</sub>) adopt chair conformations with the torsion angles N(1)–C(7)–C(6)–C(1) of –58.8° and N(3)–C(16)–C(17)–C(22) of –42.4°. The remaining five-membered rings formed by the pendant 2-pyridylmethyl groups are closely planar, with the sum of interior angles being 531.6 and 540.2° for Mn–N(4)–C(24)–C(23)–N(3) and Mn–N(2)–C(9)–C(8)–N(1) rings, respectively. The two pyridine rings are planar, and manganese is –0.55 and 0.13 Å, respectively, out of planes through N(2)–C(9)–C(10)–C(11)–C(12)–C(13) and N(4)–C(24)–C(25)–C(26)–C(27)–C(28). The dihedral angle that they form is 77.6°. The Mn–N(amine) bonds trans to the phenoxo groups are, as expected, somewhat (mean value = 2.101 (4) Å) longer than those for other known<sup>7b</sup> Mn(III) complexes containing only Mn(III)–N(amine) bonds in the equatorial plane, and this is a reflection of the weak trans effect of the shorter Mn(III)–O(phenolate) bonds (mean value = 1.867 (4) Å). Similar Mn(III)–O(phenolate) distances have been reported in some few examples of five,<sup>8b,e</sup> and six-coordinated<sup>8b,c,f,g</sup> monomeric Mn(III) species. However, in most cases, these bonds are somewhat longer ( $\approx 1.89$  Å). The stronger interaction in **1** is consistent with its lower energy phenolato-to-manganese(III) charge-transfer band at  $\lambda_{\text{max}} = 504$  nm compared with other Mn(III) complexes described in the literature for which this lower energy band lies in the 350–480-nm range.<sup>8c,g,f</sup> The axial Mn–N(py) bond distances of 2.237 (5) and 2.252 (5) Å in complex **1** are  $\approx 0.1$  Å longer than the corresponding V(III)–N(py) bond distances of 2.139 (4) and 2.144 (4) Å in the [V<sup>III</sup>(BBPEN)]<sup>+</sup> complex,<sup>20</sup> which is consistent with a Jahn–Teller distortion of this high-spin d<sup>4</sup> ion. However, it is important to note that these Mn(III)–N(py) distances in **1** are significantly shorter ( $\approx 0.2$  Å) than those found in other “Jahn–Teller elongated” Mn(III)–N(py) complexes.<sup>8c,21</sup> This unusual structural feature can be explained in terms of the ring strain caused by the rigidity of the pyridyl arms. An analysis of the planarity of the five-membered chelate rings (sum of the interior angles: 531.6 and 540.2°) containing the pyridine nitrogen atoms and the bond angles N(1)–Mn–N(2) and N(3)–Mn–N(4) of 77.6 (2)° and 78.1 (2)° respectively, give us the extent of puckering in the inner and outer region of these rings.

The crystallographically independent hexafluorophosphate anion in the structure is ordered and does not show any serious distortions from rigorous octahedral environment. The P–F bonds range from 1.543 (6) to 1.584 (5) Å and F–P–F cis angles vary between 88.8 (3) and 92.1 (3)°.

The remaining structural parameters for the ligand are as expected and will not be discussed further.

**Magnetism and Electronic Spectra.** Magnetic properties and electronic spectral data of the new ligands and complexes are

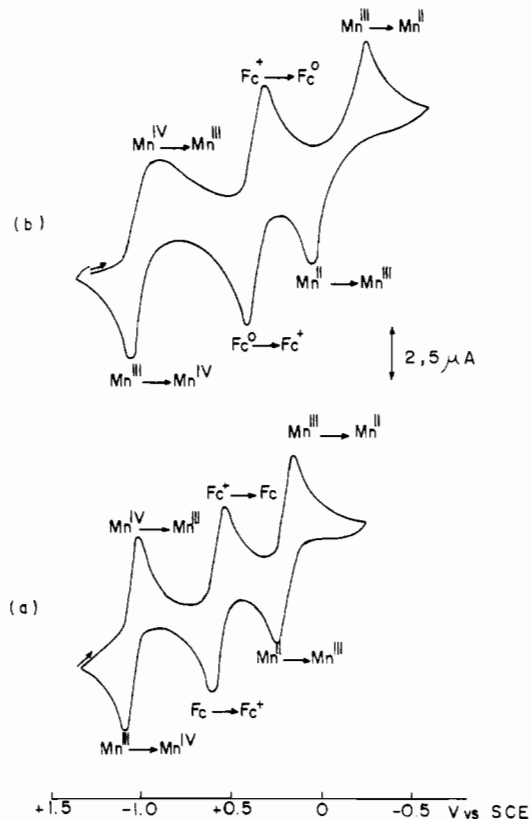


Figure 2. Cyclic voltammograms (scan rate 50 mV s<sup>-1</sup>) of  $\approx 10^{-3}$  M solutions of (a) [Mn<sup>III</sup>(BBPPN)][PF<sub>6</sub>] and (b) [Mn<sup>III</sup>(BBPEN)][PF<sub>6</sub>] in CH<sub>3</sub>CN (0.1 M [(TBA)PF<sub>6</sub>]) at a platinum electrode with the internal standard ferrocene.

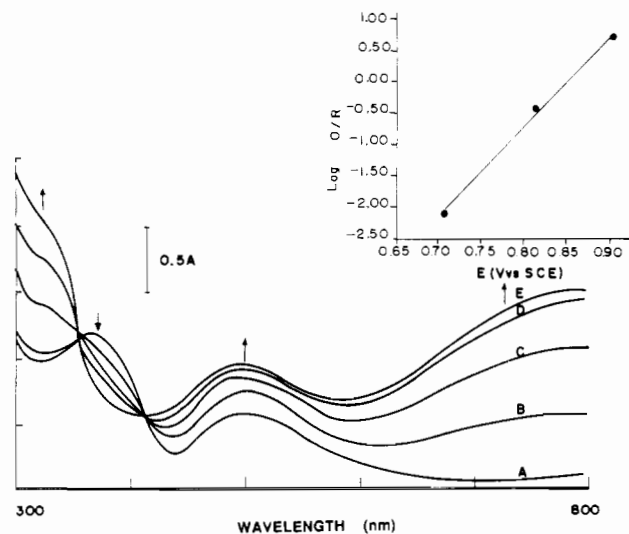
summarized in Table IV. The magnetic moments of 4.85 and 4.90  $\mu_B$  for complexes **1** and **2**, respectively fit the Curie–Weiss law between 81 and 293 K, and are in excellent agreement with the spin-only value of 4.90  $\mu_B$  for a high-spin manganese(III) ion.

The electronic spectra of the free ligands H<sub>2</sub>BBPEN and H<sub>2</sub>BBPPN in acetonitrile show various intense absorption maxima in the 200–300-nm region. These bands are assigned to  $\Pi \rightarrow \Pi^*$  transitions, and the inter- and intramolecular hydrogen bonding between the phenolic groups and the amine nitrogen atoms probably originate the observed splitting of these  $\Pi \rightarrow \Pi^*$  transitions. A similar behavior has been detected for other well-characterized ligands containing amine and phenolic groups described in the literature.<sup>22</sup>

The electronic spectrum of the [Mn<sup>III</sup>(BBPEN)]<sup>+</sup> ion complex is illustrated in Figure 3, spectrum A. The lowest energy band at 506 nm ( $\epsilon = 2100$  M<sup>-1</sup> cm<sup>-1</sup>) is assigned by analogy to other described Mn(III) complexes<sup>8c,g,22a,23</sup> as being a L  $\rightarrow$  M charge-transfer from a p $\Pi$  orbital on the phenolate oxygen to the half-filled Mn(III) d $\Pi^*$  orbitals. A second stronger transition which is absent in the free ligand, is observed at 370 nm ( $\epsilon = 4200$  M<sup>-1</sup> cm<sup>-1</sup>). We suggest that this band is originated from a second LMCT to a d $\sigma^*$  orbital. If this is so, the energy difference, 7260 cm<sup>-1</sup>, between the two transitions would then be a measure of 10Dq for this octahedral complex. A similar spectra (Table IV) has been obtained for the *rac*-[Mn<sup>III</sup>(EHPG)]<sup>-</sup> complex,<sup>23</sup> which is blue-shifted and gives a value of 5150 cm<sup>-1</sup> for 10Dq, close to that found for complex **1**. However, these values are significantly lower from that observed for other Mn(III) complexes, for which 10Dq have been determined (e.g. 17 800 cm<sup>-1</sup>

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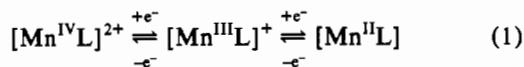


**Figure 3.** Spectra recorded during spectropotentiostatic experiment on  $5 \times 10^{-4}$  M  $[\text{Mn}^{\text{III}}(\text{BBPEN})]^+$  (0.1 M  $[(\text{TBA})\text{PF}_6]$  in  $\text{CH}_3\text{CN}$ ). Applied potentials in V vs SCE are as follows: (A) 0.6; (B) 0.7; (C) 0.8; (D) 0.84; (E) 0.88.

for  $[\text{Mn}^{\text{III}}\text{F}_6]^{3-}$  and  $17\,900\text{ cm}^{-1}$  for  $[\text{Mn}^{\text{III}}(\text{acac})_3]$ .<sup>24</sup> From this information, we suggest that the energy gap for **1** measures the splitting of the  $t_{2g}$  orbital ( ${}^5E_g \rightarrow {}^5B_{1g} + {}^5A_{1g}$ ), in a tetragonal environment, for which  $[\text{Mn}^{\text{III}}\text{F}_6]^{3-}$  and  $[\text{Mn}^{\text{III}}(\text{acac})_3]$  display respectively an energy difference of  $9000$  and  $9500\text{ cm}^{-1}$  (the majority of Mn(III) complexes show values between  $9000$  and  $11\,000\text{ cm}^{-1}$ )<sup>23</sup> in relatively good agreement with the value calculated for complex **1**. Ligand field bands were not observable in complexes **1** and **2**. The  $[\text{Mn}^{\text{III}}(\text{BBPPN})]^+$  complex exhibits a similar spectrum with their maxima shifted to lower energies (Table IV). However, the spectrum displays an additional band at  $353\text{ nm}$ , which is also assigned to a LMCT process. If we proceed with the same calculation as for complex **1**, an energy difference of  $9800\text{ cm}^{-1}$  is found, again in good agreement with the energy values for the  ${}^5A_{1g} \leftarrow {}^5B_{1g}$  transition detected for other Mn(III) complexes.<sup>24</sup>

Since the magnetic, spectral and electrochemical properties of the  $[\text{Mn}^{\text{III}}(\text{BBPPN})]^+$  are closely analogous to those of **1**, it is reasonable to assume that they also have similar coordination spheres, in which the halves of the symmetrical hexadentate ligands are in a facial arrangement (*fac*- $\text{N}_2\text{O}$  set).

**Electrochemistry and Spectroelectrochemistry.** Cyclic voltammograms of complexes **1** and **2** were recorded in acetonitrile with  $[\text{TBA}(\text{PF}_6)]_6$  as supporting electrolyte in the potential range  $-0.5$  to  $1.5\text{ V}$  vs SCE. The results are summarized in Table V. Typical CVs of **1** and **2** are displayed in parts a and b, respectively, of Figure 2. For both complexes, two well-defined quasi-reversible one-electron-transfer waves are detected. The anodic process corresponds to the Mn(IV)/Mn(III) couple, and the cathodic process to the Mn(III)/Mn(II) couple as shown in eq 1.



Controlled-potential coulometric measurements on the  $[\text{Mn}^{\text{III}}(\text{BBPEN})]^+$  complex at  $+0.67$  and  $-0.63\text{ V}$  vs  $\text{Fc}^+/\text{Fc}$  revealed a one-electron oxidation and a one-electron reduction, respectively. The CVs of the deep blue oxidized solution and **1** are identical under the same conditions. Its electronic spectrum consists of two very intense bands at  $506$  and  $790\text{ nm}$  (see Table IV). The

**Table V.** Electrochemical Data for the Redox Couples Mn(IV)/Mn(III) and Mn(III)/Mn(II) at  $298\text{ K}$ <sup>a</sup>

complex	Mn(IV)/Mn(III)			Mn(III)/Mn(II)			ref
	$E^{\circ'}$ , V	$(\Delta E_p)$ , mV <sup>b</sup>	$n^c$	$E^{\circ'}$ , V	$(\Delta E_p)$ , mV <sup>b</sup>	$n^c$	
$[\text{Mn}^{\text{III}}(\text{BBPEN})]\text{PF}_6^d$	0.49	(90)	0.94	-0.37	(90)	0.82	this work
$[\text{Mn}^{\text{III}}(\text{BBPPN})]\text{PF}_6$	0.61	(170)	0.92	-0.44	(240)	0.97	this work
$[\text{Mn}^{\text{III}}(\text{EHPG})]^-$	0.14			-0.40			8g, 23
$[\text{Mn}^{\text{IV}}(\text{als})_2]$	0.16			-0.22			9d
$[\text{Mn}^{\text{III}}(\text{BHBB})(\text{py})_2]^-$	0.16						8c

<sup>a</sup> Measured in  $\text{CH}_3\text{CN}$  with  $0.1\text{ M}$   $[\text{TBA}][\text{PF}_6]$  as supporting electrolyte; all  $E^{\circ'}$  values are given vs  $\text{Fc}^+/\text{Fc}$ ; working electrode is platinum; reference electrode is SCE; scan rate of  $50\text{ mV/s}$ . <sup>b</sup> Data from cyclic voltammetric measurements;  $E^{\circ'}$  is calculated as the average of anodic ( $E_{pa}$ ) and cathodic ( $E_{pc}$ ) peak potentials;  $\Delta E_p = E_{pa} - E_{pc}$ . <sup>c</sup> Data from coulometric measurements. <sup>d</sup> Data from spectroelectrochemical measurements;  $E^{\circ'} = 0.41\text{ V}$  vs  $\text{Fc}^+/\text{Fc}$  and  $n = 0.94$  are calculated from the Nernst plot.

chemical reversibility of this process was confirmed through electroreduction of the oxidized species by the application of the appropriate potential and the full recovery of the original spectrum of  $[\text{Mn}^{\text{III}}(\text{BBPEN})]^+$ .

Because of the stability of the Mn(IV) form of the  $[\text{Mn}(\text{BBPEN})]^{2+/+}$  couple, a spectroelectrochemical study at the same experimental conditions as employed in the CVs and coulometric experiments was carried out. Figure 3 shows the potential spectral change in the  $300$ – $800\text{-nm}$  range during the oxidation of  $[\text{Mn}^{\text{III}}(\text{BBPEN})]^+$  to  $[\text{Mn}^{\text{IV}}(\text{BBPEN})]^{2+}$  in an optically transparent thin-layer electrode (OTLE). The Mn(IV) complex exhibit maxima at  $506$  and  $790\text{ nm}$ , in excellent agreement with values obtained from the coulometric experiments. These two bands are also assigned as charge-transfer transitions, probably from the phenolic oxygen(s) to the d orbital of the manganese(IV) ion.<sup>25</sup> The maintenance of two strict isobestic points in successive spectra strongly corroborates the presence of a single product throughout the course of the electrolysis. Data for the Nernst plot shown in the inset of Figure 3 were obtained by recording the absorbance of the  $506\text{-nm}$  band after equilibrium was established following selected potential steps. The  $E^{\circ'} = 0.41\text{ V}$  vs  $\text{Fc}^+/\text{Fc}$  and  $n = 0.9 \pm 0.1$  electron values obtained from this plot are in very good agreement with the CV and coulometric results. Under an argon atmosphere, solutions of the  $[\text{Mn}^{\text{IV}}(\text{BBPEN})]^{2+}$  species are stable for at least  $24\text{ h}$ . From this information, we conclude that the  $[\text{Mn}^{\text{IV}}(\text{BBPEN})]^{2+}$  ion complex can be electrochemically generated in solution without changing the coordination sphere at the manganese center.

Coulometric and spectropotentiostatic measurements for the reduction of **1** confirm the results obtained from cyclic voltammetric studies, indicating that this is also an one-electron transfer process, possibly involving the Mn(II) complex. However, the reduced pale red solution undergoes decomposition in few minutes. Thus, the exact nature of the Mn(II) species is unclear at present.

The  $[\text{Mn}(\text{BBPPN})]^+$  complex exhibits similar redox behavior like that described above for complex **1** but with the Mn(IV) species being less stable (see Table V). The  $130\text{-mV}$  anodic shift in the Mn(IV)/Mn(III) redox couple in **2**, the lower stability of the electrochemically generated  $[\text{Mn}^{\text{IV}}(\text{BBPPN})]^{2+}$  species, and the blue shift of their maxima in the electronic spectra probably result from the additional methylene group, which requires the formation of a six-membered chelate ring rather than the five-membered ring formed by the ethylenediamine "backbone" in complex **1**. Somewhat similar behavior has recently been reported for a series of Mn(IV) hydroxyl-rich salicylaldehyde complexes.<sup>9c</sup> In addition, it is important to note that the high redox potentials for the Mn(IV)/Mn(III) couple exhibited by complexes **1** and **2** demonstrate the ability of the  $\text{H}_2\text{BBPEN}$

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and H<sub>2</sub>BBPPN ligands to stabilize preferentially the Mn(III) oxidation state. The comproportionation constant of  $3.5 \times 10^{14}$  for the equilibrium  $\text{Mn(IV)} + \text{Mn(II)} \rightleftharpoons 2 \text{Mn(III)}$ , calculated from the separation of the redox potentials of the MnBBPEN complex, strongly corroborates this assignment.

In several mononuclear Mn(III) and Mn(IV) complexes with N<sub>2</sub>O<sub>4</sub> and N<sub>3</sub>O<sub>3</sub> donors, such as hydroxyl-rich salicylaldehydes,<sup>9e</sup> *N*-(hydroxyphenyl)salicylamides,<sup>26</sup> bis-*N*-(2-carboxyethyl)salicylideneaminato,<sup>9d</sup> 1,4,7-tris(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane,<sup>22a</sup> EHPG,<sup>8g</sup> and BHBB,<sup>8c</sup> the Mn(IV)/Mn(III) redox potentials are all shifted by 300–1300 mV to more negative potentials, relative to complexes 1 and 2. This fact shows us clearly that N<sub>2</sub>O<sub>4</sub> ligands stabilize preferentially the Mn(IV) oxidation state, as is the case of most of the described Mn(IV)–N<sub>2</sub>O<sub>4</sub> complexes.<sup>9d,e,f,26</sup> However, in some instances Mn(III)–N<sub>2</sub>O<sub>4</sub> complexes have been also isolated.<sup>8b,g,9d,23</sup> At this point, we take particular notice of the fact that in the carboxylato-coordinated [Mn<sup>III</sup>(EHPG)]<sup>–8g</sup> and [Mn<sup>IV</sup>(als)<sub>2</sub>]<sup>9d</sup> complexes, the redox potentials are  $\approx 350$  mV more negative than those detected in complexes 1 and 2. This result can be qualitatively understood in terms of the relative softness of pyridyl groups in 1 and 2 compared to the more hard carboxylato function in [Mn<sup>III</sup>(EHPG)]<sup>–</sup> and [Mn<sup>IV</sup>(als)<sub>2</sub>]. Obviously, therefore, H<sub>2</sub>BBPEN and H<sub>2</sub>BBPPN would be expected to stabilize Mn(III) relative to Mn(IV). The electrochemically generated [Mn<sup>IV</sup>-(EHPG)] species undergoes intramolecular oxidative decarboxylation.<sup>8g</sup> On the other hand, mononuclear Mn(III) complexes with N<sub>4</sub>O<sub>2</sub> donors (octahedral geometry with two cis Mn–N bonds, two cis Mn–O bonds, and two axial Mn–N bonds) are exceedingly rare. To date, the [Mn<sup>III</sup>(BHBB)(py)<sub>2</sub>]<sup>–8c</sup> complex<sup>8c</sup> is the unique structurally characterized Mn(III) complex which contains a N<sub>4</sub>O<sub>2</sub> coordination geometry similar to that in 1. In this case, the redox potential for the Mn(IV)/Mn(III) couple is 0.166 V vs Fc<sup>+</sup>/Fc and therefore is cathodic shifted by 324 and 444 mV relative to those for complexes 1 and 2, respectively. However, the authors<sup>8c</sup> have pointed out that a [Mn<sup>III</sup>(BHBB)]<sup>–</sup> complex, probably solvated by DMF rather than by pyridine, would be the redox-active species.

Finally, the well-defined one-electron nearly reversible response of the Mn(IV)/Mn(III) couple for complex 1 can be interpreted in terms of stability of the Mn(III) species, in which the Jahn–Teller elongation is inhibited by the close planar five-membered rings formed by the pyridyl arms. The Mn(IV) species (d<sup>3</sup> system) is evidently less distorted. According to the Marcus theory,<sup>27</sup> this fact could contribute significantly to the inner-sphere rearrangements, diminishing the activation barrier of the heterogeneous electron-transfer process, and so causing an approximation to the electrochemical reversibility of this system.

**EPR Spectroscopy.** In order to confirm the manganese (IV) formulation of [Mn<sup>IV</sup>(BBPEN)]<sup>2+</sup>, an EPR measurement on the electrochemically generated species was carried out. The X-band EPR spectrum of a frozen solution in acetonitrile obtained after exhaustive electrolysis was measured at 110 K. The spectrum is shown in Figure 4 and displays signals at  $g_1 = 5.84$ ,  $g_2 = 4.77$ , and  $g_3 = 1.99$  with well-resolved <sup>55</sup>Mn hyperfine structure on each of the observed resonances which are attributed to rhombic distortions. The magnitude of the <sup>55</sup>Mn hyperfine coupling (89 G) for the  $g = 1.99$  signal is fully consistent with that expected for a d<sup>3</sup> ion and therefore strongly supports the [Mn(BBPEN)]<sup>2+</sup> as a Mn(IV) complex.<sup>9e,28</sup> Interestingly, whereas axial distortions

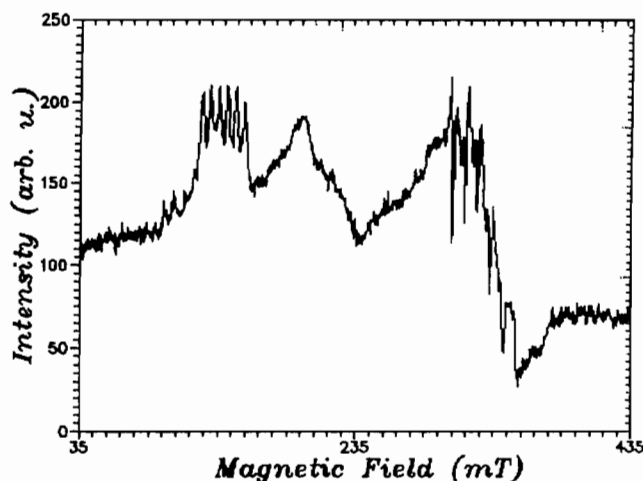


Figure 4. X-Band (9.15-GHz) EPR spectrum of [Mn<sup>IV</sup>(BBPEN)]<sup>2+</sup> in CH<sub>3</sub>CN at 110 K (power 80 mW, gain  $1.25 \times 10^4$ ).

in the two limiting cases ( $2D \gg h\nu^{9c-d,26,29}$  or  $2D \ll h\nu^{30}$ ) occur in a number of mononuclear Mn(IV) complexes, well-resolved <sup>55</sup>Mn hyperfine structures with rhombic electronic distortions have so far been documented only in hydroxyl-rich Schiff base Mn(IV) complexes<sup>9e</sup> and now in [Mn<sup>IV</sup>(BBPEN)]<sup>2+</sup>.

#### Concluding Remarks and Future Directions

A novel Mn(III) species with a N<sub>4</sub>O<sub>2</sub> coordination environment has been isolated and characterized by X-ray crystallography, magnetic susceptibility, electrochemical, and spectroscopic measurements. The corresponding Mn(IV) complex exhibits EPR spectra in the  $g = 4$ –6 range, although it is more rhombic than the biological signal at  $g \approx 4.1$ , which has been attributed to an approximately axially symmetric mononuclear manganese(IV) center.<sup>6c</sup>

The accessibility of [Mn<sup>IV</sup>(BBPEN)]<sup>2+</sup> species, evidenced by spectroelectrochemical and EPR data, and the high redox potential of the Mn(IV)/Mn(III) couple ( $E^{\circ'} = 0.90$  V vs NHE) reveal that the complex is biomimetic of photosystem II.

Finally, the synthetic route described for preparation of H<sub>2</sub>BBPEN and H<sub>2</sub>BBPPN can be used as a general way for preparation of multidentate bioinorganic relevant N, O donor ligands derived from alkyldiamines. The synthesis of binucleating ligands derived from 2-hydroxy-1,3-diaminopropane containing phenolate and  $\alpha$ -pyridyl or phenolate and methylimidazolyl as pendant arms and their manganese, iron, and vanadium complexes are under current investigation in our group and will be the subject of future reports.

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**Supplementary Material Available:** Tables VI and VII, listing anisotropic temperature factors and hydrogen atom coordinates (3 pages). Ordering information is given on any current masthead page.

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