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Superoxide and Manganese(III).[†] Reactions of Mn-EDTA and Mn-CyDTA Complexes with O₂⁻. X-ray structure of KMnEDTA·2H₂O

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The reactions of Mn^{III}EDTA⁻, Mn^{II}EDTA²⁻, and Mn^{III}CyDTA⁻ with superoxide have been studied in both aqueous and nonaqueous solvents. In anhydrous Me₂SO, the reduction of Mn^{III}EDTA⁻ to Mn^{II}EDTA²⁻ by superoxide has been characterized by stopped-flow kinetic measurements, rapid-scan spectrophotometry, electron paramagnetic resonance, and cyclic voltammetry. The reaction is second order with a rate constant of $5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C. The reaction of Mn^{III}CyDTA⁻ is analogous, having a rate constant of $\sim 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Addition of superoxide to a Mn^{II}EDTA²⁻ solution in Me₂SO produces a green intermediate which changes to a yellow-brown final product. Although manganese aminocarboxylate complexes do not catalyze the dismutation of superoxide in aqueous solution, the complexes do react with superoxide. Mn^{III}EDTA⁻ is reduced to Mn^{II}EDTA²⁻ by superoxide in water. Mn^{II}EDTA²⁻ and superoxide interact to form a blue intermediate which dissociates to regenerate Mn^{II}EDTA²⁻ and the spontaneous dismutation products. The reactions of manganese aminocarboxylate complexes with hydrogen peroxide, sodium peroxide, and dioxygen in Me₂SO are also discussed. The crystal and molecular structure of KMnEDTA·2H₂O has been determined by single-crystal X-ray diffraction techniques by using 1684 unique reflections in the range $2^\circ \leq 2\theta \leq 50^\circ$. KMnEDTA·2H₂O crystallizes in the orthorhombic space group *P*2₁2₁2₁, with $a = 6.579$ (1) Å, $b = 23.161$ (7) Å, and $c = 10.054$ (3) Å. There are four molecules in the unit cell. Refinement of the nonhydrogen atoms by least-squares procedures gave a final R_1 value of 0.065. In the complex anion, the manganese is coordinated by the hexadentate EDTA ligand producing a distorted octahedral MnN₂O₄ geometry. The closest water molecule is greater than 4 Å away from the manganese. The potassium counterion is coordinated to six oxygens from carboxylate and water groups. Average Mn-N and Mn-O (two types) bond lengths are 2.22 (1), 2.03 (1), and 1.90 (1) Å. The presence of two short Mn-O bonds and four long Mn-O and Mn-N bonds is opposite to the distortions observed in the 3d⁹ CuN₂O₄ complexes, wherein the metal-oxygen bonds are generally longest, a result thought to be consistent with Jahn-Teller effects. The diffusion coefficients of chemically prepared O₂⁻ solutions and of dioxygen in Me₂SO have been determined by single-step chronoamperometry. These values, 1.1×10^{-5} and $2.93 \times 10^{-5} \text{ cm}^2/\text{s}$, respectively, are in good agreement with less accurate values reported previously by other workers. We also report the electrochemistry of the aforementioned manganese aminocarboxylate complexes.

Introduction

The presence of the manganese(III) ion in biological redox reactions has become increasingly apparent in recent years. It is known that manganese ions are required for the photosynthetic evolution of dioxygen from green plant chloroplasts.¹ A manganese metalloenzyme, superoxide dismutase, is responsible for the disproportionation of superoxide anion to molecular oxygen and hydrogen peroxide in procaryotes and in the mitochondria of eucaryotes.² The results of circular dichroism,³ electron spin resonance and magnetic susceptibility,⁴ and electron absorption spectroscopy,² suggest that the enzyme contains manganese(III) in its resting state. The protein has also been the subject of nuclear magnetic resonance⁵ and pulse radiolysis^{6,58} examination of its mechanism of catalysis.

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Although a chemical model for superoxide dismutase is potentially useful, the problems encountered in studying various manganese(III) species have resulted in only a few investigations to date. Kono et al.⁸ have reported that a manganese(II) pyrophosphate complex is oxidized to Mn(III) by superoxide although this result has recently been refuted by Bielski and Chan.⁹ Di- and trivalent manganese quinolinol complexes have been proposed as a redox model for mitochondrial superoxide dismutase.¹⁰ Valentine¹¹ has studied the reaction of superoxide with Mn^{III}TPP (TPP = tetraphenylporphyrin) and has shown that Mn^{III}TPP is reduced by superoxide. Our continued interest in the structural chemistry of manganese(III) species and the relationships between dynamic behavior and structure, particularly with Jahn-Teller and pseudo-Jahn-Teller systems,¹² has prompted these studies.

The reactions of manganese complexes with hydrogen peroxide and dioxygen have received considerable study. Mn^{III}CyDTA⁻ (CyDTA⁻ = diaminocyclohexane-*N,N,N',N'*-tetraacetic acid) is reduced by hydrogen peroxide in acidic

aqueous solution.¹³ Basolo et al.¹⁴ have reported recently that a manganese(II) porphyrin complex and dioxygen interact reversibly at -78°C to form an adduct formulated as $\text{TTPMn}^{\text{IV}}\text{O}_2^{2-}$. Matsushita¹⁵ has investigated the reactions of $\text{Mn}^{\text{II}}(\text{salen})$ compounds with oxygen. Three types of complexes were obtained: $[\text{LMn}^{\text{III}}\text{O}_2\text{Mn}^{\text{III}}\text{L}]$, $[\text{LMn}^{\text{IV}}\text{OMn}^{\text{IV}}\text{L}]$, and $[\text{LMn}^{\text{IV}}=\text{O}]$. Taylor¹⁶ has reported on oxygenation studies of $\text{Mn}(\text{II})$ complexes containing pentadentate ligands. Sawyer¹⁷ has shown by cyclic voltammetry and spectroscopic techniques that dioxygen is reversibly bound by $[\text{tris}(3,5\text{-di-}t\text{-butylcatecholato})]\text{manganese}(\text{III})$ in Me_2SO .

Previously, superoxide radical has been generated by electrochemical methods¹⁸ or by pulse radiolysis.¹⁹ In 1975, Valentine²⁰ reported a convenient preparation of superoxide anion in aprotic media by the solubilization of potassium superoxide with crown ethers. We have used solutions of superoxide generated in this manner to study the reactions of $\text{Mn}^{\text{III}}\text{EDTA}^-$, $\text{Mn}^{\text{III}}\text{CyDTA}^-$, and $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ with superoxide in nonaqueous solvents and in aqueous solutions by means of a liquid mixing system designed to mix a miscible organic solvent with water in ~ 10 ms.³⁰ We have studied the reactions of $\text{Mn}^{\text{III}}\text{EDTA}^-$ with hydrogen peroxide in water and $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ with dioxygen and sodium peroxide in water and Me_2SO .

We report here our determination of the crystal and molecular structure of $\text{KMnEDTA}\cdot 2\text{H}_2\text{O}$ with Mo radiation. A brief description of the structure obtained with Cu radiation has been published by Lis.²¹

The diffusion coefficients of O_2 and O_2^- in Me_2SO measured by chronoamperometric techniques are reported.

Experimental Section

Manipulations were carried out under an atmosphere of dry nitrogen or argon except where otherwise noted.

Reagents. EDTA was purchased from J. T. Baker Chemical Co., Inc. CyDTA was obtained from Aldrich Chemical Co., Inc. Potassium superoxide was purchased from K & K Chemicals, Inc. TEAP (tetraethylammonium perchlorate) was obtained from Fisher Scientific, recrystallized twice from a water-ethanol mixture, and dried at 80°C over P_2O_5 before use. Me_2SO (dimethyl sulfoxide) was purchased from Fischer Scientific and purified by fractional crystallization followed by distillation from CaH_2 . The distillate was stored under N_2 for periods up to 1 week. 18-Crown-6 was prepared by literature methods.²² O_2 gas was purchased from Matheson Co. Sodium peroxide was purchased from Mallinckrodt Chemicals.

Preparation of Superoxide Solutions. Essentially, the method of Valentine was used.²⁰ A weighed amount of KO_2 (~ 0.004 g) and excess 18-crown-6 were placed in a Schlenk flask under an inert atmosphere. Standard bench top techniques for air-sensitive compounds²³ were used to syringe Me_2SO (~ 50 mL) into the flask. The solution was stirred for several hours until it became clear yellow. Concentrations of superoxide were determined either by quantitative EPR methods²⁴ or by using an oxygen electrode.²⁵

Preparation of Complexes. $\text{KMnEDTA}\cdot 2\text{H}_2\text{O}$,²⁶ $\text{KMnCyDTA}\cdot \text{H}_2\text{O}$,²⁷ and $\text{Na}_2\text{MnEDTA}\cdot 2\text{H}_2\text{O}$ ²⁸ were prepared by literature methods.

Titrations. To 3.0 mL of a 1 mM metal complex solution in Me_2SO in a cell filled with N_2 were added successive aliquots of a superoxide solution by a syringe. The UV-visible spectrum was recorded after each addition.

Reaction with Dioxygen. EDTA^{2-} was dissolved in Me_2SO , and the solution was kept under an atmosphere of oxygen unprotected from sunlight for 2 days. Solutions protected from light appeared to react more slowly. The reaction was monitored by changes in the UV-visible spectrum.

Reaction with Na_2O_2 . $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ was dissolved in distilled water. A solution of Na_2O_2 in water was then added. Changes in color and homogeneity were noted.

Cyclic Voltammetry. A Parr electrochemical cell was equipped with three electrodes, a bubbler, and a gas outlet. A solution of 1 mM $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ and 0.1 M TEAP was introduced. Successive aliquots of superoxide solution were added. The spectrum of the solutions was recorded within 1 min after each addition. Electrochemical rate constants for the reduction of the manganese(III)

complexes were determined by the variation in peak potential as a function of sweep rate.

Kinetic Measurements. The rate of the reactions of manganese complexes in Me_2SO and water with O_2^- was studied at 20°C by stopped-flow spectrophotometry.³⁰ The decrease in absorbance of the d-d transition at 500 nm of the manganese(III) complexes was monitored during the reaction. Error is estimated at $\pm 20\%$. Rapid-scan spectra were also recorded during the course of all reactions.³²

Catalysis Reactions. Micromolar quantities of the metal complex were reacted with Me_2SO solutions of O_2^- in water. The decrease in the superoxide absorbance at 275 nm was monitored to determine whether the metal complex accelerated disproportionation of O_2^- into O_2 and H_2O_2 .

Diffusion Coefficient Measurements. The diffusion coefficients of O_2 and chemically prepared solutions of O_2^- in Me_2SO with 0.1 M TEAP as the supporting electrolyte were determined by single-step chronoamperometry.²⁹ The electrochemical equipment was interfaced to a PDP-11/45 minicomputer, and all data were computer collected. In a typical experiment, the potential is stepped from one in which no current flows to a potential where either an electrochemical oxidation or reduction occurs. After a time τ the potential was returned to its initial value. The area of the platinum electrode and the diffusion coefficients were obtained by extrapolation of $it^{1/2}$ vs. t curves to $(it^{1/2})_0$. A 2.0 mM KCl, 4.0 mM potassium ferrocyanide solution for which the diffusion coefficient is accurately known²⁹ was used for the electrode area determination. For O_2 , the potential was stepped from 0.0 to -1.0 V and the converse step was used for O_2^- . The diffusion coefficient was then determined by using the value of $(it^{1/2})_0$ obtained above in the equation

$$D^{1/2} = (it^{1/2})_0 / 54500nAC$$

where $D^{1/2}$ is the square root of the diffusion coefficient, $(it^{1/2})_0$ is the current extrapolated to time "0", n is the number of electrons transferred, A is the area of the electrode, and C is the concentration of electroactive species.

Equipment. UV-visible spectra were recorded on a Cary 14 spectrophotometer. EPR measurements were recorded at 77 K on either a Varian E-3 (flat cells) or E-12 instrument (round cells). Electrochemical measurements were obtained with a locally constructed potentiostat, a Hewlett-Packard Model 3300A function generator, and a Hewlett-Packard Model 7035B-01 XY recorder. An SCE prepared by the method of Adams²⁹ served as the reference electrode. The auxiliary electrode was platinum foil and the working electrode was a platinum wire. The electrodes were pretreated before use by soaking in hot nitric acid, rinsing with distilled water, and sweeping the potential cyclicly for several minutes in Me_2SO . All solutions were made 0.1 M in TEAP as the supporting electrolyte. A Yellow Springs oxygen electrode was used to determine superoxide concentrations. Kinetic measurements were made with a stopped-flow spectrophotometer having a mixing chamber of special design.³⁰ The stopped flow was interfaced to a Nova 2/10 computer.

Crystallography. Deep red crystals of $\text{KMnEDTA}\cdot 2\text{H}_2\text{O}$ were isolated from a 1:3 water/ethanol mixture. They were elongated and generally irregularly shaped. A small crystal, approximately 0.1 mm \times 0.06 mm \times 0.05 mm, was chosen for crystallographic analysis. It was sprayed with an acrylic plastic coating to prevent loss of water of hydration and sealed inside a capillary. Intensity data and cell parameters were determined by using a Syntex P₂ diffractometer. The space group was determined uniquely as $P2_12_12_1$ by systematic absences. A total of 1684 reflections were collected with hkl positive in the $0^{\circ} \leq 2\theta \leq 50^{\circ}$ range. Two standard reflections, monitored every 50 reflections, showed no significant change in reflection intensity.

The data were reduced by using the CORR6 program of A. Schmonses modified for a PDP-11/45 computer by J. Winniczek. Values of $\sigma(I)$ and I were corrected for Lorentz and polarization effects. Atomic scattering factors for neutral atoms were taken from Cromer and Waber.⁵⁵ A Wilson plot was obtained to verify the noncentricity of the crystal. Phasing was determined by a Patterson synthesis using only reflections with $I/\sigma(I) \geq 10$. Location of the manganese atom at the general position 0.28, 0.089, and 0.160 gave an initial R value of 0.362 after three cycles of refinement. The structure was solved by using difference Fourier syntheses and full-matrix least-squares refinements with the FORDP and ORFLS programs, respectively. All programs were modified for use with a PDP-11/45 minicomputer. The final refinement of all nonhydrogen atoms with anisotropic temperature factors except C3 and C9 gave an R_1 value

Table I. Summary of Crystal Data for KMnEDTA·2H₂O

formula wt = 418.03	space group: $D_2^4 P2_12, 2_1$ (No. 19)
$d_{\text{calcd}} = 1.82 \text{ g/cm}^3$	crystal system: orthorhombic
$d_{\text{obsd}} = 1.81 \text{ g/cm}^3$	cell constants ^a
$Z = 4$	$a = 6.579$ (1) Å
$\mu = 12.23 \text{ cm}^{-1}$	$b = 23.161$ (7) Å
$\lambda(\text{Mo K}\alpha) = 0.71073$ Å	$c = 10.054$ (2) Å
crystal dimensions: $0.1 \times 0.06 \times 0.05 \text{ mm}^3$	$V = 1532.15$ (74) Å ³
systematic absences	$F(000) = 856$
00 l ($l = 2n + 1$)	scan rate: $2.02\text{--}29.3^\circ/\text{min}$ in 2θ
0 $k0$ ($k = 2n + 1$)	bgd scan time: 0.5 s
$h00$ ($h = 2n + 1$)	2θ scan: $0^\circ \leq 2\theta \leq 50^\circ$

^a Determined by a least-squares fit of 15 reflections with $2\theta > 7.59^\circ$.

Table II. Summary of Refinement Information for KMnEDTA·2H₂O^a

molecular formula	KMn(C ₁₀ H ₁₂ N ₂ O ₈)·2H ₂ O
data collected	1684
data with $I/\sigma(I) \geq 3$	964
R	0.065
R_w	0.067

^a $I = [I_g - (\text{sum of background counts})/(\text{background time to scan time ratio})] \times \text{scan rate}$; $\sigma_c = [I_g + (\text{sum of background counts})/(\text{background time to scan time ratio})]^{1/2} \times \text{scan rate}$; $\sigma^2 = \sigma_c^2 + (P)^2 + [I(\sigma(\text{DCF})/\text{DCF})^2]$; $\sigma(I) = (\sigma^2)^{1/2}$; $\sigma(F) = 1/2[\sigma(I)] \times (1/LpI)^{1/2}$; I = net count; I_g = total scan count; background time to scan ratio = 0.5; DCF = decay factor; Lp = Lorentz and polarization correction; P = electronic instability (usually 0.02); $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2\}^{1/2}$; $w_i = 1/\sigma_i^2(F)$.

Table III. Positional Parameters for KMnEDTA·2H₂O

atom	x/a	y/b	z/c
Mn	0.2811 (4)	0.0893 (1)	0.1603 (3)
K	0.7835 (7)	0.1526 (2)	0.5961 (4)
O1	0.3775 (19)	0.0085 (5)	0.2144 (12)
O2	0.3746 (17)	-0.0825 (5)	0.1461 (12)
O3	0.4353 (17)	0.0817 (6)	0.0006 (12)
O4	0.5298 (19)	0.1193 (6)	-0.1910 (11)
O5	0.4178 (22)	0.1635 (5)	0.2173 (13)
O6	0.3824 (23)	0.2576 (5)	0.2347 (13)
O7	0.1031 (17)	0.0974 (5)	0.3065 (11)
O8	-0.1807 (21)	0.0718 (5)	0.4050 (13)
O9	0.7904 (22)	0.2243 (6)	0.3730 (13)
O10	0.3629 (23)	0.1643 (5)	0.5240 (13)
N1	0.0315 (21)	0.0351 (6)	0.0822 (16)
N2	0.1219 (19)	0.1556 (6)	0.0362 (14)
C1	-0.0710 (29)	0.0664 (8)	-0.0265 (19)
C2	-0.0897 (29)	0.1323 (7)	0.0156 (20)
C3	0.1302 (28)	-0.0201 (8)	0.0454 (16)
C4	0.3068 (30)	-0.0306 (8)	0.1420 (17)
C5	0.2415 (37)	0.1627 (8)	-0.0882 (19)
C6	0.4186 (26)	0.1189 (8)	-0.0937 (19)
C7	0.1259 (28)	0.2079 (7)	0.1145 (18)
C8	0.3236 (31)	0.2111 (8)	0.1933 (17)
C9	-0.1113 (27)	0.0245 (7)	0.1997 (15)
C10	-0.0583 (36)	0.0670 (9)	0.3148 (19)

of 0.068 and an R_w of 0.086; the 964 observed reflections with $I/\sigma(I) \geq 3.0$ were used. Refinement was continued on a UNIVAC 1108 using anomalous scattering factors for both Mn and K. Conversion produced final R_1 and R_w values of 0.065 and 0.067. Refinement with inverted coordinates gave R_1 and R_w values of 0.068 and 0.071, respectively. Refinement was terminated at this stage.²¹ No parameter shift during the last cycle was greater than 0.2σ . A final difference Fourier map indicated no density greater than $0.8 \text{ e}/\text{\AA}^3$. Crystallographic data are given in Tables I and II. Positional parameters are given in Table III. Molecular distances and angles are given in Tables IV–VIII.

Results

The electronic spectrum of KMn^{III}EDTA·2H₂O displays a band maximum at 500 nm in Me₂SO. Addition of CaH₂ to

Table IV. Significant Bond Lengths (Å) for KMnEDTA·2H₂O

Mn–O1	2.050 (12)	O4–C6	1.222 (22)	N2–C2	1.507 (23)
Mn–O3	1.907 (12)	O5–C8	1.287 (22)	N2–C5	1.487 (23)
Mn–O5	2.022 (13)	O6–C8	1.218 (22)	N2–C7	1.446 (22)
Mn–O7	1.889 (11)	O7–C10	1.277 (25)	C1–C2	1.589 (25)
Mn–N1	2.211 (14)	O8–C10	1.219 (25)	C3–C4	1.534 (26)
Mn–N2	2.237 (14)	N1–C1	1.475 (24)	C5–C6	1.546 (25)
O1–C4	1.252 (22)	N1–C3	1.482 (23)	C7–C8	1.525 (27)
O2–C4	1.283 (23)	N1–C9	1.530 (22)	C9–C10	1.559 (26)
O3–C6	1.285 (22)				

Table V. Significant Bond Angles (deg) for KMnEDTA·2H₂O

Mn–O1–C4	113.1 (11)	O7–Mn–N1	82.7 (6)
O1–Mn–O3	88.5 (6)	Mn–N1–C1	108.9 (11)
Mn–O3–C6	120.9 (10)	Mn–N1–C3	104.7 (11)
O1–Mn–O5	124.2 (6)	Mn–N1–C9	105.9 (10)
O3–Mn–O5	94.6 (6)	O1–Mn–N2	156.7 (6)
Mn–O5–C8	117.4 (11)	O3–Mn–N2	81.0 (6)
O1–Mn–O7	94.4 (6)	O5–Mn–N2	77.5 (6)
O3–Mn–O7	173.8 (6)	O7–Mn–N2	94.3 (6)
O5–Mn–O7	88.3 (6)	N1–Mn–N2	81.0 (7)
Mn–O7–C10	120.8 (11)	Mn–N2–C2	105.3 (11)
O1–Mn–N1	78.8 (6)	Mn–N2–C5	107.3 (11)
O3–Mn–N1	92.5 (6)	Mn–N2–C7	105.2 (10)
O5–Mn–N1	156.0 (7)		

Table VI. Average Bond Lengths and Angles for KMnEDTA·2H₂O

	no.	length, Å
Mn–O	2	2.036 (12)
Mn–O	2	1.898 (11)
Mn–N	2	2.223 (14)
O _c –C	4	1.275 (23)
O _n –C	4	1.235 (23)
C _{sp³} –C _{sp³}	1	1.589 (25)
C _{sp³} –C _{sp²}	4	1.541 (26)
N–C	6	1.488 (23)
	no.	angle, deg
Mn–O–C	4	118.1 (11)
Mn–N–C	6	106.2 (11)
O–C–O	4	122.8 (13)
O–C–C	8	118.6 (13)
N–C–C	6	109.0 (12)
C–N–C	6	112.4 (11)

Table VII. Positional Parameters and Bond Distances of Oxygens Coordinated to a Single K on KMnEDTA·2H₂O

	x/a	y/b	z/c	K–D dist, Å
K	0.7835 (7)	0.1526 (2)	0.5961 (4)	
O9	0.7904 (22)	0.2243 (6)	0.3730 (13)	2.790 (14)
O10	0.3629 (23)	0.1643 (6)	0.5240 (13)	2.873 (16)
O4	0.5298 (19)	0.1193 (6)	-0.1910 (11)	2.822 (13)
O8	-0.1807 (21)	0.0718 (6)	0.4050 (13)	2.693 (14)
O2	0.3746 (17)	-0.0825 (5)	0.1461 (12)	2.819 (13)
O6	0.3824 (23)	0.2576 (5)	0.2347 (13)	2.764 (14)

remove water from the solution does not alter the spectrum, nor does the addition of water to the Me₂SO solution. The solution has an absorbance in the UV region, and a broad low-energy band occurs in the near-IR region at 950 nm. The presence of these three bands indicates a substantial distortion from octahedral geometry about the Mn(III). As will be discussed later, the crystal structure of KMnEDTA·2H₂O shows a distorted MnO₄N₂ octahedron with four long and two short bonds.⁶⁴

The ground state of the high-spin 3d⁴ ion is ⁵D which splits into ⁵E_g and ⁵T_{2g} components in an octahedral field. In accord with the Jahn–Teller theorem, distortion of the complex removes the degeneracy associated with the ⁵E_g ground state. Assuming, then, an idealized D_{4h} symmetry for the coordination geometry about Mn(III), we assigned the two highest

Table VIII. Some Least-Squares Planes in $\text{KMnEDTA}\cdot 2\text{H}_2\text{O}$ A. Deviations from Least-Squares Planes^a

Plane 1

atoms determining plane: O5, -0.0044; O6, -0.0047; C7, -0.0035; C8, 0.0126

other atoms: Mn, -0.1993; N1, -0.5454; N2, 0.4988

Plane 2

atoms determining plane: O3, 0.0068; O4, -0.0071; C5, 0.0054; C6, -0.0192

other atoms: Mn, -0.2709; N1, 1.8944; N2, -0.0205

Plane 3

atoms determining plane: O1, -0.0028; O2, -0.0025; C3, -0.0021; C4, 0.0074

other atoms: Mn, 0.3979; N1, -0.4033; N2, 0.9558

Plane 4

atoms determining plane: O7, 0.0075; O8, 0.0077; C9, 0.0058; C10, -0.0210

other atoms: Mn, 0.0192; N1, 0.3027; N2, 2.2497

B. Equations of the Planes^b

plane no.	L	M	N	D
1	0.5205	0.1231	-0.8450	0.0552
2	-0.5998	-0.6385	-0.4823	-2.9364
3	0.6571	0.2279	-0.7185	0.1311
4	-0.4898	0.7211	-0.4901	-0.2225

C. Dihedral Angle between Planes (deg)

1-2, 89.0; 1-3, 12.3; 1-4, 75.6; 2-3, 101.3; 2-4, 86.0; 3-4, 78.8

^a The number given for each atom represents the distance in Å of that atom from the calculated plane. ^b In the form $LX + MY + NZ = D$.

energy transitions, which are in the UV and visible regions, to ${}^5\text{B}_{1g} \leftrightarrow {}^5\text{B}_{2g}$ and ${}^5\text{B}_{1g} \leftrightarrow {}^5\text{E}_g$. The near-IR band can be assigned³¹ to the ${}^5\text{B}_{1g} \leftrightarrow {}^5\text{A}_{1g}$ transition in which both states are components of the ${}^5\text{E}_g$ ground state of octahedral symmetry. The visible spectrum of $\text{Na}_2\text{Mn}^{\text{II}}\text{EDTA}\cdot 2\text{H}_2\text{O}$ in Me_2SO also exhibits an absorption maximum at 500 nm although with reduced intensity, since d-d transitions in a high-spin d^5 system are spin forbidden.

Addition of superoxide anion to a solution of $\text{Mn}^{\text{III}}\text{EDTA}^-$ in Me_2SO results in the rapid reduction of the complex to $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$, as determined by changes in the visible spectrum. A one-to-one stoichiometry of oxidant to reductant is indicated.

$\text{Mn}^{\text{III}}\text{EDTA}^-$ does not exhibit an EPR spectrum either at 77 K or at room temperature, a result attributable to a large zero field splitting of the Mn(III) ion.²⁴ The spectrum of $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ in Me_2SO at 77 K exhibits a broad transition at $g \sim 2$. A similar but not identical spectrum is obtained upon addition of superoxide to a $\text{Mn}^{\text{III}}\text{EDTA}^-$ solution.

The cyclic voltammogram of $\text{KMnEDTA}\cdot 2\text{H}_2\text{O}$ in Me_2SO shows a peak for the one-electron reduction at $E_p = -0.25$ V at slow sweep rates. The couple is quasi-reversible. The cyclic voltammogram of superoxide in Me_2SO shows an oxidation at $E_{1/2} = -0.75$ V. The cyclic voltammogram of a 1:1 mixture of superoxide and $\text{Mn}^{\text{III}}\text{EDTA}^-$ indicates that all of the superoxide is converted to dioxygen by the time the first scan is completed. No new electroactive species are formed and, indeed, the voltammogram of the degassed solution is identical with that of $\text{Na}_2\text{Mn}^{\text{II}}\text{EDTA}\cdot 2\text{H}_2\text{O}$.

The reaction of $\text{KMn}^{\text{III}}\text{CyDTA}\cdot \text{H}_2\text{O}$ in Me_2SO proceeds in a comparable fashion to that of $\text{Mn}^{\text{III}}\text{EDTA}^-$. The cyclic voltammogram of $\text{KMn}^{\text{III}}\text{CyDTA}\cdot \text{H}_2\text{O}$ in Me_2SO indicates that this complex is reduced to the Mn(II) species at $E_p = -0.30$ V vs. the SCE.

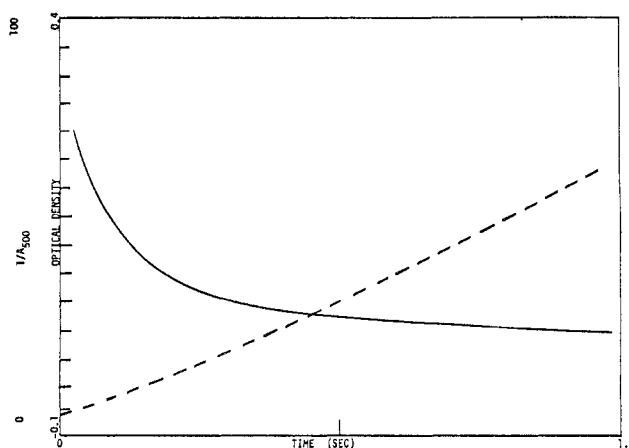


Figure 1. Decay plot for the reaction of O_2^- with $\text{Mn}^{\text{III}}\text{EDTA}^-$ in Me_2SO .

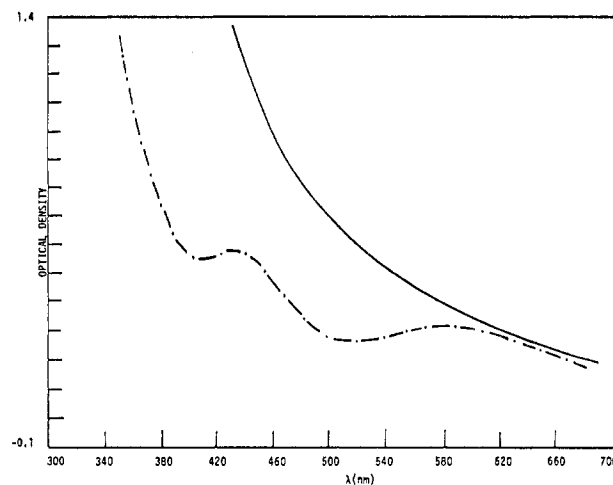


Figure 2. UV-visible spectra of the intermediate (---) and the product (—) of the reaction of $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ with O_2^- .

The rates of the reaction of O_2^- with $\text{Mn}^{\text{III}}\text{EDTA}^-$ and $\text{Mn}^{\text{III}}\text{CyDTA}^-$ in Me_2SO have been determined at 20 °C by stopped-flow and rapid-scan spectrophotometry. The reactions appear to be second order with rate constants of 5×10^4 and $\sim 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively; however, there is a slight curvature in the inverse absorbance plot. A typical decay plot is shown in Figure 1.

The reaction of superoxide with $\text{Na}_2\text{MnEDTA}\cdot 2\text{H}_2\text{O}$ is more complicated. Addition of superoxide to a solution of $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ in Me_2SO produces several spectral changes. When equivalent portions of $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ and O_2^- are mixed, a green intermediate is immediately formed with peaks at 430 and 580 nm as shown in Figure 2. Within several seconds of its formation, the intermediate has disappeared and a yellow-brown final product is obtained that has an absorbance tail through this visible region. The same results are produced by addition of an excess solution of superoxide to $\text{Mn}^{\text{II}}\text{EDTA}^-$. All attempts to obtain an EPR spectrum for the yellow-brown solution at 77 K failed, as did attempts to isolate a product. The cyclic voltammogram of the resultant solution indicates that some oxygen is evolved, but there is no electrochemical evidence for peroxide formation. However, it is well-known that peroxide reacts with Me_2SO to produce Me_2SO_2 .³² Hence, any peroxide formed may be consumed and not be electroactive. Addition of HCl to the above solution generates $\text{Mn}^{\text{III}}\text{EDTA}^-$ and gas is liberated. The stoichiometry of the reaction of $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ and O_2^- as determined spectroscopically is 1:2. Analogously, addition of O_2^- to $\text{Mn}^{\text{II}}\text{CyDTA}^{2-}$ in Me_2SO produces an intermediate with λ_{max} 580 nm which

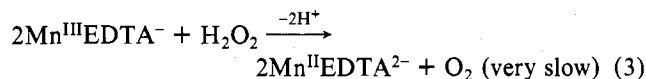
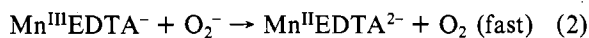
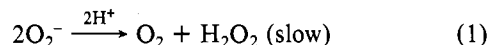
also changes to a yellow-brown final product solution after a few seconds.

In aqueous solution, $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ reacts with Na_2O_2 to produce a green intermediate which slowly (~ 10 s) gives a yellow-brown solution that precipitates MnO_2 upon standing. Reaction with dilute HCl gives a deep pink solution which rapidly becomes colorless. Gas (presumably $\text{Cl}_2(\text{g})$) is evolved.

Bubbling oxygen through solutions of $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ in Me_2SO in the presence of sunlight forms a brownish product whose spectrum is qualitatively similar to that produced by $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ and superoxide, except that a shoulder appears in the spectrum at 540 nm.

We have also examined the reaction of superoxide with the EDTA complexes in buffered aqueous media at pH 10.0. Superoxide spontaneously dismutates at 20 °C by a process which is initially second order with a rate constant of $500 \text{ M}^{-1} \text{ s}^{-1}$.⁶⁰ Later, the reaction deviates from second order. We have found that although $\text{Mn}^{\text{III}}\text{EDTA}^-$ and $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ react with superoxide in aqueous solution, neither complex catalyzes the dismutation. Indeed, the rate of disproportionation in the presence of the metal complex appears to be slightly slower than the rate in the absence of added metal complex.

$\text{KMn}^{\text{III}}\text{EDTA}\cdot 2\text{H}_2\text{O}$ in 0.2 M borate buffer at pH 10.0 is straw yellow with an absorbance maximum at 445 nm. It is probably present as the hydroxo species.²⁶ When an aqueous solution of $\text{Mn}^{\text{III}}\text{EDTA}^-$ is mixed with a Me_2SO solution of superoxide anion in the stopped-flow spectrophotometer, the $\text{Mn}^{\text{III}}\text{EDTA}^-$ is reduced to $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$. No intermediate is observed to have a visible spectrum different from either starting materials or products. The reduction has a second-order rate constant of $\sim 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C. During the course of the reaction, superoxide is spontaneously dismutating to produce dioxygen and hydrogen peroxide. In a later reaction, peroxide at pH 10.0 reduces $\text{Mn}^{\text{III}}\text{EDTA}^-$ to $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$. Hence, at pH 10.0 we have the following concomitant reactions occurring, albeit at different rates. (The stoichiometry of reaction 3 is not known.)



$\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ also interacts with superoxide in aqueous solution. Upon the addition, a blue intermediate ($\lambda_{\text{max}} 620 \text{ nm}$) is formed within the dead time of the stopped flow. This intermediate decays within 2 s to give a final solution having no absorption in the visible region.

The diffusion coefficients of O_2 and O_2^- in Me_2SO have been determined by a chronoamperometric technique.²⁹ The diffusion coefficient of O_2 has been determined to be $2.93 \times 10^{-5} \text{ cm}^2/\text{s}$. Using the Ilkovic equation, Hamm³³ has calculated the diffusion coefficient as $2.81 \times 10^{-5} \text{ cm}^2/\text{s}$. Sawyer³⁴ has used chronopotentiometry to determine the diffusion coefficient as $3.23 \times 10^{-5} \text{ cm}^2/\text{s}$. As the $(i^{1/2})_0$ and the rotating-disk-electrode procedures are preferred methods, we believe that the technique we have used has given the most accurate value. We have measured the diffusion coefficient of O_2^- as $1.1 \times 10^{-5} \text{ cm}^2/\text{s}$. This is in good agreement with Sawyer's first determination³⁴ and that reported by Patkan.⁶¹

We have studied the rates of the electrochemical reduction of $\text{KMn}^{\text{III}}\text{CyDTA}\cdot\text{H}_2\text{O}$ and $\text{KMn}^{\text{III}}\text{EDTA}\cdot 2\text{H}_2\text{O}$ by cyclic voltammetric techniques.³⁵ We have found that the electrochemical rate constants for reduction are roughly equivalent.

The molecular structure of $\text{KMn}^{\text{III}}\text{EDTA}\cdot 2\text{H}_2\text{O}$ is shown in Figure 3. The Mn(III) ion is coordinated to the hexadentate EDTA ligand via four carboxylate oxygens atoms and two

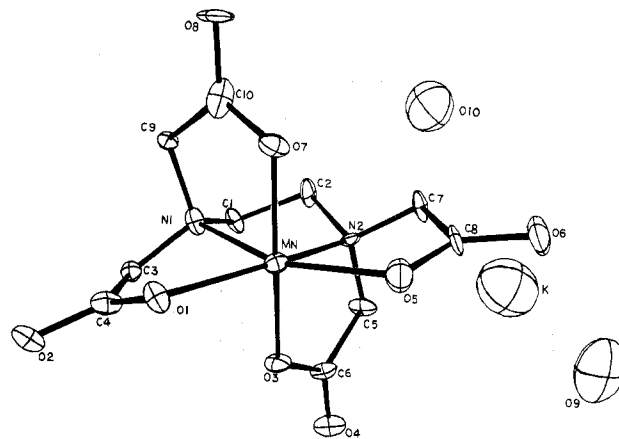


Figure 3. ORTEP drawing of $\text{KMnEDTA}\cdot 2\text{H}_2\text{O}$.

nitrogen atoms. The structure about the manganese atom is that of a highly distorted octahedron with N-Mn-N bond angles of 81.0°. The molecule has approximately C₂ symmetry with the axis of rotation bisecting the ethylenediamine portion of the ligand and passing through the manganese ion. The gross stereochemistry and space group of $\text{KMn}^{\text{III}}\text{EDTA}\cdot 2\text{H}_2\text{O}$ are the same as in other six-coordinate EDTA complexes⁶² such as $\text{NH}_4\text{Co}^{\text{III}}\text{EDTA}\cdot 2\text{H}_2\text{O}$.

Following the terminology of Hoard,³⁶ the less strained glycinate rings (N1-Mn-O7 and N2-Mn-O3) are called L and the more strained (N1-Mn-O1 and N2-Mn-O5) are called M. Oxygen atoms coordinated to manganese are odd numbered and are designated as O_c. The five-membered ring containing the two nitrogen atoms, the manganese atom, and the two methylene carbons is designated as E.

There are two types of Mn-O bonds. The Mn-O bonds of the coordinated oxygens of the L rings are significantly shorter than the Mn-O bonds of the M rings with average lengths of 1.90 (1) and 2.04 (1) Å, respectively. The two Mn-N bond lengths are equivalent within experimental error with an average bond length of 2.21 (1) Å. This distance is shorter than in $\text{Mn}^{\text{III}}\text{CyDTA}^-$.³⁷ The observation of four long and two short bonds is not unexpected. Crystallographic investigations of other Jahn-Teller molecules have shown distorted octahedral geometries. One form of $\text{Mn}^{\text{III}}(\text{acac})_3$ contains two short (1.95 Å) and four long (2.00 Å) Mn-O bonds.^{38,64}

The coordination about the manganese in $\text{KMn}^{\text{III}}\text{EDTA}\cdot 2\text{H}_2\text{O}$ is very similar to that in $\text{KMn}^{\text{III}}\text{CyDTA}\cdot 2\text{H}_2\text{O}$,³⁷ where bond lengths of 1.89 and 2.01 Å are observed for the short and long Mn-On bonds, respectively. The average C_{sp³}-N bond length of 1.49 (2) Å is in close agreement with the value of 1.49 Å reported for the $\text{Mn}^{\text{III}}\text{CyDTA}^-$ complex.³⁷ The C_{sp³}-N bonds of the L ring are slightly longer than in the M rings. The C_{sp³}-C_{sp³} bond in the E ring is 1.59 (2) Å which is somewhat longer than the 1.55 Å reported for $\text{Mn}^{\text{III}}\text{CyDTA}^-$ in which the ethylenediamine fragment is replaced by the more rigid cyclohexylamine moiety. The average C_{sp³}-C_{sp³} bond length in the L and M rings is 1.54 (3) Å, a value which compares favorably with the length found in other amino-carboxylate complexes.³⁹ The angle formed by the two coordinated oxygen atoms of the L rings and the manganese is 173.8 (6)° in the EDTA complex, whereas this ring is 178° in the CyDTA complex.³⁶ The angle formed by the coordinated oxygen atoms of the M rings with the manganese is 124.2 (6) and 128.5° for $\text{Mn}^{\text{III}}\text{EDTA}^-$ and $\text{Mn}^{\text{III}}\text{CyDTA}^-$, respectively.³⁷ In seven-coordinate $\text{Mn}^{\text{II}}_3(\text{HEDTA})_2\cdot 10\text{H}_2\text{O}$ the corresponding O-Mn-O angle of the M rings is 154.8°.⁴⁰ The O-C-C average bond angles are identical for both L and M rings but larger than those found in corresponding seven-coordinate complexes such as $\text{Fe}^{\text{III}}\text{CyDTA}\cdot\text{H}_2\text{O}$.³⁷ Ideally, the M and L rings should be planar with a sum of the interior

angles equal to 540°. This sum is ~538 and ~527° for the L and M rings, which is similar to the values found for Mn^{III}CyDTA⁻.³⁷ The Mn–N–C angles of the E, L, and M rings are 107.3, 105.3 and 105.2°, respectively.

The average of the O_c–C (ring oxygens) bond lengths is 1.27 (2) Å, which is longer than the value of 1.22 Å for the O–C distances. This is consistent with a decrease in double-bond character of the O_c–C bond upon complexation of the O_c's to the metal. All of the carboxylate groups are planar with the sum of the angles about the central carbon being ~360°. The two CCO₂ planes of the two L rings are roughly perpendicular to each other with a value of 86.0°. The angle between the CCO₂ planes in the M rings is 12.3°. The L rings lie on opposite sides of the Mn–N–N plane as do the carbon atoms of the E ring. For a nondistorted octahedral arrangement, two of the M–O bonds should lie in the Mn–N–N plane. However, the coordinated oxygens of the L rings are +1.86 and –1.86 Å from this plane and the coordinate oxygens of the M ring are 0.41 and –0.36 Å away from the plane.

In KMn^{III}CyDTA·H₂O, the individual L and M rings are not equivalent. Rettig and Trotter³⁷ account for the differences by assuming an asymmetric interaction occurs between the uncomplexed oxygen atoms and the water molecule with the cationic potassium. In KMn^{III}EDTA·2H₂O, the potassium ion is six-coordinate and coordinates two water molecules as well as O4 and O8 of the L rings and O2 and O6 of the M rings. The average potassium–oxygen distance is 2.8 Å. The closest water molecule to the manganese in KMn^{III}EDTA·2H₂O is 4.1 Å away, whereas it is only 3.68 Å away in KMn^{III}CyDTA·2H₂O. In Mn^{III}₃(HEDTA)₂·10H₂O, the metal–water bond distance⁴⁰ is 2.225 Å.

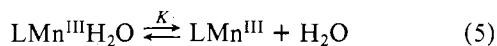
Discussion

Mn^{III}CyDTA⁻ and Mn^{III}EDTA⁻ are rapidly reduced by superoxide in aprotic media to produce Mn^{II}CyDTA²⁻ and Mn^{II}EDTA²⁻ according to eq 4. Although their strength as



oxidizing agents⁶³ is not significantly different, as seen by comparing the thermodynamic reduction potentials (0.814 vs. 0.823 V), the reduction of Mn^{III}CyDTA proceeds at a rate which is 2 orders of magnitude faster than that of Mn^{III}EDTA.

A possible explanation is related to the difference in the water exchange of the two complexes according to eq 5.



Combining (5) with (4), one obtains rate expression 6, where

$$d[\text{LMn}^{\text{III}}]/dt = kK[\text{LMn}^{\text{III}}\text{H}_2\text{O}][\text{O}_2^-] \quad (6)$$

K is 2 orders of magnitude larger for Mn^{III}CyDTA⁻ than for Mn^{III}EDTA⁻. However, this conclusion seems unlikely. The solid-state structures of both KMn^{III}EDTA·2H₂O and KMn^{III}CyDTA·2H₂O indicate that the water molecule is not coordinated to the manganese ion. The shortest Mn(III)–H₂O interactions are at 3.6–4.1 Å. Unfortunately, ¹⁷O NMR studies⁴² have proved to be nondefinitive although they are consistent with the interpretation that water is not exchanging in the first coordinate sphere.

Whether the reduction by O₂⁻ proceeds by an inner or outer sphere mechanism is not known. It has been reported⁴³ that the reaction of excess EDTA with Mn^{III}EDTA⁻ produces CO₂, formaldehyde, and the Mn^{II}EDTA²⁻ complex. This reaction proceeds by oxidation of free rather than complexed ligand. Although Poh and Stewart⁴⁴ indicate that a convenient pathway for the reaction of Mn^{III}CyDTA⁻ with MeOH to produce formaldehyde might be ligand substitution (methanol for carboxylate), this is unlikely to be operative in our reactions.

Table IX. Rate Constants for Water Exchange for Mn(III) Superoxide Dismutase⁴¹ as a Function of the Mn–H Distance

<i>r</i> , ^a Å	<i>τ</i> _m ¹ , ^b s	<i>τ</i> _m , ^c s	1/ <i>τ</i> _m , s ⁻¹
2.61	7.12 × 10 ⁻⁶	6.88 × 10 ⁻⁶	1.4 × 10 ⁵
2.71	8.92 × 10 ⁻⁶	5.08 × 10 ⁻⁶	2.0 × 10 ⁵
2.74	9.53 × 10 ⁻⁶	4.47 × 10 ⁻⁶	2.2 × 10 ⁵
2.90	1.34 × 10 ⁻⁵	6 × 10 ⁻⁷	1.7 × 10 ⁶

^a *r* = metal ion to proton distance. ^b *τ*_m¹ = longitudinal relaxation time. ^c *τ*_m = residence time.

Hamm and Templeton⁴⁵ have shown that ligand substitution of Mn^{III}CyDTA(CN)⁻ to produce Mn^{III}CyDTA(CN)₂²⁻, in which there is an uncoordinated carboxylate arm, proceeds with a rate constant of 0.034 M⁻¹ s⁻¹ at 25 °C. This rate is much slower than the rates we have observed for the redox reaction. In reactions in which ligand substitution is involved in the rate-determining step, it has been reported that Mn^{III}EDTA⁻ reacts faster than Mn^{III}CyDTA⁻. This difference in reactivity is anticipated for ligand-substitution reactions on the basis of the values of the formation constants of both complexes. Thus, our observation of an inverse order of rates is in direct contradiction with a ligand-substitution process as the rate-determining step. Shepherd and Nelson⁴⁶ have recently concluded that the reaction of Mn^{III}EDTA⁻ with oxovanadium(IV) complexes proceeds via an outer sphere mechanism.

Villafranca⁵ has studied the proton relaxation rate for the manganese superoxide dismutase enzyme and has postulated that the rate of water exchange is too slow to accommodate an inner sphere mechanism for the reaction of superoxide with the enzyme. However, his calculation used as the Mn–O bond distance the value reported by Morosin and Brathovde⁴⁷ for Mn(acac)₃. This structure was actually that of Co(acac)₃ and the correct structure³⁸ has Mn–O bond lengths of 1.95 and 2.00 Å. Other Mn(III) structures have Mn–O bond lengths up to 2.4 Å. With longer Mn–O distances, a faster rate of water exchange, 1/*τ*_m, is obtained (Table IX). With manganese superoxide dismutase, pulse radiolysis studies give⁵⁸ an apparent rate constant of 1.5 × 10⁹ M⁻¹ s⁻¹. Thus, *k*₂, the water exchange rate, should be ~2.5 × 10⁷ s⁻¹. Unfortunately, experimental error limits can lead to the order of magnitude difference between the NMR data using a Mn–O distance of 2.15 Å (Mn–H = 2.90 Å) and the *k*₂ for the enzyme. Thus the NMR water exchange results are not conclusive. In addition, Villafranca has pointed out that proton results do not necessarily represent the rate associated with water exchange. Hence ¹⁷O NMR studies might be expected to be informative. Unfortunately, ¹⁷O NMR studies of the water exchange with the Mn^{III}EDTA⁻ and Mn^{III}CyDTA⁻ complexes have not led to meaningful estimates of the rate of water exchange.

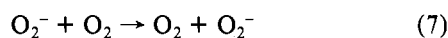
The 2 order of magnitude rate enhancement of O₂⁻ with Mn^{III}CyDTA⁻ compared with Mn^{III}EDTA appears to be related to steric factors.

Margerum et al.⁴⁸ have studied the oxidations of amino-carboxylate complexes with halogens. They used a steric-compression argument to explain their kinetic differences between CyDTA and EDTA complexes. A similar argument based on the structures of the reactants and products, but expressed as the difference in reorganizational energy for Mn^{III}EDTA⁻ and Mn^{III}CyDTA⁻ upon reduction, can account for our observed kinetic differences.

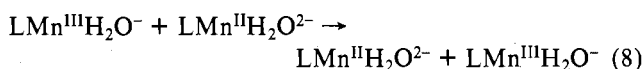
According to Marcus' theory,⁴⁹ there are four contributions to the rate constants of redox reactions. These are (a) interaction energy which is usually insignificant and can be ignored, (b) formation of the precursor complex, (c) inner shell reorganizational energy, and (d) solvent reorganizational energy. Because of the similar structures, it is unlikely that the equilibrium constant for the formation of the precursor complex

will vary significantly between MnEDTA and MnCyDTA complexes.

The electron-transfer process which is being considered is comprised of the two self-exchange reactions



and



The free energy change of the cross-reaction, ΔG_{12}^{**} , is given⁴⁹ by

$$\Delta G_{12}^{**} = \frac{\Delta G_1^{**} + \Delta G_2^{**}}{2} + \frac{\Delta G^{\circ}}{2} + \frac{(\Delta G^{\circ})^2}{8(\Delta G_1^{**} + \Delta G_2^{**})} \quad (9)$$

where ΔG_1^{**} and ΔG_2^{**} refer to the self-exchange reactions, $\Delta G^{**} = \Delta G_1^* + \Delta G_o^*$ (where ΔG_1^* is the inner sphere reorganizational energy and ΔG_o^* is solvent shell reorganizational energy), and ΔG° is the free energy change for the cross-reaction when the two reactants are a distance r apart. Since we are comparing the free energy change upon reaction of two different oxidants that have nearly the same thermodynamic potential (hence, the difference of ΔG° for the two cross-reactions is negligible) with the same reductant, it will suffice to compare only the self-exchange reactions of the two manganese aminocarboxylate complexes.⁴⁹

ΔG_o^* is composed of

$$\Delta G_o^* = \frac{n^2}{4r} \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) \quad (10)$$

where n is the number of electrons transferred and D_{op} is the dielectric constant at optical frequencies. It is evident that the difference in the outer shell reorganizational energy for the $\text{Mn}^{\text{III}}\text{CyDTA}^-$ and $\text{Mn}^{\text{III}}\text{EDTA}^-$ reactions is small. *Another indication of the insignificance of the difference in outer shell reorganizational energy for the two complexes is the fact that the rate constants for reduction of $\text{Mn}^{\text{III}}\text{EDTA}^-$ are the same regardless of the medium.*

For the inner shell reorganizational energy⁴⁹

$$\Delta G_i^* = \frac{f_1 f_2}{2(f_1 + f_2)} (\Delta r^0)^2 \quad (11)$$

where f_1 and f_2 are the force constants for the oxidized and reduced forms, respectively, and Δr^0 is the difference in the equilibrium metal-ligand distance for the two oxidation states. The difference in force constants between $\text{Mn}^{\text{III}}\text{EDTA}^-$ and $\text{Mn}^{\text{III}}\text{CyDTA}^-$ and $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ and $\text{Mn}^{\text{II}}\text{CyDTA}^{2-}$ is expected to be small. The force constants for the M-O stretch in a series of $\text{M}(\text{acac})_2$ complexes ($\text{M} = \text{Cu}, \text{Fe}$) range from 1.45 to 1.30 mdyn/Å.⁵⁹ The value of Δr^0 is the same for both the EDTA and CyDTA complexes if only the metal-chelate bonds are considered. The Mn(III)-H₂O interaction is at 4.08 Å for $\text{Mn}^{\text{III}}\text{EDTA}^-$ and 3.68 Å for $\text{Mn}^{\text{III}}\text{CyDTA}^-$. The water-metal bond length in $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ is 2.225 Å. It can be assumed to have the same value in $\text{Mn}^{\text{II}}\text{CyDTA}^{2-}$. Thus Δr^0 for the water-metal bond in the $\text{Mn}^{\text{III}}\text{EDTA}^{2-}$ couple is 1.97 Å and Δr^0 for the water-metal bond for the $\text{Mn}^{\text{III}}\text{CyDTA}^-/\text{Mn}^{\text{II}}\text{CyDTA}^{2-}$ couple is 1.58 Å. Since there is a squared dependence on Δr^0 in the energy of reorganization expression, it is evident that the kinetic differences as expressed by $k = K\nu_0 e^{-\Delta G^{**}/RT}$ may be accounted for by the greater reorganization necessary in the reduction of $\text{Mn}^{\text{III}}\text{EDTA}^-$ relative to $\text{Mn}^{\text{III}}\text{CyDTA}^-$.

In basic aqueous solution, the reactions of manganese(III) aminocarboxylate complexes are similar to those in aprotic

Table X. Final Anisotropic Thermal Parameters ($\times 10^4$)^a for $\text{KMnEDTA} \cdot 2\text{H}_2\text{O}$

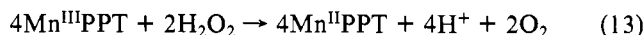
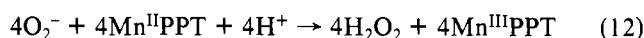
atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	95 (7)	9 (2)	31 (2)	-1 (2)	1 (4)	1 (2)
K	196 (13)	15 (2)	61 (5)	-0.5 (4)	4 (8)	-4 (3)
O1	170 (40)	1 (3)	40 (15)	9 (9)	-25 (20)	-2 (5)
O2	125 (30)	13 (3)	77 (15)	16 (9)	-8 (20)	-7 (7)
O3	131 (32)	13 (3)	43 (15)	12 (9)	39 (18)	12 (6)
O4	118 (35)	25 (4)	44 (16)	8 (10)	-6 (20)	6 (6)
O5	213 (42)	11 (3)	78 (18)	-6 (10)	6 (22)	-1 (6)
O6	376 (56)	9 (3)	73 (17)	-20 (11)	17 (27)	-13 (6)
O7	109 (32)	14 (3)	53 (16)	3 (9)	0 (18)	-11 (5)
O8	245 (44)	22 (3)	72 (15)	-7 (11)	112 (24)	-13 (6)
O9	253 (40)	20 (3)	125 (21)	-9 (11)	-11 (28)	8 (7)
O10	306 (53)	15 (3)	85 (19)	0 (11)	11 (25)	7 (6)
N1	142 (42)	8 (3)	57 (19)	7 (10)	-50 (25)	-1 (6)
N2	39 (34)	9 (3)	51 (18)	-1 (9)	16 (22)	3 (7)
C1	144 (56)	8 (4)	67 (24)	20 (13)	-52 (32)	-1 (8)
C2	159 (59)	7 (4)	113 (29)	-7 (14)	-53 (36)	-9 (9)
C3	1.8 (4) ^b					
C4	142 (51)	14 (4)	30 (22)	1 (15)	9 (32)	-9 (9)
C5	107 (57)	15 (4)	66 (22)	26 (14)	7 (32)	13 (9)
C6	44 (45)	17 (5)	39 (20)	-1 (12)	-25 (29)	3 (9)
C7	177 (53)	6 (4)	60 (24)	3 (12)	-75 (32)	-10 (8)
C8	258 (68)	3 (4)	40 (22)	-4 (14)	58 (33)	-6 (7)
C9	163 (51)	8 (4)	21 (20)	-4 (13)	17 (26)	-7 (7)
C10	239 (70)	13 (5)	56 (26)	-19 (17)	-64 (36)	5 (9)

^a The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^b Isotropic value (in Å²). Anisotropic constants not all positive definite.

media but are believed to involve manganese hydroxo species of the form $\text{Mn}^{\text{III}}\text{L}(\text{OH})$.²⁶ Fackler and Chawla⁵⁶ also have shown that the dominant form of Mn(III) in dilute perchloric acid is a hydroxo species. In water, the Mn(III) complexes react with both superoxide and hydrogen peroxide, one of the dismutation products. The reaction of hydrogen peroxide with $\text{Mn}^{\text{III}}\text{CyDTA}^-$ in acidic media to give $\text{Mn}^{\text{II}}\text{CyDTA}^{2-}$ and O_2 has been studied by Hamm and Jones.¹³ In their proposed mechanism, a manganese peroxo intermediate is formed, although without spectral evidence. We were also unable to detect any intermediate in the reaction of $\text{Mn}^{\text{III}}\text{EDTA}^-$ with O_2^- or H_2O_2 at pH 10.0. At pH 10.0, $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ did not react with hydrogen peroxide.

In basic aqueous solution, $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ interacts with superoxide to form a blue intermediate which decomposes to produce $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ and the dismutation products. We believe this intermediate to be of the form $[\text{LMn}^{\text{II}}\text{O}_2^-]$. The water exchange rate of $4.4 \times 10^8 \text{ s}^{-1}$ as determined by ¹⁷O NMR is compatible with the formation of an intermediate.⁵⁰

Kono et al.⁸ have reported that manganese(II) pyrophosphate (PPT) was oxidized to manganese(III) pyrophosphate by superoxide but manganese(III) pyrophosphate was not reduced by superoxide, eq 12 and 13. We see no



evidence for oxidation of $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ by superoxide. Indeed, by using pulse radiolysis techniques, Bielski and Chan⁹ have demonstrated that O_2^- is not capable of oxidizing MnSO_4 at pH 6.0.

It has been shown that $\text{Fe}^{\text{II/III}}\text{EDTA}$ complexes^{51,52} catalyze the dismutation of superoxide as does hydrated Cu^{2+} ion.⁵³ The basic difference between the FeEDTA and the MnEDTA systems lies in the values of the M(III)/M(II) redox couples. The standard redox potential of the $\text{Mn}^{\text{III}}\text{EDTA}/\text{Mn}^{\text{II}}\text{EDTA}$ system is 0.82 V, whereas for $\text{Fe}^{\text{III}}\text{EDTA}/\text{Fe}^{\text{II}}\text{EDTA}$ this value is 0.11 V. The reduction and oxidation potentials of superoxide are given in Figure 4. It is evident from this figure that O_2^- is capable of reducing $\text{Mn}^{\text{III}}\text{EDTA}^-$ and $\text{Fe}^{\text{III}}\text{EDTA}^-$ in any

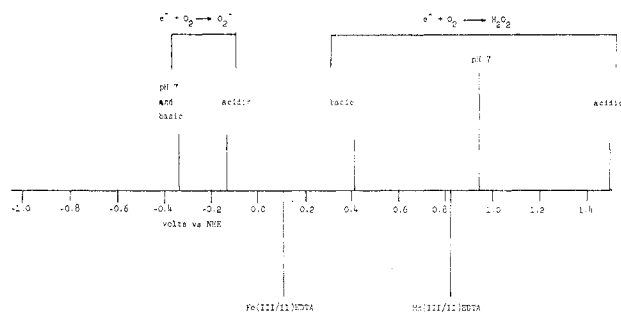


Figure 4. A scale of important redox potentials, in volts.^{54,57}

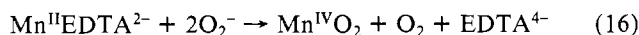
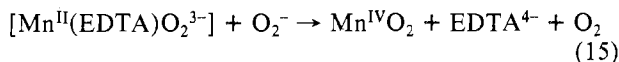
pH region. However, $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ can be oxidized to Mn^{III} by O_2^- only in acidic media, whereas $\text{Fe}^{\text{II}}\text{EDTA}^{2-}$ can be oxidized by O_2^- at any reasonable pH. It is also evident from this figure that in order to be an effective dismutase at pH 7.0, the metal complex is limited to be a maximum redox potential of 0.9 V, a limit which MnEDTA approaches. However, there are also kinetic barriers to the reaction of $\text{Mn}^{\text{III}}\text{EDTA}^-$ with superoxide.

Even though it is thermodynamically possible at a low pH for superoxide to oxidize $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ to $\text{Mn}^{\text{III}}\text{EDTA}^-$, this does not appear to occur. Instead, $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ is oxidized to Mn^{IV} which then is reduced to $\text{Mn}^{\text{III}}\text{EDTA}^-$ in acid media. (It is well-known that the combination of Mn^{II} and Mn^{IV} in acid solutions gives Mn^{III} .)

In aprotic media, $\text{Mn}^{\text{II}}\text{EDTA}^-$ interacts with superoxide to form a green intermediate and then a yellow-brown final product which is stable indefinitely in Me_2SO . Some dioxygen is evolved but we observed no electrochemical evidence for peroxide formation. Addition of acid to the product solution generates $\text{Mn}^{\text{III}}\text{EDTA}^-$. A spectrophotometric titration indicated that the reaction was complete (by the absence of any additional spectral changes) upon the addition of 2 equiv of superoxide. The solution did not exhibit any EPR spectrum of O_2^- until at least 2 equiv of O_2^- was added. Consistent with these facts, there are at least two possible products that can be formulated, either $\text{Mn}^{\text{II}}\text{EDTAO}_2^{2-}$ or an oxo Mn^{IV} . We believe that our product is an oxo Mn^{IV} for several reasons. First, one would not expect that a peroxo species would be stable in Me_2SO since peroxide itself oxidizes Me_2SO to Me_2SO_2 . The spectrum of freshly prepared manganese(IV) oxide from KMnO_4 , ROH , and H_2O is qualitatively similar to the above. Addition of EDTA and acid to a manganese(IV) oxide solution in Me_2SO also produces $\text{Mn}^{\text{III}}\text{EDTA}^-$.

The reaction of Na_2O_2 with $\text{Mn}^{\text{II}}\text{EDTA}^{2-}$ also produces a green solution which turns yellow-brown upon standing for several seconds. A brown precipitate is formed. Addition of acid produces $\text{Mn}^{\text{III}}\text{EDTA}^-$ and gas is liberated.

A set of equations consistent with the above results is



Although our results indicate that MnEDTA is not an effective model of mitochondrial or procaryotic superoxide dismutases, the study of its reaction with superoxide is nonetheless enlightening in the sense that a model for enzyme function is more narrowly defined. Clearly the protein must either lower the $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ redox couple to a value near or below 0.4 V, a rather difficult constraint with nitrogen and oxygen ligands, or supply the system with very acidic protons. This latter process might be accomplished with nearby protonated imidazole groups. In addition, it is apparent that protein/substrate reorganizational energies must be small. Structural

rigidity about the metal ion can lead to enhanced electron-transfer rates for the oxidation of O_2^- . The stereochemical flexibility of the Jahn-Teller-active manganese(III) apparently accommodates the appropriate structural coordination induced by the protein which is necessary to make fast electron transfer possible.

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Registry No. $\text{KMnEDTA} \cdot 2\text{H}_2\text{O}$, 66615-87-0; KMnCyDTA , 38127-69-4; Na_2MnEDTA , 15375-84-5; O_2^- , 11062-77-4.

Supplementary Material Available: A listing of observed and calculated structure factors for $\text{KMn}^{\text{III}}\text{EDTA} \cdot 2\text{H}_2\text{O}$ (4 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and the University of Santander, Bucaramanga, Colombia

Structure and Electron Paramagnetic Resonance Spectrum of the Product of the Reaction of Aqueous Pyridine with Copper(II) Hexafluoroacetylacetonate. Tetrakis(pyridine)bis(trifluoroacetato)copper(II)

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Relationships between structure and EPR spectroscopic parameters for copper(II) coordination are of interest due to the diversity of coordination geometries found with this ion. Often EPR parameters are the only available spectroscopic information concerning the ion, especially in proteins. Tetragonal CuN_4O_2 coordination in the title compound for a copper-doped zinc sample produces high g_{\parallel} (2.288) and A_{\parallel} ($169 \times 10^{-4} \text{ cm}^{-1}$) values. The sample is obtained by decomposition of copper(II) and zinc(II) hexafluoroacetylacetonate complexes in aqueous pyridine. Single-crystal X-ray analysis was used to identify the product as tetrakis(pyridine)bis(trifluoroacetato)copper(II), $\text{Cu}(\text{py})_4(\text{CF}_3\text{CO}_2)_2$, a compound first encountered as a byproduct during the synthesis of copper(II)-doped $\text{Zn}(\text{F}_6\text{acac})_2(\text{py})_2$ and subsequently prepared by reaction of pyridine with copper(II) trifluoroacetate. The title compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.528$ (6) Å, $b = 9.218$ (5) Å, $c = 18.471$ (10) Å, $\alpha = 104.57$ (5)°, $\beta = 98.50$ (6)°, and $\gamma = 118.65$ (4)°. Least-squares refinement of 3126 reflections resulted in a final conventional R factor of 0.067. The molecule contains a tetragonally elongated CuN_4O_2 geometry with an average Cu-N bond distance of 2.046 (6) Å and an average Cu-O bond distance of 2.367 (7) Å. The four pyridine molecules occupy the equatorial positions, and the two monodentate trifluoroacetate ligands occupy the axial positions. The tetragonality parameter T is larger (0.86) than for any CuN_4O_2 complex previously reported.

Introduction

Systematic studies of the stereochemistry of copper(II) complexes have been pursued by Hathaway and co-workers¹ and others². The copper(II) ion has an $[\text{Ar}]3d^9$ electron configuration which leads to a Jahn-Teller electronic degeneracy in complexes of high symmetry.³ Bersuker^{2a} has attempted to systematize the stereochemical features observed in copper(II) complexes containing CuO_6 , CuN_6 , and CuN_4O_2 coordination. The metal-ligand equatorial, R_S , and axial, R_L , distances appear to be correlated,⁴ and the tetragonality parameter $T = R_S/R_L$ for CuN_4O_2 geometries is less than 0.81 for all complexes heretofore reported.^{1,2} Interest in copper(II) coordination stems, in part, from the prevalence of this ion in several metalloenzyme systems^{5,6a} and industrially important catalytic reactions.^{6b}

Our own group has presented results of magnetic and crystallographic studies⁷ wherein certain complexes with a CuO_4N_2 coordination geometry are fluxional in the solid state at temperatures down to 70 K and below. These studies involved complexes containing the 1,1,1,5,5,5-hexafluoro-2,4-pentane-

dionato ligand (F_6acac) and pyridine (py). During attempts to synthesize copper-doped $\text{Zn}(\text{F}_6\text{acac})_2(\text{py})_2$ with excess pyridine, blue crystals were isolated which appeared from IR studies to contain uncoordinated carbonyl⁸ and from electron paramagnetic resonance (EPR) studies, four equivalent nitrogen atoms. A monodentate F_6acac coordination was postulated.⁹ Structural studies¹⁰ revealed that the correct stoichiometry for this material is $\text{Cu}(\text{py})_4(\text{O}_2\text{CCF}_3)_2$. The hexafluoroacetylacetonate ligand apparently hydrolyzes with C-C bond rupture under the conditions of the synthesis, a somewhat surprising result since anhydrous hexafluoroacetylacetonate is usually dried (it is a dihydrate when moist) by distillation from sulfuric acid. Subsequent studies by one of us^{10b} (J.P.S.) have shown that the hydrolysis to trifluoroacetate is catalyzed by both Cu(II) and Zn(II).

Experimental Section

Synthesis. A pyridine solution of $\text{Cu}(\text{F}_6\text{acac})_2$ in contact with the atmosphere for several weeks produces blue crystals of $\text{Cu}(\text{py})_4(\text{CF}_3\text{CO}_2)_2$ along with some green crystals of $\text{Cu}(\text{F}_6\text{acac})_2(\text{py})_2$.

Upon addition of water to a pyridine solution of $\text{Cu}(\text{F}_6\text{acac})_2$, a blue phase is produced which separates from a green phase. When the blue solution is mixed with an equal amount of benzene, blue crystals of $\text{Cu}(\text{py})_4(\text{CF}_3\text{CO}_2)_2$ are obtained upon slow evaporation in air.

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