

solvent afforded pure **3** (15 mg, 0.05 mmol, 30%) as a slightly air-sensitive orange solid. UV-visible wavelength maxima (nm, in CH₂Cl₂): 422, 310, 282. Exact mass (*m/z*): calcd for ⁵⁶Fe³²S¹²C₁₄¹¹B₃¹H₂₇⁺, 316.1462; found, 316.1466.

Synthesis of (η⁶-HNMe₂C₈H₄)Fe(Et₂C₂B₄H₄) (4**).** In a thick-walled Pyrex tube were placed 0.500 g (1.71 mmol) of **1** and ca. 1.0 g of 2,3-dimethylindole (Aldrich). The tube was sealed under vacuum and heated in an oven at 180 °C for 2.5 h, after which it was opened in air and the contents extracted with dichloromethane. The solvent was removed and the residue washed with a minimum volume of hexane and suction-filtered through silica gel with hexane as eluent, until all of the 2,3-dimethylindole was removed (ca. 1 L). Elution of the column with dichloromethane gave a red filtrate which upon evaporation gave **4** (0.49 g, 1.47 mmol, 86%). UV-visible wavelength maxima (nm, in CH₂Cl₂): 358, 278. Exact mass (*m/z*): calcd for ⁵⁶Fe¹⁴N¹²C₁₆¹¹B₄¹H₂₅⁺, 331.1709; found, 331.1709.

Deprotonation of **4 and Synthesis of (η⁶-MeNMe₂C₈H₄)Fe(Et₂C₂B₄H₄) (**6**).** A 74-mg (0.22-mmol) sample of **4** was placed in a 50-mL two-neck round-bottom flask equipped with a rubber septum and a vacuum line attachment. The flask was evacuated and placed in a liquid-nitrogen bath, and 40 mL of dry DME was added via vacuum distillation, after which the reactor was warmed to ca. 0 °C, affording an orange solution. A 10-mL quantity of 2.5 M *n*-butyllithium was introduced via the septum, causing an immediate color change to dark red. The flask was warmed to room temperature, and 0.50 mL of methyl iodide was added via syringe, producing a color change to orange. The mixture was stirred for 10 min, the reactor was opened to air, and the solvent was removed by rotary evaporation. The residue was extracted with dichloromethane, and the extract was suction-filtered through silica gel with dichloromethane as eluent, affording a single orange band. Evaporation to dryness gave orange crystals of **6** (74 mg, 0.21 mmol, 96%). UV-visible wavelength maxima (nm, in CH₂Cl₂): 466, 294, 250. Exact mass (*m/z*): calcd for ⁵⁶Fe¹⁴N¹²C₁₇¹¹B₄¹H₂₇⁺, 345.1865; found, 345.1874.

Acknowledgment. This work was supported in part by the National Science Foundation, Grant CHE 8721657.

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Structures and Spectroscopic Characteristics of Iron(III) Diethylenetriaminepentaacetic Acid Complexes. A Non-Heme Iron(III) Complex with Relevance to the Iron Environment in Lipoyxygenases

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Received September 21, 1990

Certain enzymes, including lipoyxygenase and phenylalanine hydroxylase, contain iron in an unusual non-heme environment. Solutions of the versions of these enzymes containing iron(III) display an EPR signal at *g* = 6.^{1,2} While the *g* = 6 signal is usually associated with high-spin ferric heme,³ the enzymes have none of the other distinguishing spectroscopic properties of heme proteins. The ligand environments of the iron atoms in these proteins are presently unknown in spite of substantial characterization efforts. In the case of lipoyxygenase, the nature of the iron site has been probed in a number of investigations employing magnetic susceptibility,⁴ paramagnetic NMR effects,⁵ EXAFS,⁶ EPR,⁷ Mössbauer,⁸ and MCD.⁹ The enzyme isolated from soybeans (native) contains high-spin iron(II), probably in an octahedral field of six oxygen and/or nitrogen atoms. An evolutionarily conserved cluster of histidine residues has been proposed to be a part of the ligand field.¹⁰ Treatment of the native enzyme

with 1 equiv of the hydroperoxide product of catalysis converts the iron site to the high-spin iron(III) species with the characteristic *g* = 6 EPR signal. There is evidence that water oxygen is one of the ligands to iron in the oxidized form of the enzyme.¹¹

In a study of the incorporation of iron-57 into lipoyxygenases by a tissue culture technique, we used iron as the diethylenetriaminepentaacetic acid (DTPA) chelate.¹² We were intrigued by the finding that this iron complex had Mössbauer spectroscopic properties similar to those of the iron in lipoyxygenase and, like the metal in the enzyme, was resistant to oxidation by molecular oxygen.⁸ While numerous investigations of the structures and spectroscopic properties of Fe^{III}EDTA complexes have been carried out,¹³ we could find only one structural study and limited spectroscopic characterization of the corresponding DTPA compounds.^{14,15} The structures of Fe^{III}EDTA complexes have been obtained under a wide variety of conditions. At low pH, the iron was found in a six-coordinate, roughly octahedral field, consisting of two nitrogen and three oxygen atoms from the ligand and one oxygen atom from water solvent.¹⁶ At high pH, an additional ligand carboxyl was found to join the coordination sphere, making the iron seven coordinate and roughly pentagonal bipyramidal.¹⁷ Like nearly all high-spin non-heme iron(III) species, the EDTA complexes displayed EPR signals at *g* = 4.3 irrespective of pH.¹⁸ The single structure report on Fe^{III}DTPA found the iron in a seven-coordinate pentagonal-bipyramidal geometry made up of three ligand nitrogen atoms and four ligand oxygens.¹⁴ Like the EDTA complexes, Fe^{III}DTPA has been characterized by the observation (at pH 9–10) of the *g* = 4.3 EPR feature.¹⁵ This report describes the discovery of the interesting effect of conditions on both the solid-state (structural) and solution (spectroscopic) properties of the complexes of iron(III) with DTPA.

Experimental Section

Synthesis. H₅DTPA (Aldrich), Fe(NO₃)₃·9H₂O (Fisher), FeCl₃·6H₂O (Fisher), NaHCO₃ (Malinkrodt), and 40% aqueous (C₂H₅)₃NOH (Alfa) were used as supplied without further purification. The Fe^{III}DTPA complexes were prepared by a modification of the procedure of Sievers and Bailar.¹⁹

[FeH₂DTPA]₂·2H₂O (**I**). Fe(NO₃)₃·9H₂O (4.04 g, 0.01 mol) was added to a solution of H₅DTPA (3.93 g, 0.01 mol) in deionized H₂O (20 mL), and the mixture was heated to 70 °C. The clear orange solution turned bright yellow and turbid during the heating process. The pH of

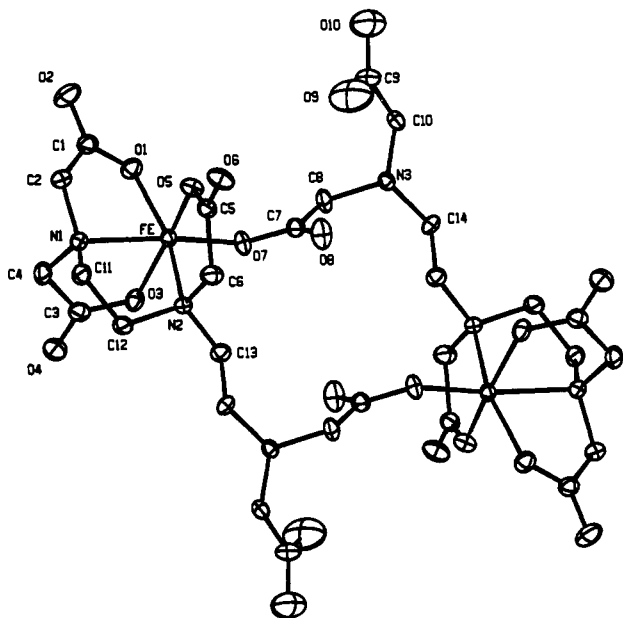
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Table I. Summary of Data Collection and Structure Solution and Refinement

	I	II	III
formula	C ₂₈ H ₄₄ Fe ₂ N ₆ O ₂₂	C ₁₄ H ₂₂ FeNa ₂ N ₃ O ₁₂	C ₃₀ H ₄₆ FeN ₅ O ₁₄
fw	928.38	526.17	776.73
F(000)	964	542	1676
dimensions, mm	0.31 × 0.20 × 0.05	0.25 × 0.11 × 0.10	0.59 × 0.20 × 0.18
space group	P2 ₁ /c	P1	P2 ₁ /c
a, Å	12.681 (3)	7.080 (3)	18.061 (2)
b, Å	12.929 (3)	10.118 (5)	15.350 (4)
c, Å	12.225 (3)	14.549 (3)	13.970 (4)
α, deg		104.26 (3)	
β, deg	105.63 (2)	93.17 (2)	94.67 (1)
γ, deg		89.77 (3)	
V, Å ³	1930.2	1008.5	3860.2
Z	2	2	4
ρ, g/cm ³	1.60	1.73	1.34
μ, cm ⁻¹	8.4	8.5	4.5
reflens			
total	4143	4305	8196
unique	3962	3967	7867
R _{int} , %	2.9	2.4	2.7
decay	0.919–1.078	0.974–1.047	0.950–1.143
absorption	0.86–1.00	0.91–1.00	0.95–1.00
minimization function		Σw(F _o - F _c) ²	
reflens included, F _o ² > 3.0σF _o ²)	1877	2597	3148
param refined	277	295	475
R	0.046	0.036	0.043
R _w	0.055	0.045	0.048
S	1.62	1.31	1.37

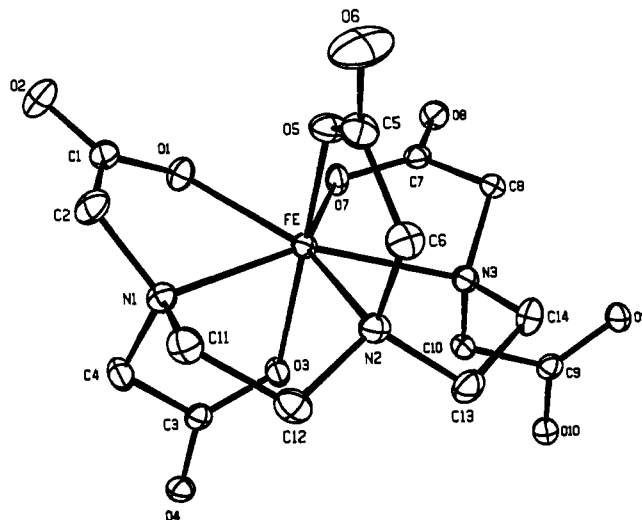
Figure 1. ORTEP drawing of the [FeH₂DTPA]₂ (I) molecule.

the solution was 1.4. Heating was discontinued, and absolute ethanol (12 mL) was added, producing a bright yellow precipitate. The solid was collected, dried, and recrystallized (yellow-orange square plates) by slow evaporation from H₂O.

Na₂[FeDTPA]·2H₂O (II). An aqueous solution (20 mL) containing equivalent amounts of Fe(NO₃)₃·9H₂O (5.0 g, 0.0124 mol) and H₂DTPA (4.88 g, 0.0124 mol) was heated to 100 °C and neutralized with NaHCO₃ (5.38 g, 0.064 mol) to give a clear mustard yellow solution with pH 6.5. A dark red liquid separated upon addition of absolute ethanol (75 mL). The red liquid was transferred to a dish and allowed to evaporate. Amber rectangular plate shaped crystals were obtained.

[(C₂H₅)₄N]₂[FeDTPA]·4H₂O (III). Aqueous solutions of FeCl₃·6H₂O (3.35 g, 0.0124 mol, 10 mL) and H₂DTPA (4.88 g, 0.0124 mol, 25 mL) were combined, heated to 100 °C, and neutralized with (C₂H₅)₄NOH (23.4 mL, 0.064 mol). Addition of base was accompanied by a color change from yellow to dark red. The pH of the solution was 8.9. Addition of absolute ethanol (500 mL) and slow evaporation produced red-orange hexagonal plate shaped crystals.

Structure Determination. Crystals for X-ray measurements were mounted in glass capillaries. Preliminary examination and intensity data

Figure 2. ORTEP drawing of the [FeDTPA]²⁻ (II) dianion.

collection were carried out with an Enraf-Nonius CAD-4 automatic diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Intensity data were collected by using ω - 2θ scans to $2\theta_{\max}$ of 52.0° and corrected for absorption and decay. All three structures were solved by Patterson and Fourier techniques and refined in full-matrix least-squares analyses on F with $w = 4F_o^2/\sigma^2(F_o^2)$. In the final cycles all non-hydrogen atoms were refined anisotropically with ligand hydrogen atoms riding in ideal positions. Scattering factors for the neutral atoms and anomalous scattering coefficients for non-hydrogen atoms were taken from ref 20. All calculations were carried out with a VAX 11/750 computer using SDP/VAX,²¹ and the figures were prepared with ORTEP.²² A summary of data collection and structure solution is given in Table I, final atomic coordinates of non-hydrogen atoms are listed in Tables II–IV, selected bond lengths and angles are detailed in Tables V–VII, and drawings of the molecules are presented in Figures 1 and 2.

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Table II. Positional Parameters for I (Non-Hydrogen Atoms)^a

atom	x	y	z	B, Å ²
Fe	0.21457 (6)	0.40518 (6)	0.33041 (6)	1.76 (1)
O1	0.3735 (3)	0.4200 (3)	0.3489 (3)	2.73 (9)
O2	0.5007 (3)	0.4381 (4)	0.2557 (4)	4.2 (1)
O3	0.2139 (3)	0.2627 (3)	0.3889 (3)	2.50 (9)
O4	0.2394 (3)	0.0947 (3)	0.3641 (4)	3.7 (1)
O5	0.1895 (3)	0.5314 (3)	0.2362 (3)	2.53 (9)
O6	0.0767 (4)	0.6308 (3)	0.1086 (3)	3.4 (1)
O7	0.1987 (3)	0.4606 (3)	0.4709 (3)	2.66 (9)
O8	0.0889 (3)	0.5995 (4)	0.4516 (3)	3.7 (1)
O9	0.2678 (5)	0.7824 (6)	0.4974 (5)	8.7 (2)
O10	0.4165 (5)	0.8473 (5)	0.6071 (5)	8.1 (2)
O11	0.4001 (5)	-0.0564 (5)	0.4157 (4)	7.7 (2)
O12	0.4910 (7)	0.3540 (6)	0.5876 (7)	13.7 (3)
N1	0.2381 (4)	0.3175 (4)	0.1859 (4)	2.0 (1)
N2	0.0392 (3)	0.3856 (3)	0.2364 (3)	1.86 (9)
N3	0.2085 (3)	0.6823 (3)	0.6574 (3)	1.8 (1)
C1	0.4084 (4)	0.4131 (5)	0.2592 (5)	2.7 (1)
C2	0.3264 (5)	0.3722 (5)	0.1525 (5)	2.6 (1)
C3	0.2390 (4)	0.1849 (5)	0.3349 (5)	2.5 (1)
C4	0.2721 (5)	0.2117 (5)	0.2274 (5)	3.1 (1)
C5	0.0961 (5)	0.5549 (5)	0.1707 (5)	2.4 (1)
C6	0.0017 (5)	0.4845 (5)	0.1769 (5)	2.9 (1)
C7	0.1669 (4)	0.5481 (5)	0.5016 (4)	2.3 (1)
C8	0.2403 (4)	0.5806 (4)	0.6166 (5)	2.5 (1)
C9	0.3267 (5)	0.7959 (6)	0.5848 (6)	4.5 (2)
C10	0.3056 (5)	0.7503 (5)	0.6973 (5)	2.9 (1)
C11	0.1305 (4)	0.3161 (5)	0.0977 (4)	2.6 (1)
C12	0.0393 (4)	0.3011 (5)	0.1536 (4)	2.4 (1)
C13	-0.0262 (4)	0.3598 (5)	0.3152 (4)	2.3 (1)
C14	0.1448 (4)	0.6695 (5)	0.7442 (4)	2.1 (1)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter. Estimated standard deviations are given in parentheses.

Table III. Positional Parameters for II (Non-Hydrogen Atoms)^a

atom	x	y	z	B, Å ²
Fe	0.08202 (7)	0.33956 (5)	0.25651 (3)	1.539 (9)
Na1	0.2448 (2)	0.9780 (1)	0.5022 (1)	2.15 (3)
Na2	0.4237 (2)	0.2975 (1)	0.4379 (1)	2.17 (3)
O1	0.2808 (3)	0.1906 (2)	0.2829 (2)	2.13 (5)
O2	0.4117 (4)	-0.0109 (3)	0.2283 (2)	3.14 (6)
O3	-0.0985 (3)	0.3266 (2)	0.3511 (2)	1.91 (5)
O4	-0.2752 (3)	0.2017 (2)	0.4189 (2)	2.17 (5)
O5	0.2040 (3)	0.3311 (3)	0.1375 (2)	2.53 (5)
O6	0.1809 (5)	0.2993 (4)	-0.0189 (2)	5.17 (8)
O7	0.3011 (3)	0.4421 (2)	0.3464 (2)	2.14 (5)
O8	0.4798 (3)	0.6285 (2)	0.3937 (2)	2.44 (5)
O9	-0.0131 (3)	0.8602 (2)	0.4018 (2)	2.22 (5)
O10	-0.1766 (3)	0.7968 (2)	0.5094 (2)	2.29 (5)
O11	-0.5059 (4)	-0.0899 (3)	0.3967 (2)	2.73 (6)
O12	0.5469 (5)	0.2641 (4)	-0.0968 (3)	6.7 (1)
N1	-0.0470 (4)	0.1206 (3)	0.1963 (2)	1.80 (6)
N2	-0.1725 (4)	0.3661 (3)	0.1557 (2)	1.90 (6)
N3	0.0161 (4)	0.5752 (3)	0.2950 (2)	1.73 (6)
C1	0.2811 (5)	0.0709 (4)	0.2292 (2)	2.12 (7)
C2	0.1114 (5)	0.0305 (4)	0.1626 (3)	2.54 (8)
C3	-0.1710 (4)	0.2129 (3)	0.3561 (2)	1.78 (7)
C4	-0.1219 (5)	0.0873 (3)	0.2816 (3)	2.21 (7)
C5	0.1118 (5)	0.3273 (4)	0.0584 (3)	2.60 (8)
C6	-0.0939 (5)	0.3659 (4)	0.0629 (2)	2.43 (8)
C7	0.3404 (5)	0.5660 (3)	0.3483 (2)	1.83 (7)
C8	0.2057 (4)	0.6323 (3)	0.2909 (2)	1.88 (7)
C9	-0.0826 (4)	0.7705 (3)	0.4371 (2)	1.86 (7)
C10	-0.0520 (5)	0.6190 (3)	0.3936 (2)	1.87 (7)
C11	-0.1979 (5)	0.1180 (4)	0.1221 (3)	2.35 (8)
C12	-0.3070 (5)	0.2496 (4)	0.1448 (3)	2.43 (8)
C13	-0.2686 (5)	0.4961 (4)	0.1953 (3)	2.31 (8)
C14	-0.1250 (5)	0.6098 (4)	0.2263 (3)	2.36 (7)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter. Estimated standard deviations are given in parentheses.

EPR Spectroscopy. The EPR spectra were taken on a Varian E-line Century Series EPR spectrometer equipped with a gas-phase, liquid helium flow cooling apparatus. Frequency measurements were made on

Table IV. Positional Parameters for III (Non-Hydrogen Atoms)^a

atom	x	y	z	B, Å ²
Fe	0.29276 (3)	0.04330 (4)	0.41890 (5)	2.35 (1)
O1	0.2102 (2)	-0.0285 (2)	0.4721 (2)	3.05 (7)
O2	0.1301 (2)	-0.0573 (2)	0.5808 (2)	4.76 (8)
O3	0.3774 (2)	-0.0232 (2)	0.4720 (2)	3.16 (7)
O4	0.4204 (2)	-0.1141 (2)	0.5874 (3)	5.64 (9)
O5	0.2203 (2)	0.1308 (2)	0.3627 (2)	3.10 (7)
O6	0.1942 (2)	0.2673 (2)	0.3190 (2)	4.49 (8)
O7	0.2618 (1)	-0.0450 (2)	0.3126 (2)	2.69 (6)
O8	0.2263 (2)	-0.0624 (2)	0.1583 (2)	4.11 (8)
O9	0.5260 (2)	-0.0400 (3)	0.2050 (2)	6.2 (1)
O10	0.4583 (2)	0.0643 (2)	0.1276 (3)	5.6 (1)
O11	0.2393 (2)	0.4433 (2)	0.3693 (3)	4.97 (9)
O12	0.3881 (2)	0.4294 (2)	0.4391 (3)	4.88 (9)
O13	0.1544 (2)	0.0545 (3)	0.0326 (3)	6.2 (1)
O14	0.1479 (3)	0.2249 (3)	0.1197 (3)	8.8 (1)
N1	0.2931 (2)	0.0677 (2)	0.5901 (3)	3.06 (8)
N2	0.3522 (2)	0.1745 (2)	0.4549 (3)	2.82 (8)
N3	0.3622 (2)	0.0732 (2)	0.2846 (3)	2.93 (8)
N4	0.3164 (2)	0.7116 (2)	0.4027 (3)	3.61 (9)
N5	0.0118 (2)	0.5488 (3)	0.7515 (3)	3.24 (8)
C1	0.1812 (2)	-0.0151 (3)	0.5521 (3)	3.0 (1)
C2	0.2156 (2)	0.0592 (3)	0.6111 (3)	3.6 (1)
C3	0.3828 (2)	-0.0519 (3)	0.5595 (3)	3.6 (1)
C4	0.3373 (3)	-0.0063 (3)	0.6304 (3)	4.0 (1)
C5	0.2316 (2)	0.2131 (3)	0.3665 (3)	2.9 (1)
C6	0.2955 (3)	0.2430 (3)	0.4362 (3)	3.5 (1)
C7	0.2618 (2)	-0.0236 (3)	0.2237 (3)	2.7 (1)
C8	0.3075 (2)	0.0548 (3)	0.2028 (3)	3.2 (1)
C9	0.4735 (3)	0.0145 (3)	0.1961 (4)	4.2 (1)
C10	0.4260 (2)	0.0124 (3)	0.2833 (3)	3.3 (1)
C11	0.3260 (3)	0.1515 (3)	0.6226 (4)	4.4 (1)
C12	0.3836 (2)	0.1774 (3)	0.5566 (3)	3.8 (1)
C13	0.4129 (2)	0.1872 (3)	0.3908 (3)	3.9 (1)
C14	0.3869 (3)	0.1648 (3)	0.2880 (3)	3.8 (1)
C15	0.2645 (3)	0.7662 (3)	0.4580 (3)	3.6 (1)
C16	0.1987 (3)	0.7201 (4)	0.4948 (4)	5.5 (1)
C17	0.3538 (3)	0.6399 (3)	0.4654 (4)	5.4 (1)
C18	0.3998 (3)	0.6722 (4)	0.5532 (4)	6.9 (2)
C19	0.3715 (3)	0.7750 (3)	0.3666 (4)	3.9 (1)
C20	0.4311 (3)	0.7355 (4)	0.3089 (4)	6.3 (2)
C21	0.2740 (3)	0.6633 (3)	0.3200 (4)	5.5 (1)
C22	0.2285 (3)	0.7204 (4)	0.2494 (4)	6.7 (2)
C23	0.0711 (2)	0.4893 (3)	0.7980 (4)	4.3 (1)
C24	0.0439 (3)	0.4276 (3)	0.8730 (4)	5.5 (1)
C25	-0.0208 (3)	0.6066 (3)	0.8258 (4)	4.5 (1)
C26	0.0339 (3)	0.6644 (4)	0.8819 (4)	6.8 (2)
C27	0.0492 (3)	0.6028 (3)	0.6781 (4)	4.6 (1)
C28	0.0015 (3)	0.6702 (4)	0.6253 (4)	7.0 (2)
C29	-0.0525 (3)	0.4989 (3)	0.7029 (4)	4.7 (1)
C30	-0.0308 (4)	0.4316 (4)	0.6307 (4)	7.4 (2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter. Estimated standard deviations are given in parentheses.

Table V. Selected Bond Distances (Å) and Angles (deg) for I^a

Distances			
Fe-O1	1.975 (4)	Fe-O7	1.921 (4)
Fe-O3	1.976 (4)	Fe-N1	2.186 (5)
Fe-O5	1.973 (4)	Fe-N2	2.226 (4)
Angles			
O1-Fe-O3	98.8 (2)	O3-Fe-N2	88.8 (2)
O1-Fe-O5	89.2 (2)	O5-Fe-O7	100.0 (2)
O1-Fe-O7	102.2 (2)	O5-Fe-N1	89.6 (2)
O1-Fe-N1	77.6 (2)	O5-Fe-N2	79.1 (2)
O1-Fe-N2	156.5 (2)	O7-Fe-N1	170.4 (2)
O3-Fe-O5	165.0 (1)	O7-Fe-N2	100.0 (2)
O3-Fe-O7	90.8 (2)	N1-Fe-N2	81.9 (2)
O3-Fe-N1	79.8 (2)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

a Hewlett-Packard frequency counter (Model 5340A), and field measurements were made with a Systron Donner digital NMR gaussmeter (Model 3193). The data were collected on a Tracor Northern digital

Table VI. Selected Bond Distances (Å) and Angles (deg) for II^a

Distances			
Fe-O1	2.147 (2)	Fe-N1	2.341 (3)
Fe-O3	1.957 (2)	Fe-N2	2.317 (3)
Fe-O5	1.960 (3)	Fe-N3	2.362 (3)
Fe-O7	2.077 (2)		
Angles			
O1-Fe-O3	98.5 (1)	O5-Fe-O7	96.4 (1)
O1-Fe-O5	87.9 (1)	O5-Fe-N1	91.2 (1)
O1-Fe-O7	72.10 (9)	O5-Fe-N2	78.0 (1)
O1-Fe-N1	70.46 (9)	O5-Fe-N3	97.6 (1)
O1-Fe-N2	141.80 (9)	O7-Fe-N1	141.4 (1)
O1-Fe-N3	143.41 (9)	O7-Fe-N2	144.1 (1)
O3-Fe-O5	164.16 (9)	O7-Fe-N3	71.34 (9)
O3-Fe-O7	99.34 (9)	N1-Fe-N2	74.5 (1)
O3-Fe-N1	77.47 (9)	N1-Fe-N3	144.90 (9)
O3-Fe-N2	88.2 (1)	N2-Fe-N3	74.25 (9)
O3-Fe-N3	85.9 (1)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Selected Bond Distances (Å) and Angles (deg) for III^a

Distances			
Fe-O1	2.043 (3)	Fe-N1	2.421 (4)
Fe-O3	1.935 (3)	Fe-N2	2.318 (3)
Fe-O5	1.991 (3)	Fe-N3	2.385 (4)
Fe-O7	2.054 (3)		
Angles			
O1-Fe-O3	98.8 (1)	O5-Fe-O7	91.7 (1)
O1-Fe-O5	91.8 (1)	O5-Fe-N1	103.5 (1)
O1-Fe-O7	75.1 (1)	O5-Fe-N2	77.1 (1)
O1-Fe-N1	70.6 (1)	O5-Fe-N3	86.0 (1)
O1-Fe-N2	136.8 (1)	O7-Fe-N1	142.7 (1)
O1-Fe-N3	146.8 (1)	O7-Fe-N2	145.5 (1)
O3-Fe-O5	168.6 (1)	O7-Fe-N3	71.8 (1)
O3-Fe-O7	95.1 (1)	N1-Fe-N2	71.8 (1)
O3-Fe-N1	76.4 (1)	N1-Fe-N3	142.0 (1)
O3-Fe-N2	92.1 (1)	N2-Fe-N3	74.9 (1)
O3-Fe-N3	87.4 (1)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

signal averager (Model NS 570) and transferred to a computer for analysis.

Results and Discussion

The EPR spectra obtained for solutions of Fe^{III}DTPA as a function of pH are displayed in Figure 3. For comparison, the spectra of the oxidized form (treated with an equimolar amount of product hydroperoxide) of one isoenzyme of soybean lipoxygenase (P4) obtained at pH 7 and 9 are also presented. The striking feature of this EPR analysis is the *apparent* similarity of the low and high pH spectra of the model compound and the low and high pH spectra of the oxidized enzyme. As in the case of the enzyme, the EPR spectrum obtained for the DTPA complex depends critically on the pH at which the measurement was made. The spectrum for the complex at low pH is a clear example of a $g = 6$ axial signal with a large rhombic distortion³ originating from a compound that does not have a planar and/or cyclic ligand. Depending on the conditions of measurement, lipoxygenase can have two $g = 6$ forms with differing rhombic distortions.⁷ For the low pH form of Fe^{III}DTPA, the distortion from "pure axial" is strong enough to allow transitions from the other Kramers' doublets in the $S = 5/2$ multiplet. The high-pH spectrum with its $g = 4.3$ or purely rhombic signal is the expected result for non-heme iron in the high-spin state. These EPR observations prompted the following investigation of the structures of the complexes determined on crystals obtained from solutions at different pH values. A more detailed interpretation of the EPR (and Mössbauer) spectroscopy of the Fe^{III}DTPA complexes that includes matrix diagonalization of the 6×6 electronic spin Hamiltonian will be presented elsewhere.

Iron(III) forms three (at least) DTPA complexes, depending on solution pH. At low pH the [FeH₂DTPA] form is isolated

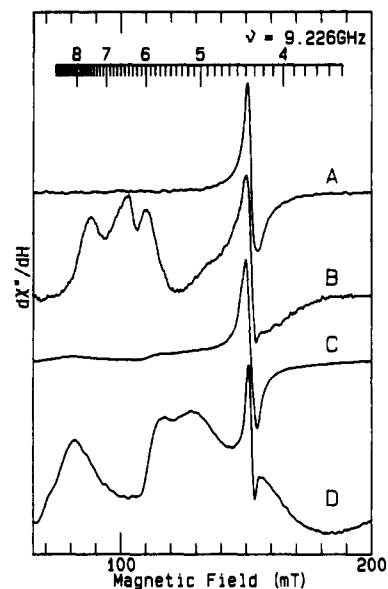


Figure 3. Low-temperature EPR spectra of lipoxygenase and Fe^{III}DTPA: (A) 800 μ M soybean lipoxygenase (P4) oxidized with 1.1X 13-hydroperoxy-9Z,11E-octadecadienoic acid, pH 9.5; (B) 800 μ M soybean lipoxygenase (P4) oxidized with 1.1X 13-hydroperoxy-9Z,11E-octadecadienoic acid, pH 6.5; (C) 2.5 mM Fe^{III}DTPA, pH 10, 50% glycerol; (D) 2.5 mM Fe^{III}DTPA, pH 3, 50% glycerol. The EPR running conditions were as follows: 40°K; microwave power, 5 mW; modulation amplitude, 1 mT; sweep time, 4 min. Scaling factors were chosen to make the vertical ranges the same for each spectrum.

as the crystalline dimer, [FeH₂DTPA]₂·2H₂O (I). At high pH the [FeDTPA]²⁻ form can be isolated as both the sodium salt dihydrate (II) or the tetraethylammonium salt tetrahydrate (III). The intermediate form, [FeHDTPA]⁻, has been previously isolated as Ba[FeHDTPA]ClO₄·4H₂O.¹⁴

The unusual neutral dimeric complex [FeH₂DTPA]₂ (Figure 1) lies on a crystallographic center of symmetry. One end of the DTPA ligand functions much like EDTA, attaching three carboxylate oxygen and two nitrogen atoms to one metal center. This leaves a pendant aminocarboxylate group free to bind to the second metal. The intramolecular iron center to iron center distance in the crystals is 8.061 Å. The iron environment, FeN₂O₄, in the dimers thus formed is pseudo-cis-octahedral. The distortion from octahedral is due to the constraints imposed by the formation of five-membered chelate rings with angles at iron of less than 90°. The cis configuration is also imposed by ligand constraints. We note that the pendant arm of the ligand is much less constrained and is thus able to move the carboxylate oxygen closer to the iron. The observed shortening of this Fe-O bond is 0.05 Å.

The structure of the deprotonated dianionic complex [FeDTPA]²⁻ is almost identical with that of the analogous monoanion. The iron atom is seven coordinate, FeN₃O₄, and the coordination polyhedron is a pentagonal bipyramid. The two axial atoms are oxygens, and the equatorial plane has a cis arrangement of oxygen atoms (Figure 2). As expected, the axial Fe-O bonds are shorter than the equatorial ones. The complex is formed by a most efficient wrapping of the ligand around the metal ion, only one of the carboxylate groups not realizing its potential as a ligand. Complete coordination of DTPA has only been previously observed with the larger Nd³⁺ ion.¹³

As expected from charge density arguments, the metal-ligand bond lengths in the six-coordinate species are shorter than those of the seven-coordinate analogues. A more subtle effect concerns the influence of the counterion on the bond lengths of the dianion. The Fe-O distances are longer in the sodium salt compared to the tetraethylammonium analogue, and the opposite is true for the Fe-N bonds. We attribute this to the polarization effect due to the closer approach of the Na⁺ ions to the exclusively monodentate carboxylate groups, whereas the Et₄N⁺ ions, which are larger with a more diffuse charge, would have a much smaller effect.

All of the present structures contain lattice water molecules. Most of these are strongly hydrogen bonded to either carboxylate groups or to other water molecules. Where no hydrogen bond exists, we were unable to locate the hydrogen atoms and the thermal parameters of the water oxygen atoms were significantly higher. One further consequence of the hydrogen bonding is the compactness of the crystal packing, as evidenced by the high values for the crystal densities.

In conclusion we find that iron(III) forms interesting complexes with the poly(aminocarboxylate) ligand DTPA as a function of solution pH. Further, the low-pH solution of Fe^{III}DTPA represents an example of an iron complex incorporating biologically relevant ligand atoms (N, O) that has some of the spectroscopic properties that are characteristic of the iron environment in lipoxigenases. In extending the present results to the enzyme, we hypothesize that the active form has a structure in the first-coordination sphere of the iron that is very similar to the low-pH form of Fe^{III}DTPA, while at high pH the axial component of the cis-octahedral coordination is reduced in magnitude, possibly by ligand addition as it is in the case of FeDTPA.

Acknowledgment. This research was supported financially by the National Science Foundation (Grant DMB-8713537).

Supplementary Material Available: For compounds I-III, text describing data collection and reduction and structure solution and refinement and tables giving crystallographic details, positional parameters, and bond distances and angles (64 pages); listings of structure factor amplitudes (39 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic and Magnetic Properties of a Unique Diamagnetic Binuclear μ -Oxo Vanadium(IV) Complex. Crystal Structure of $[(\text{tpa})\text{VO}(\mu\text{-O})\text{VO}(\text{tpa})](\text{ClO}_4)_2$ (tpa = Tris(2-pyridylmethyl)amine)

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Received October 16, 1990

Introduction

Oxo-bridged transition-metal complexes have received much attention in recent years, as these complexes may serve as structural models for metalloproteins involved in oxygen transport and oxygen metabolism.

Examples of homobinuclear single-oxo-bridged metal complexes are known for the first elements of the transition periods. Reviews covering the newer literature^{2,3} have been published. Although there are a few examples of single- μ -oxo binuclear vanadium complexes reported in the literature, there are no reports on mono(μ -oxo) vanadium(IV) complexes. Four binuclear V(III) systems have been reported.^{4,5} Mixed-valence IV,V systems

Table I. Crystallographic Data and Refinement Results for $[(\text{tpa})\text{VO}(\mu\text{-O})\text{VO}(\text{tpa})](\text{ClO}_4)_2$

formula	V ₂ C ₃₆ Cl ₂ H ₃₆ N ₈ O ₁₁	γ , deg	81.41 (3)
fw	929.53	V , Å ³	1935 (1)
space group	$P\bar{1}$	Z	2
T , K	110	λ , Å	0.710 73
a , Å	12.244 (6)	d_{calc} , g cm ⁻³	1.595
b , Å	12.299 (2)	μ , cm ⁻¹	6.75
c , Å	13.370 (2)	$R(F_o)$	0.037
α , deg	77.418 (13)	$R_w(F_o)$	0.044
β , deg	83.15 (2)		

having tripodal doubly or triply negatively charged ligands have been characterized.⁶⁻⁹ Binuclear vanadium(V) complexes of enolato¹⁰ or phenolato-based¹¹ ligands are known also. This paper reports the synthesis, physicochemical properties, and crystal structure of the first example of a diamagnetic mono(μ -oxo) vanadium(IV) complex. The nonbridging donor atoms are provided by the quadridentate tripodal ligand tris(2-pyridylmethyl)amine (tpa). The fact that this is a neutral ligand with good σ -donor properties seems to be essential for the stabilization of the V(IV) oxidation state in a binuclear structure.

Experimental Section

Syntheses. **Tris(2-pyridylmethyl)amine (tpa).** This ligand was prepared by the method described by Højland et al.¹⁵ The crude product was purified by recrystallization of the $\text{tpaH}_3(\text{ClO}_4)_3$ salt.

(μ -Oxo)bis{[tris(2-pyridylmethyl)amine]vanadyl(IV)} perchlorate. Tris(2-pyridiniummethyl)amine perchlorate (1.2 g, 2.0 mmol) was dissolved in a 1:1 mixture of acetonitrile and 0.5 M aqueous sodium hydroxide (24 mL). An aqueous solution of oxovanadium(IV) sulfate (10 mL, 0.2 M) was added with stirring at room temperature. The solution immediately turned dark purple and became strongly acidic. During 1 h an aqueous sodium hydroxide solution (1 mL, 1 M) was added dropwise with stirring. The reaction mixture yielded dark maroon crystals of the title compound over 18 h. The product was filtered out and dried in air. Yield: 0.73 g (78.6%). The crude product was recrystallized from a 1:2 mixture of acetone and water. Anal. Found: C, 42.66; H, 3.87; N, 10.98; Cl, 7.22. Calc for $[\text{V}_2\text{O}_3\text{C}_{36}\text{H}_{36}\text{N}_8](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$: C, 44.78; H, 4.17; N, 11.60; Cl, 7.34.

Physical Measurements. Infrared spectra were recorded on a Hitachi 270-30 infrared spectrophotometer, UV-visible absorption spectra on a Cary 219 spectrophotometer at room temperature, and ¹H NMR spectra on a Bruker 250-MHz spectrometer at room temperature in a 1:1 mixture of (CD₃)₂CO and D₂O. Magnetic susceptibilities were measured (at Monash University) down to liquid-helium temperature on an automated Faraday balance using a superconducting magnet.¹² The molar susceptibilities were corrected for ligand diamagnetism by using Pascal's constants. C, H, N, and Cl analyses were performed by the microanalytical laboratory at the H. C. Ørsted Institute, Copenhagen.

X-ray Crystallography. The compound forms compact crystals. Room-temperature Weissenberg photographs showed that they belong to the triclinic system. Low-temperature diffraction data were collected with an Enraf-Nonius CAD-4 diffractometer using Mo K α radiation obtained from a graphite monochromator. An Enraf-Nonius gas-flow low-temperature device was used to cool the crystal (0.15 \times 0.2 \times 0.2

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