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Contribution from the Department of Chemistry,
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Coordination Chemistry of Microbial Iron Transport Compounds. 26. Dimeric Dialkoxo-Bridged Iron(III) Complexes of Linear Dihydroxamate Ligands[1]

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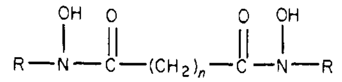
For a series of dihydroxamate ligands of the general formula $RN(OH)C({=}O)(CH_2)_nC({=}O)N(OH)R$ (H_2L) the dimeric complexes Fe_2L_3 contain pseudooctahedral tris(hydroxamato)iron(III) centers that are separated by many angstroms and are analogous to complexes of the microbial ferric ion chelating agent (siderophore) rhodotorulic acid. Certain of the synthetic Fe_2L_3 complexes display anomalous behavior in alcohol solutions, due to the formation of the μ-alkoxo-bridged species $Fe_2L_2(OR')_2$. Solution equilibria are reported for several such complexes as the ligand and alcohol are varied. Three of the alkoxo-bridged dimers were characterized in the solid state: **1** ($n = 5$, R = isopropyl, R' = CH_3); **2** ($n = 5$, R = phenyl, R' = CH_3); **3** ($n = 5$, R = phenyl, R' = CH_2CH_3). The coupling of the $S = {}^5/_2$ iron centers has been fit by using the Hamiltonian $\hat{H} = -2J\vec{S}_1\cdot\vec{S}_2$ to give values of J (esd) of −10.92 (4), −13.25 (3), and −12.16 (2) cm^{-1} for **1**–**3**, respectively. The structure of **1** has been determined by single-crystal X-ray diffraction. The space group is $P2_1/n$ with $Z = 2$, such that the center of the Fe_2O_2 dimer unit lies on a crystallographic inversion center (C_i symmetry). The approximate symmetry of the complex is C_{2h} and is composed of dihydroxamate ligands that span the two iron atoms, in addition to the μ-alkoxide bridges. The Fe–O distances average 2.002 (4) (alkoxide), 2.003 (2) (N–O), and 2.038 (8) Å (C–O). The O–Fe–O bond angles average 77.72 (4) (intra-ring) and 75.42 (5)° (alkoxide). The distortion of the FeO_6 centers from octahedral symmetry results in the three trans O–Fe–O angles 163.3, 165.6, and 158.3°. Red-orange monoclinic crystals of **1** have $a = 11.453$ (1) Å, $b = 14.986$ (2) Å, $c = 11.948$ (1) Å, $\beta = 119.046$ (8)°, and $V = 1792.8$ (7) Å^3. For two formula units of **1** per cell, d(calcd) = 1.32 and d(obsd) = 1.33 (3) g cm^{-3}. Of 4122 measured reflections, 3023 were used to refine 199 variables, with resultant standard and weighted agreement factors (on F) of $R = 2.7$ and $R_w = 3.9\%$.

Introduction

Rhodotorulic acid is a naturally occurring iron(III) chelating agent of microbial origin in which the two hydroxamate groups of this tetradentate ligand are separated by a maximum chain length extension of up to 10 Å.[2,3] We have prepared a series of analogous dihydroxamate ligands whose synthesis and general iron(III) coordination chemistry,[4] as well as use as synthetic analogues in studying microbial iron transport,[5] we report elsewhere. The general formula of these synthetic ligands is



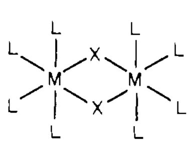
$$R-N(OH)-C({=}O)-(CH_2)_n-C({=}O)-N(OH)-R$$

L^1: R = isopropyl, $n = 5$
L^2: R = phenyl, $n = 5$

In the following text we will designate as H_2L the free acid form of these ligands. The particular dianion designated L^1 has five bridging methylene groups in the chain ($n = 5$) and terminal isopropyl groups (R = i-C_3H_7). For the ligand dianion L^2, $n = 5$ and R = phenyl.

In the process of characterizing the iron(III) complexes of the series of dihydroxamic acid ligands for which R = i-C_3H_7 and n = 3–6, 8, and 10, it was found that compounds of stoichiometry $Fe_2L_3{\cdot}H_2O$ may be isolated from aqueous solutions containing the ratio Fe^{3+}:L of 2:3.[4] The compounds are dimeric in solution and appear to be polymeric in the solid state. Their physical properties are typical of ferric tris(hydroxamato) complexes such as that formed by rhodotorulic acid itself.[3] Upon dissolution in methanol, however, the iron complex with ligand L^1 ($n = 5$, R = isopropyl) exhibits anomalous spectroscopic and magnetic properties. All efforts to isolate the anomalous species from methanol solutions containing the ratio Fe^{3+}:L of 2:3 led ultimately to the tris(hydroxamato) complex $Fe_2(L^1)_3{\cdot}H_2O$. This paper describes the isolation and X-ray crystal structure of the dimeric methoxy-bridged iron(III) complex $Fe_2(L^1)_2(\mu\text{-}OCH_3)_2$, as well as the synthesis of the related complexes $Fe_2(L^2)_2(\mu\text{-}OCH_3)_2$ and $Fe_2(L^2)_2(\mu\text{-}OCH_2CH_3)_2$, and the temperature-dependent magnetic properties of these compounds. The solution chemistry of these unusual dimeric compounds, which are stable over only a narrow range of conditions, has been explored as a function of the bridging alkoxide group's basicity.

The fundamental property of spin exchange[6] in multinuclear complexes containing more than one paramagnetic center has been explored in detail[7-20] in dimeric complexes of the type



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In particular, there has been extensive study of the structural and magnetic properties of bridged Cu(II) dimers,[9,21-25] in which a linear correlation between the coupling constant J and the Cu–O–Cu bridge angle has been reported. The value of J has also been found to be correlated with the electron density at the bridging oxygen atoms. Molecular orbital analysis is in agreement with these observations.[26] In contrast, the origin of the variations of J with these parameters in weakly antiferromagnetically coupled Fe(III) dimers has remained unknown.[11-19]

We report here the comparative magnetic behavior of the dimeric, alkoxo-bridged, dihydroxamate ferric complexes $Fe_2(L^1)_2(\mu\text{-}OCH_3)_2$ (**1**), $Fe_2(L^2)_2(\mu\text{-}OCH_3)_2$ (**2**), and $Fe_2(L^2)_2(\mu\text{-}OCH_2CH_3)_2$ (**3**). The detailed crystal and molecular structure of the first member of this series, **1**, is described. A preliminary account of portions of this study has been communicated.[27]

Experimental Section

Infrared spectra were obtained as KBr pellets with a Perkin-Elmer 597 spectrophotometer. Mössbauer spectra were measured by Professor B. H. Huynh, Emory University, using the procedure described elsewhere.[28] Visible spectra were recorded by using a Hewlett-Packard 8450A UV/vis spectrophotometer. Melting points were taken in open capillaries with a Mel-Temp apparatus and are uncorrected. Microanalyses were performed by Analytical Services, Chemistry Department, University of California, Berkeley.

Preparation of Compounds. The pimelyl bis(*N*-isopropyl- and pimelyl bis(*N*-phenylhydroxamic acids) were prepared using the method of Smith and Raymond.[29] The μ-alkoxo-bridged complexes of these ligands were prepared by using stoichiometric amounts of $Fe(NO_3)_3\cdot 9H_2O$ and ligand (Fe:L = 1:1) with the appropriate alcohol as solvent. The apparent pH (from a glass electrode calibrated to aqueous buffers) was adjusted to ~7–8 by using methanolic KOH or NaOH. The methoxo-bridged complex with pimelyl bis-*N*-isopropyl hydroxamic acid was isolated by precipitation of KNO_3 from the methanol solution using diethyl ether and concentration of the solution in vacuo to obtain the microcrystalline, analytically pure product. The methoxo- and ethoxo-bridged complexes with pimelyl bis(*N*-phenylhydroxamic acid) precipitated directly from the alcoholic solutions as (apparently pure) crystalline solids when the pH was raised to ~7–8 with methanolic or ethanolic NaOH. These compounds were not purified further due to their low solubility in alcoholic solutions.

Table I. Crystallographic Summary for $Fe_2(L^1)_2(\mu\text{-}OCH_3)_2$ (1)

mol formula	$C_{28}H_{54}Fe_2N_4O_{10}$
space group	$P2_1/n$[a] (No. 14)
fw	718.46
cell const	
a, Å	11.453 (1)
b, Å	14.986 (2)
c, Å	11.948 (1)
β, deg	119.046 (8)
V, Å^3	1792.8 (7)
Z	2
2θ range for cell constants, deg	23.6–26.8[b]
d(obsd), g cm^{-3}	1.33 (3)[c]
d(calcd), g cm^{-3}	1.32
syst reflcn absences	$0k0, k = 2n + 1$; $h0l, h + l = 2h + 1$
$F(000)$	764 electrons
p	0.035
2θ range for data collcn, deg	3.0–55.0
total reflcns measd	4122
data crystal dimens, mm	0.14 × 0.20 × 0.38
abs coeff[d] (μ(Mo Kα)), cm^{-1}	8.60

[a] Nonstandard setting of space group $P2_1/c$ with equivalent positions $\pm(x, y, z)$ and $\pm(^1/_2 - x, ^1/_2 + y, ^1/_2 - z)$. [b] A total of 6 sets of 4 reflections per set were related by Laue symmetry $2/m$. [c] Flotation in a mixture of CCl_4/heptane. [d] Examination of reflections with $\chi = 90 \pm 10°$ at approximately regular intervals ($5° < \Delta 2\theta < 10°$) within the 2θ range of data collection by the χ-scan technique gave normalized transmission factors for the data crystal of 0.98–1.00; hence, an absorption correction was not applied to these data.

Table II. Fractional Coordinates of Non-Hydrogen Atoms of **1**[a]

atom	x	y	z
Fe	−0.00235 (2)	0.10482 (2)	0.01573 (2)
O(1)	−0.0514 (1)	0.17956 (9)	0.1256 (1)
O(2)	0.1756 (1)	0.11468 (9)	0.1821 (1)
O(3)	0.0364 (1)	0.19810 (9)	−0.0820 (1)
O(4)	−0.1851 (1)	0.12649 (9)	−0.1370 (1)
O(5)	−0.0730 (1)	−0.00871 (8)	0.0475 (1)
N(1)	0.0473 (1)	0.1796 (1)	0.2504 (1)
N(2)	−0.0666 (1)	0.2035 (1)	−0.2058 (1)
C(1)	0.1637 (2)	0.1460 (1)	0.2752 (1)
C(2)	−0.1801 (2)	0.1655 (1)	−0.2290 (1)
C(3)	−0.1975 (2)	−0.0144 (2)	0.0442 (2)
C(4)	0.0096 (2)	0.2169 (1)	0.3418 (2)
C(5)	−0.0298 (2)	0.3139 (2)	0.3111 (2)
C(6)	−0.0998 (2)	0.1607 (2)	0.3414 (2)
C(7)	−0.0316 (2)	0.2481 (1)	−0.2951 (2)
C(8)	0.0772 (2)	0.1957 (2)	−0.3026 (2)
C(9)	0.0085 (2)	0.3439 (2)	−0.2554 (2)
C(10)	0.2795 (2)	0.1415 (1)	0.4097 (2)
C(11)	0.2638 (2)	0.0683 (1)	0.4910 (2)
C(12)	0.2260 (2)	−0.0235 (1)	0.4281 (2)
C(13)	0.3332 (2)	−0.0654 (1)	0.4049 (2)
C(14)	0.3018 (2)	−0.1622 (1)	0.3589 (2)

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 3 for identity of the atoms.

$Fe_2(L^1)_2(\mu\text{-}OCH_3)_2$ (**1**): IR (ν, cm^{-1}) 2807 (C—H, OCH_3), 1564 (C═O), in the deuterated complex 2050 (C-D, OCD_3; calcd 2059); mp 233 °C dec; yield 95%. Anal. Calcd for $Fe_2(C_{13}H_{24}N_2O_4)_2(OCH_3)_2$: C, 46.80; H, 7.52; N, 7.80; Fe, 15.60. Found: C, 46.77; H, 7.52; N, 7.76; Fe, 15.7.

$Fe_2(L^2)_2(\mu\text{-}OCH_3)_2$ (**2**): IR (ν, cm^{-1}) 2804 (C—H, OCH_3), 1540 (br, C═O); mp 227 °C dec; yield 96%. Anal. Calcd for $Fe_2(C_{19}H_{20}N_2O_4)_2(OCH_3)_2\cdot H_2O$: C, 55.05; H, 5.28, N, 6.42; Fe, 13.08. Found: C, 55.15; H, 5.45; N, 6.34; Fe, 12.8.

$Fe_2(L^2)_2(\mu\text{-}OC_2H_5)_2$ (**3**): IR (ν, cm^{-1}) 2860 (C—H) 1540 (br, C═O); mp 198 °C dec; yield 98%. Anal. Calcd for $Fe_2(C_{19}H_{20}N_2O_4)_2(OC_2H_5)_2$: C, 57.14; H, 5.67; N, 6.35; Fe, 12.7. Found: C, 56.97; H, 5.88; N, 6.26; Fe, 12.4.

Magnetic Susceptibility Measurements. Temperature-dependent magnetic susceptibility measurements were made with a S.H.E. Model 805 variable-temperature susceptometer (capable of a maximum field

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strength of 50 kG) in conjunction with a S.H.E. Model 868 susceptometer control system. The powdered samples were contained in sample holders machined from high-purity aluminum (with 3% Si; Varian) or Kel-F. Susceptibility measurements were recorded over the temperature range 5–300 K at a field strength of 10 kG. Diamagnetic corrections for these compounds were calculated by using Pascal's constants. The susceptibility data were analyzed by using a general least-squares program (ORGLS, obtained from Oak Ridge National Laboratory) that minimized the sums of $(\mu_{eff}(\text{obsd})^2 - \mu_{eff}(\text{calcd})^2)^2$ or $(\chi_g(\text{obsd}) - \chi_g(\text{calcd}))^2$, as described.

X-ray Crystallography. Excellent single crystals of **1** form from methanol solution at room temperature as red-orange plates. Due to its moisture sensitivity, a well-formed crystal was wedged into a thin-walled capillary and then examined by precession photography. This established the space group as $P2_1/n$.[30,31] Crystal data and those variables of data collection,[32] which are relevant to this study, are summarized in Table I. The structure was solved by standard heavy-atom procedures and refined by full-matrix least-squares methods using only reflections with $F_o^2 > 3\sigma(F_o^2)$, as described previously.[32] The least-squares refinement, in which non-hydrogen atoms were treated anisotropically, converged with $R = 2.7$ and $R_w = 3.9\%$, with an error in an observation of unit weight of 1.49[33] for 3023 observations[34] and 199 variables. The hydrogen atoms were located from a difference Fourier map (at densities of 0.3–0.7 e Å^{-3}) and were fixed at idealized positions during the concluding cycles of refinement.[35] In the final cycle of refinement no shift in a parameter exceeded 0.70 of its estimated standard deviation. The largest peaks on a final difference Fourier were 0.3–0.4 e Å^{-3} and were associated with the carbon atom of the bridging methoxide group. Comparison of F_o vs. F_c as a function of the magnitude of F_o, setting angle, and Miller index showed minor disagreement among only the very weak reflections. Positional parameters with esd's as derived from the least-squares inverse matrix are given in Table II; anisotropic thermal parameters (with esd's) (Table III), hydrogen atom parameters (Table IV), and observed and calculated structure factor amplitudes (Table V) are available.[36]

Results and Discussion

The anomalous behavior of the ferric complex of ligand L^1 upon dissolution in methanol has been discussed in part elsewhere.[4,27] The quadrupole doublet observed at 4.2 K in the Mössbauer spectrum and the extremely weak EPR signal, along with the reduced magnetic moment observed in methanol solution, provided strong evidence for the formation of a μ-methoxo-bridged species. This suggested a reaction between the tris(hydroxamato) complex and the methanol solvent (eq 1). Formation of the μ-dimethoxo complex is also consistent

$$Fe_2L_3 + 2CH_3OH \rightleftharpoons Fe_2L_2(\mu\text{-}OCH_3)_2 + LH_2 \quad (1)$$

with the reduced extinction coefficient of ~2000 M^{-1} cm^{-1} (λ_{max} 414 nm), characteristic of two, rather than three, hydroxamate moieties bound per ferric ion.[4] Due to the stability of ferric tris(hydroxamato) complexes, reaction 1 is unexpected, especially at neutral pH; this is the first time that such behavior has been reported.

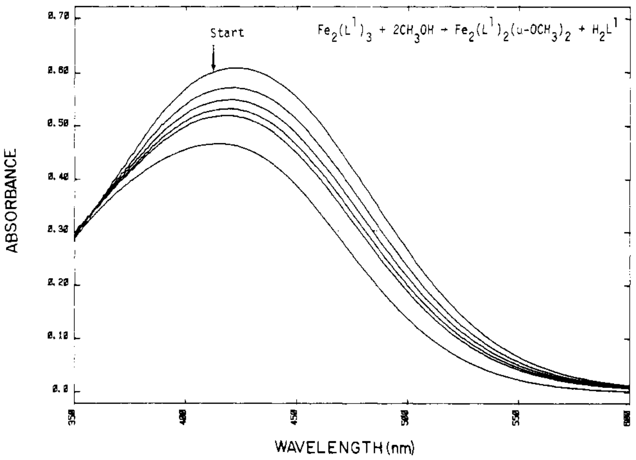

Figure 1. Spectral changes with time for $Fe_2(L^1)_3$ ($n = 5$) in 2-propanol as CH_3OH is added. Spectra are recorded every 20 min and, ultimately, after 20 h.

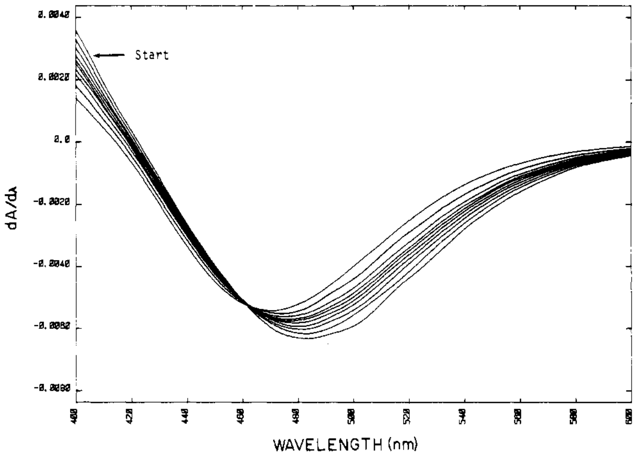

Figure 2. Derivative spectra (of those spectra shown in Figure 1) plotted every 10 min for $Fe_2(L)_3 + CH_3OH$.

The visible spectrum of the $Fe_2(L^1)_3$ complex in 2-propanol is characteristic of a simple tris(hydroxamato) complex (Fe_2L_3, λ_{max} 424 nm, ϵ 3000 M^{-1} cm^{-1} per Fe^{3+}), indicating that the μ-isopropoxo-bridged species does not form. Dilution of the 2-propanol solution with methanol produces a gradual shift in the λ_{max} to higher energies, accompanied by a decrease in extinction coefficient, until ultimately the spectrum is that of the bis(hydroxamato) μ-dimethoxo complex. Figure 1 shows the spectral changes as a function of time for dilution of a 2-propanol solution of $Fe_2(L^1)_3$ by 50% with methanol. The spectrum at $t = 0$ s is of a solution of $Fe_2(L^1)_3$ in 2-propanol, which is of identical Fe^{3+} concentration as the solution in 50% methanol/2-propanol. The spectra are recorded every 20 min, and finally after 20 h. Figure 2 shows the derivative spectra for this reaction plotted every 10 min. The presence of the isosbestic point indicates that there are two absorbing species in solution, $Fe_2(L^1)_3$ and $Fe_2(L^1)_2(\mu\text{-}OMe)_2$, consistent with reaction 1. This behavior is not observed for the other ligands in the series.

With the identity of the anomalous species reasonably established, it was possible to isolate it in the solid state. Previous attempts to obtain this complex as a solid led ultimately to $Fe_2(L^1)_3 \cdot H_2O$ due to equilibrium 1 and the presence of an additional equivalent of ligand. In the absence of excess ligand (Fe:L = 1:1) the μ-dimethoxo-bridged diiron complex $Fe_2(L^1)_2(\mu\text{-}OCH_3)_2$ (**1**) may be isolated from methanol solution in quantitative yield.

The infrared spectrum of **1** shows a medium-intensity band at 2807 cm^{-1}. This band, which is absent in the tris(hydroxamato) complex, $Fe_2(L^1)_3$, shifts to 2050 cm^{-1} when **1** is

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(30) An alternate setting of space group $P2_1/c$ with equivalent positions $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$.

(31) Preliminary study of intense, low-angle ($2\theta \leq 17°$) reflections from this crystal with an Enraf-Nonius CAD 4 automated diffractometer confirmed this symmetry and indicated that the crystal had good mosaic character; the peak widths at half-height, as determined by ω scans with a receiving aperature of 1 mm were 0.14–0.18° and thus were satisfactorily narrow. After accurately centering 24 high-angle reflections chosen from diverse regions of reciprocal space, intensity data were gathered as previously reported.[32]

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(33) The function minimized in refinement is $\sum w(F_o - F_c)^2$, where the weight w is $4F_o^2/\sigma(F_o^2)$. The error indices R and R_w and the standard deviation in an observation of unit weight are defined in ref 32.

(34) Reflection 10$\bar{1}$ appeared to be affected by secondary extinction ($F_o/F_c = 0.8$) and therefore was excluded from the final cycles of refinement.

(35) The C–H distances were constrained to 0.95 Å in accordance with a previous study: Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213. Hydrogen atoms were assigned fixed thermal parameters of 5.0 Å^2.

(36) See paragraph at end of paper regarding supplementary material.

prepared in deuterated methanol and thus is assigned as the symmetric C–H stretching mode of the μ-methoxo group. The deuterated complex also shows a weak absorbance at 2200 cm^{-1}, possibly due to the asymmetric methyl stretching mode (obscured in the OCH_3 complex by the aliphatic C–H stretching modes of the dihydroxamate ligand). These values are in agreement with those reported recently for the dimeric complex $Pd_2(\mu\text{-}OCH_3)_2(F_6acac)_2$:[37] $\nu_s(\text{C–H}) = 2830\ cm^{-1}$, $\nu_s(\text{C–D}) = 2070\ cm^{-1}$; $\nu_a(\text{C–D}) = 2320\ cm^{-1}$. The X-ray crystal structure of **1** provided the final conclusive evidence necessary to establish its identity.

Similar behavior is observed when a 2-propanol solution of $Fe_2(L^1)_3$ is diluted with ethanol. However, the final λ_{max} is unshifted (424 nm), and only a decrease in extinction coefficient (to $\epsilon \sim 2200\ M^{-1}\ cm^{-1}$ per Fe^{3+}) is observed. It is possible that the ethoxo-bridged species does not form to an appreciable extent due to the higher pK_a of ethanol (18[38] vs. pK_a(MeOH) = 16[39]). To lend support to this hypothesis, a 2-propanol solution of the $Fe_2(L^1)_3$ complex in 2-propanol was diluted by 50% with benzyl alcohol. It has been shown[40] that benzyl alcohol is of comparable acidity to methanol in 2-propanol solution, with both being more acidic than ethanol (K_e = 0.95 (EtOH), 3.8 (BzOH), 4.0 (MeOH), where for HA + $i\text{-PrO}^-$ = A^- + i-PrOH, $K_e = [A^-]/[HA][i\text{-PrO}^-]$. Therefore, the $\mu\text{-}OCH_2C_6H_5$ complex would be expected to form. Dilution of a 2-propanol solution of the $n = 5$ complex with benzyl alcohol causes λ_{max} to shift slowly to lower energy with a decrease in extinction coefficient, until a final value of 444 nm ($\epsilon \sim 1900\ M^{-1}\ cm^{-1}$, consistent with two hydroxamate groups bound per ferric ion) is obtained after approximately 24 h. Isosbestic behavior is observed in the derivative spectra during the course of the reaction, indicating that there are only two absorbing species in solution. No change in absorption spectrum is observed when a 2-propanol solution of the $n = 10$ complex is diluted by 50% with benzyl alcohol.

The EPR spectrum of the $n = 5$ complex in i-PrOH ($[Fe^{3+}]$ = 0.2 mM) exhibits a broad absorbance at $g = 4.3$, whereas no signal is observed for the solution of the same concentration with 50% benzyl alcohol. This also suggests that the $\mu\text{-}OCH_2C_6H_5$ complex forms to an appreciable extent. When 2-propanol solutions of both the $n = 5$ and $n = 10$ $Fe(L^1)_3$ complexes are diluted with trifluoroethanol, a small decrease in extinction coefficient is observed (accompanied by a slight shift, less than 4 nm, in the absorbance maximum to lower energy). This suggests simple protonation of the ferric tris(hydroxamato) complexes by the much stronger acid, trifluoroethanol, to form a small amount of bis(hydroxamato) complexes, FeL^+.

There is no evidence for the formation of hydroxo-bridged species with the $n = 5$ ligand in aqueous solutions containing ferric ion. The μ-dialkoxo-bridged ferric complexes are moisture sensitive, presumably because they yield $Fe_2(L^1)_3$ and various hydrolyzed species. Such behavior has also been observed for μ-dialkoxo-bridged ferric complexes of acetylacetonate.[16]

Although the μ-diethoxo ferric complex could not be isolated with ligand L^1, it was readily obtained by using pimelyl bis(*N*-phenylhydroxamic acid) (L^2). In fact, both the μ-dimethoxo and μ-diethoxo complexes precipitate from the alcoholic solutions even when the ratio Fe:L^2 is 2:3. This is presumably due to the much lower solubility of these complexes, which drives the equilibrium in eq 1 to the right. Ghosh and Sarkar[41] have also studied the coordination chemistry of pimelyl bis(*N*-phenylhydroxamic acid) with ferric ion. The complex that they reported was prepared in ethanolic solution (Fe:L = 1:2) and deposited as magenta red crystals. The elemental analysis that they obtained is consistent with a reported stoichiometry of $Fe_2L(LH)_2(OH)_2(OH_2)_2 \cdot 2.5H_2O$: N, 6.94 (required 6.73); Fe, 8.94 (required 8.94). The 2.5 mol of H_2O reportedly could be removed by heating to 110 °C. In contrast, none of the Fe_2L_3 ferric bis(*N*-phenylhydroxamato) complexes that have been prepared by us (for n = 4, 6, 8, 10) is crystalline or exhibits the limited solubility properties of the $n = 5$ complex. Thus, although their elemental analyses and magnetic susceptibility measurements would seem to be inconsistent with this formulation (the μ_{eff} is reported to be 5.95 μ_B at room temperature), the complex that Ghosh and Sarkar isolated may have been the ethoxo-bridged dihydroxamate complex.

Table VI. Bond Lengths (Å) and Bond Angles (deg) for **1**[a]

Fe–O(1)	2.002 (1)	N(2)–C(7)	1.471 (2)
Fe–O(2)	2.048 (1)	C(1)–C(10)	1.509 (2)
Fe–O(3)	2.004 (1)	C(2)–C(14)′	1.501 (2)
Fe–O(4)	2.027 (1)	C(4)–C(5)	1.513 (2)
Fe–O(5)	1.998 (1)	C(4)–C(6)	1.508 (2)
Fe–O(5)′	2.006 (1)	C(7)–C(8)	1.512 (3)
Fe· · ·Fe′	3.168 (1)	C(7)–C(9)	1.512 (3)
O(1)–N(1)	1.366 (1)	C(10)–C(11)	1.533 (2)
O(2)–C(1)	1.274 (2)	C(11)–C(12)	1.526 (2)
O(3)–N(2)	1.376 (1)	C(12)–C(13)	1.519 (2)
O(4)–C(2)	1.270 (2)	C(13)–C(14)	1.532 (2)
O(5)–C(3)	1.409 (2)	O(1)· · ·O(2)	2.541 (1)
N(1)–C(1)	1.317 (2)	O(3)· · ·O(4)	2.529 (1)
N(2)–C(2)	1.319 (2)	O(5)· · ·O(5)′	2.449 (2)
O(1)–Fe–O(2)	77.71 (4)	O(1)–N(1)–C(1)	117.1 (1)
O(3)–Fe–O(4)	77.73 (4)	O(1)–N(1)–C(4)	115.3 (1)
O(5)–Fe–O(5)′	75.42 (5)	C(1)–N(1)–C(4)	127.6 (1)
O(1)–Fe–O(5)′	163.26 (4)	O(2)–C(1)–N(1)	118.0 (1)
O(2)–Fe–O(4)	165.59 (5)	O(2)–C(1)–C(10)	120.1 (1)
O(3)–Fe–O(5)	158.31 (4)	N(1)–C(1)–C(10)	121.8 (1)
Fe–O(5)–Fe′	104.58 (5)	O(3)–N(2)–C(2)	116.3 (1)
O(3)–N(2)–C(7)	114.4 (1)	O(4)–C(2)–C(14)′	118.0 (1)
C(2)–N(2)–C(7)	129.2 (1)	N(2)–C(2)–C(14)′	123.8 (1)
O(4)–C(2)–N(2)	118.1 (1)		

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 3 for identity of the atoms. Coordinates of primed atom symbols are related to those of unprimed symbols of Table II by the operation $\bar{x}, \bar{y}, \bar{z}$.

Table VII. Deviations of Pseudosymmetrically Related Atoms from C_{2h} Symmetry[a]

atom 1	atom 1′[b]	dev, Å	atom 1	atom 1′[b]	dev, Å
Fe	Fe	0.14	C(10)	C(14)′	0.07
O(1)	O(3)	0.09	C(5)	C(9)	0.17
O(2)	O(4)	0.12	C(6)	C(8)	0.21
O(5)	O(5)′	0.19	C(11)	C(13)′	0.98
N(1)	N(2)	0.03	C(12)	C(12)′	0.59
C(1)	C(2)	0.07			0.22[c]
C(3)	C(3)′	0.13			0.34[d]
C(4)	C(7)	0.13			

[a] Deviations were obtained by an iterative procedure using the program BMFIT (Liu, L. K. Ph.D. Dissertation, University of Texas, Austin, 1977) and are presented as absolute values. [b] See Figure 3 for the identity of the atoms. Atom 1′ is the atom related by pseudo-C_2 symmetry to atom 1. [c] Mean deviation; given by $\Sigma_i \Delta d_i/n$, where Δd_i is the minimized distance between atom 1 and atom 1′ and n is the number of pseudosymmetrically related atom pairs. [d] Rms deviation; obtained from $[\Sigma_i(\Delta d_i)^2/n]^{1/2}$.

X-ray Crystallography. The molecules are arranged in an approximately face-centered fashion about the inversion centers of (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$), with non-hydrogen atom contacts of ~3.75 Å. Figure 3 is a stereoscopic view of the structure of **1**. A listing of selected interatomic distances and angles is presented in Table VI. As shown in Figure 3, **1** is dimeric

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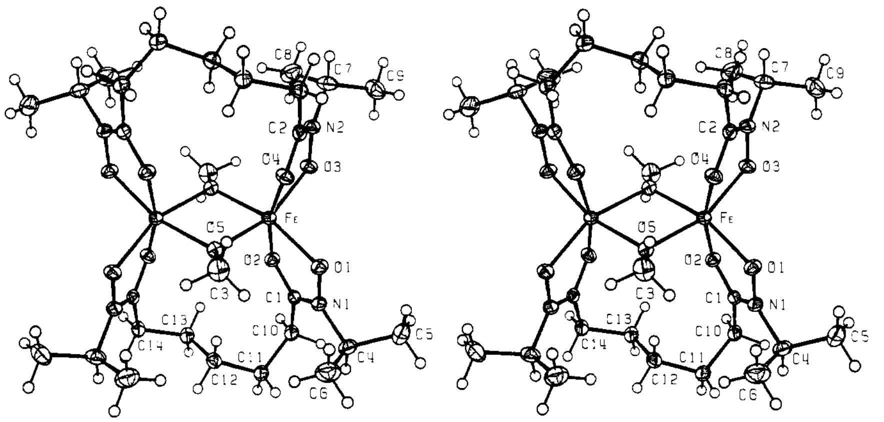

Figure 3. Stereoscopic view of the structure of $Fe_2(L^1)_2(\mu\text{-}OCH_3)_2$ ($n = 5$) (**1**) illustrating the atom-numbering scheme used herein. Atoms are drawn as ellipsoids of 30% probability; hydrogen atoms are shown as spheres of radius 0.1 Å.

and possesses rigorous C_i symmetry, although, as shown in Table VII, the approximate symmetry of the molecule is C_{2h}. The two tetradentate hydroxamate ligands bridge the two Fe^{3+} ions so that the two carbonyl oxygen atoms [O(2) and O(4)] occupy opposite positions in the Fe^{3+} coordination sphere; hence, **1** is analogous to the trans isomer of tris(hydroxamato) complexes.[42] The coordination geometry of the two Fe^{3+} ions is completed by the two methoxide oxygen atoms [O(5)] that form a nearly symmetric bridge between the metal ions [1.999 (1) and 2.006 (1) Å]. The Fe···Fe′ distance is 3.168 (1) Å, and the Fe–O(5)–Fe′ angle is 104.58 (5)°, parameters that are consistent with the weak antiferromagnetic coupling noted in this (see below) and other complexes containing the Fe_2O_2 structural unit.[20]

Magnetic Susceptibility Measurements. Solid-state, temperature-dependent magnetic susceptbility measurements were made on complexes **1**–**3** to determine what effect the nature of the ligands (alkoxide and hydroxamate) would have on the magnitude of the coupling constant (J) in these systems. The spin Hamiltonian $\tilde{H} = -2J\tilde{S}_1 \cdot \tilde{S}_2$ yields for a spin ${}^5/_2$ system such as Fe^{3+} (high spin), with $g = 2.00$ and TIP = 0, the relationship[6]

$$\mu_{\text{eff}}^2 = \frac{12.001(55 + 30z^{10} + 14z^{18} + 5z^{24} + z^{28})}{11 + 9z^{10} + 7z^{18} + 5z^{24} + 3z^{28} + z^{30}} \qquad (2)$$

where μ_{eff}^2 is calculated per metal ion and $z = \exp(-J/kT)$.

The susceptibility data for complexes **1**–**3** were fit to eq 2 by using the general nonlinear least-squares program mentioned earlier. Since the susceptibility data vs. temperature curves for complexes **2** and **3** revealed the presence of a small amount of paramagnetic impurity, only the data at higher temperatures (150–300 K) were fit to eq 2 to obtain initial estimates of the coupling constant J. There was no indication of any significant amount of impurity in complex **1**, and a good fit to eq 2 was obtained with $J = -10.92$ (4) cm^{-1}. The susceptibility data for **1** are presented as plots of μ_{eff} and χ_M' vs. temperature in Figure 4. The solid curve through the μ_{eff} data points represents the calculated values with $J = -10.92$ cm^{-1}. The J values obtained from the high-temperature data of complexes **2** and **3** are -13.57 and -12.05 cm^{-1}, respectively.

Correction for the small amount of paramagnetic impurity present in compounds **2** and **3** was achieved by using a method similar to that outlined by Ginsberg.[43] The impurity was assumed to have a molecular weight of approximately 400 (similar to that of the μ-dialkoxo-bridged complexes, calculated on the basis of one ferric ion) and to obey the Curie law ($\chi = C/T$). The gram-susceptibility of the dimer plus impurity is thus given by

$$\chi_g = \frac{4.3768(1-\alpha)}{(\text{mol wt})_{\text{imp}}T} + \alpha\left[\frac{1.5014(55 + 30z^{10} + 14z^{18} + 5z^{24} + z^{28})}{T(\text{mol wt})_{\text{d}}(11 + 9z^{10} + 7z^{18} + 5z^{24} + 3z^{28} + z^{30})} + \frac{\chi_{\text{dia}}}{(\text{mol wt})_{\text{d}}}\right] \qquad (3)$$

where (mol wt)$_{\text{imp}}$ and (mol wt)$_{\text{d}}$ are the molecular weights of the impurity and the dimer, respectively, χ_{dia} is the diamagnetic correction for the μ-dialkoxo-bridged dimer, and α is the weight fraction of dimer.

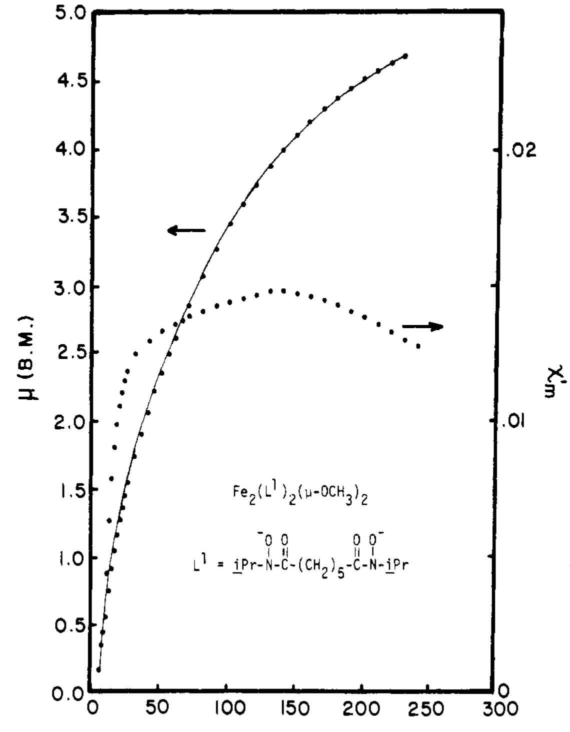

Figure 4. Susceptibility data vs. temperature for measurements made at 10 kG for $Fe_2(L^1)_2(\mu\text{-}OCH_3)_2$. The solid curve corresponds to the least-squares fit of the data with $J = -10.92$ cm^{-1}.

The J values obtained for complexes **2** and **3** by least-squares fitting of the susceptibility data to eq 3 were -13.25 (3) and -12.16 (2) cm^{-1} with $\alpha = 0.0030$ (1) and 0.0005 (1), respectively. That is, the estimated percentages, by weight, of

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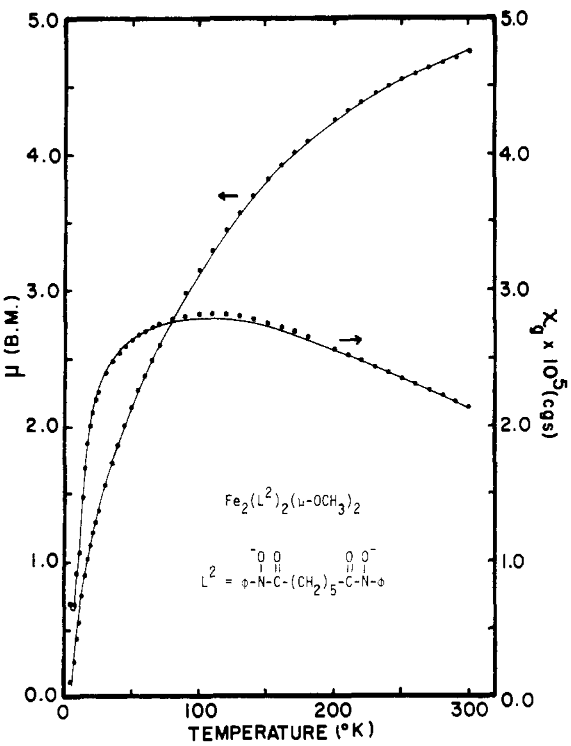

Figure 5. Susceptibility data vs. temperature for measurements made at 10 kG for $Fe_2(L^2)_2(\mu\text{-}OCH_3)_2$. The solid curves correspond to the least-squares fit of the data with $J = -13.25$ cm^{-1} and are corrected for 0.30% by weight of paramagnetic impurity.

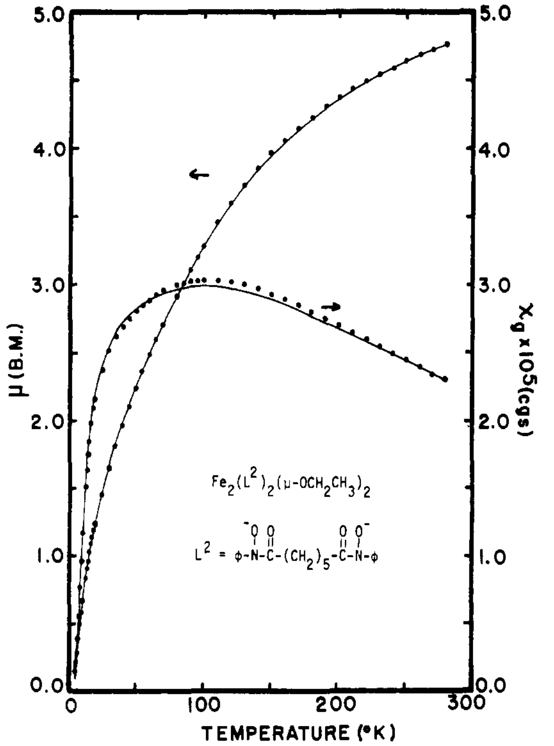

Figure 6. Susceptibility data vs. temperature for measurements made at 10 kG for $Fe_2(L^2)_2(\mu\text{-}OCH_2CH_3)_2$. The solid curves correspond to the least-squares fit of the data with $J = -12.06$ cm^{-1} and are corrected for 0.05% by weight of paramagnetic impurity.

the paramagnetic impurity are 0.3 and 0.05% for **2** and **3**, respectively. These values are in excellent agreement with the estimates obtained by using the uncorrected high-temperature susceptibility data for these complexes. Although refining on μ^2 in one case and χ in another in principle constitutes a change in weighting of the least-squares refinement, no significant difference was observed due to this change in procedure. Figures 5 and 6 show the susceptibility data plotted as μ_{eff} and χ_g vs. temperature for complexes **2** and **3**. The solid curves through the data points correspond to the theoretical values obtained from the least-squares fit. The measured and calculated susceptibilities for **1**–**3** (Tables VIII-X) are available.[36]

Chiari et al.[19] have recently published a summary of the magnetic and structural properties of the few iron(III) complexes containing four-membered iron–oxygen rings that have been characterized by X-ray diffraction. They note that the Fe–O–Fe bridging angle does not appear to play an important role in determining the extent of antiferromagnetic coupling in dihydroxo- and dialkoxo-bridged complexes of Fe(III). They also suggest that the degree of magnetic interaction is dependent upon the electron density at the bridging oxygen since $|J|$ is greater for the alkoxo- than the hydroxo- and phenoxo-bridged complexes. However, there are several other alkoxo-bridged complexes[15] that have not been structurally characterized but have J values (-8.5 to -11.0 cm^{-1}) comparable to those in complex **1**. It has been postulated[44] that the antiferromagnetic interaction in dialkoxo- and dihydroxo-bridged Fe(III) dimers is characterized only by the nature of the Fe_2O_2 structural unit and is relatively insensitive to the nature of the substituents on the bridging oxygens and the nonbridging ligands. The magnitude of the coupling constants ($|J|$) for complexes **1**–**3** increases in the order **1** < **3** < **2**. The increase in $|J|$ observed when R is the more electron-withdrawing phenyl group instead of isopropyl parallels that observed in the chromium complexes $[Cr(3\text{-}Br\text{-}acac)_2OMe]_2$ ($J = -3.55$ cm^{-1}) and $[Cr(3\text{-}Cl\text{-}acac)_2OMe]_2$ ($J = -3.67$ cm^{-1}).[8,45] This may be viewed as an acid–base effect; the electron-withdrawing power of the phenyl group leads to a strengthening of the Fe–O(R) bond due to the increased acidity of the iron center. The decrease in $|J|$ observed for the ethoxo-bridged complex **3** compared with the methoxo-bridged complex **2** is unexpected. Examples of similar systems are $[(DPM)_2Fe(OCH_3)]_2$ ($J = -8.5$ cm^{-1}) and $[(DPM)_2Fe(OCH_2CH_3)]_2$ ($J = -11$ cm^{-1}) (where DPM is dipivalomethane)[15] and the acetylacetonate complexes $[Cr(3\text{-}Br\text{-}acac)_2OMe]_2$ ($J = -3.6$ cm^{-1}) and $[Cr(3\text{-}Br\text{-}acac)_2(OCH_2CH_3)]_2$ ($J = -8.9$ cm^{-1}).[8,45] In these systems, the antiferromagnetic interaction increases with the electron density at the bridging oxygen, as predicted by molecular orbital calculations.[26]

In conclusion, the structure of **1** confirms the assignment of a μ-alkoxo-bridged dimer structure to explain the anomalous behavior of some of the ferric bis(hydroxamato) complexes in alcohol solution. These observations are relevant to the characterization of some of the hydroxamate iron chelating agents of microbial origin (siderophores), although there is as yet no evidence that the corresponding μ-hydroxo dimers form to a significant extent. Indeed, the existence of the dimeric μ-alkoxo dimers seems to rely on a delicately poised equilibrium composed of ligand acidity and geometry, as well as sensitivity to solution composition implied by eq 1.

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Supplementary Material Available: Anisotropic thermal parameters (Table III), positional and isotropic parameters for hydrogen (Table IV), observed and calculated structure factors (Table V), and magnetic susceptibility data (Tables VIII–X) (23 pages). Ordering information is given on any current masthead page.

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