

Structure, Spectra, and Redox Behavior of a μ -Dimethoxy-Bridged Diferric Complex with an Asymmetric Fe_2O_2 Bridge[†]

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Introduction

Several dimeric dialkoxo-bridged iron(III) chelates with bidentate β -diketone ligands have been synthesized and characterized.¹ On the basis of spectral and magnetic studies, they were proposed to contain the FeOFeO structural unit (Figure 1a). A feature common to them is a magnetic moment value¹ ($4.9\text{--}5.2 \mu_{\text{B}}$) somewhat lower than the spin-only value of $5.9 \mu_{\text{B}}/\text{Fe}$, which decreases with temperature, a behavior characteristic of antiferromagnetically coupled systems. The extent of antiferromagnetic interaction² ($8\text{--}11 \text{ cm}^{-1}$) is considerably smaller than that for oxo-bridged Fe(III) systems and is relatively insensitive to the nature of R(alkoxo) group and the nonbridging ligands. Further, these compounds despite considerable pairing, exhibit spectra that are very similar to isolated mononuclear complexes having similar geometry, with substantial intensity³ enhancements of the spin-forbidden $d\text{--}d$ bands. The presence of the symmetrical Fe_2O_2 unit was recently established in $[\text{Fe}(\text{acac})_2(\text{OEt})]_2$ ⁴ and $[\text{Fe}(3,6\text{-DBSQ})_2(\mu\text{-OMe})]_2$ ⁵ using an X-ray crystal structure determination. Several other such bridges (Figure 1b and c) with R = methyl have been characterized; in addition, one or two extended bridges are possible in the form of a large ring whose nitrogen atoms (R' = alkyl) are bound to the metal.^{4,6–8} To understand the origin of the novel spectral and magnetic behavior of these complexes, we have undertaken a structural study of dimethoxydiferric complexes. In the present paper, we are reporting the structure and properties of such a complex containing an asymmetric Fe_2O_2 bridge. Such polynuclear iron complexes are of additional interest because of the occurrence of iron "clusters" in several enzymes⁹ involved in biochemical redox reactions and in oxygen-carrying proteins.¹⁰

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[†] Dedicated to Professor P. T. Manoharan on the occasion of his sixtieth birth anniversary.

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Experimental Section

Synthesis of $[\text{Fe}_2\text{L}_2(\mu\text{-OCH}_3)_2]\cdot 2\text{CH}_3\text{OH}$ [$\text{LH}_2 = 1,2\text{-bis}(2'\text{-hydroxybenzyl})\text{ethane-1,2-diamine}$]. To a THF solution (25 mL) of ethylenediamine (0.24 g, 4 mmol) was added salicylaldehyde (0.98 g, 8 mmol) and the resultant mixture refluxed for 30 min. The solution was cooled, NaBH_4 (0.30 g, 2 mmol) was added with stirring, and the mixture was then filtered. To the filtrate was added Et_3N (0.80 g, 8 mmol) and then a methanolic solution (5 mL) of FeCl_3 (0.65 g, 4 mmol) with stirring. The brown precipitate obtained was filtered off, washed with cold methanol, and then dried under vacuum. Yield, 2.15 g (76%). X-ray-quality fine red crystals were obtained by recrystallization of the crude product from acetonitrile. Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}_3\text{Fe}\cdot\text{CH}_3\text{OH}$: C, 55.54; H, 6.47; N, 7.20. Found: C, 55.32; H, 6.62; N, 7.04.

Physical Measurements. Electronic spectra were recorded on a Hitachi U-3410 double-beam UV–vis–NIR spectrophotometer. EPR spectra were obtained on a Varian E 112 X-band spectrometer, the field being calibrated with diphenylpicrylhydrazyl (DPPH). All voltammetric experiments were performed in a single-compartment cell with a three-electrode system on a EG&G PAR 273 potentiostat/galvanostat equipped with an IBM PS2 computer and a HILOT DMP-40 series digital plotter. The working electrode was a glassy carbon disk (area 0.283 cm^2) and the reference electrode saturated calomel. A Pt plate was used as the counter electrode. The supporting electrolyte used was 0.1 M THAP. Solutions were deoxygenated by purging with N_2 gas for 15 min prior to measurements, and during measurements, a stream of N_2 was passed over the solution. The temperature of the methanol solution was maintained at $25 \pm 0.2 \text{ }^\circ\text{C}$ by a Haake D8 G circulating bath. The potential of Fc/Fc^+ couple (0.087 V, Ag/Ag^+) was measured in methanol under the same conditions to enable future correction for junction potentials.

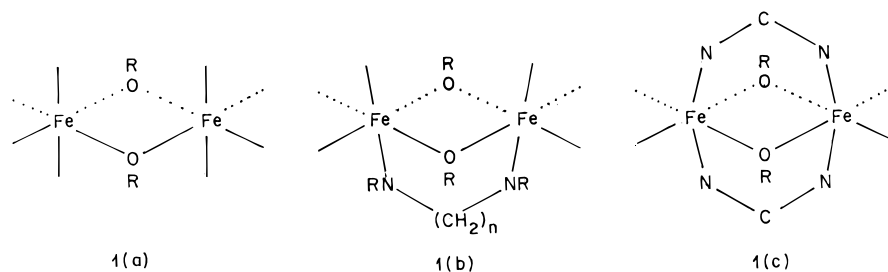
X-ray Data Collection and Crystal Structure Determination of $[\text{Fe}_2\text{L}_2(\mu\text{-OCH}_3)_2]\cdot 2\text{CH}_3\text{OH}$. A crystal fragment was mounted on an Enraf-Nonius CAD-4 diffractometer using a graphite-crystal monochromator. The space group and cell parameters were determined by a least-squares refinement of 25 reflections within a θ range of $2\text{--}25^\circ$. More crystallographic details are given in Table 1. A total of 1806 independent "observed" reflections were used in the structure analysis. The structure was solved with the SHELXS-86 program¹¹ and refined against all F^2 (SHELXL 93).¹² All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms, except for those of the methoxy group, C9, and methyl group of the methanol solvate were located in the difference Fourier map.

Results and Discussion

Description of the Crystal Structure. The crystal structure of the title compound consists of discrete complex molecules. The molecular structure of the complex molecule and labeling scheme are shown in Figure 2. Each molecule consists of two iron(III) centers which are related by a crystallographic inversion center. Each iron is coordinated by two *cis*-phenolate oxygen atoms and the two *cis*-tertiary nitrogen atoms of the tetradentate ligand, and the octahedral environment is completed by a pair of methoxy groups which asymmetrically bridge the two ferric ions. The two iron and two methoxy oxygen atoms constitute a perfect plane, with no deviation from the least-squares Fe_2O_2 plane.

The bridge angles $\text{FeO3Fe}'$ [$103.7(2)^\circ$] and $\text{FeO3}'\text{Fe}'$ and $\text{O3FeO3}'$ [$76.3(2)^\circ$] and $\text{O3Fe}'\text{O3}'$ are equal. The $\text{Fe}\text{--}\text{Fe}$

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**Figure 1.** Different dialkoxo bridge units.**Table 1.** Crystallographic Data for $[\text{Fe}_2\text{C}_{34}\text{H}_{42}\text{N}_4\text{O}_6]\cdot 2\text{CH}_3\text{OH}$

chemical formula	$\text{Fe}_2\text{C}_{36}\text{H}_{50}\text{N}_4\text{O}_8$
formula weight	778.5
space group	$P2_1/n$ (monoclinic No. 14)
a , Å	11.126(3)
b , Å	11.823(5)
c , Å	14.639(5)
β , deg	107.92(2)
V , Å ³	1832.2(11)
Z	2
T , °C	20
$\lambda\text{Mo K}\alpha$, Å	0.710 69
$\rho(\text{calc})$, g/cm ³	1.411
μ , cm ⁻¹	8.47
residuals	
R^a	0.0485
R_w^b	0.1350

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = \{ \sum w[(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2] \}^{1/2}.$$

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å² $\times 10^3$) for $[\text{Fe}_2\text{C}_{34}\text{H}_{42}\text{N}_4\text{O}_6]\cdot 2\text{CH}_3\text{OH}$

atom	x	y	z	$U(\text{eq})$
Fe	4997(1)	1235(1)	414(1)	37(1)
O(1)	4336(4)	904(3)	1458(3)	47(1)
O(2)	6301(4)	2216(3)	1168(3)	43(1)
O(3)	6121(3)	-85(3)	501(3)	44(1)
O(4)	6260(6)	2431(5)	3199(5)	81(2)
N(1)	3643(5)	2623(4)	-6(3)	41(1)
N(2)	5416(5)	1966(5)	-852(4)	46(1)
C(1)	3188(6)	1150(5)	1536(4)	47(2)
C(2)	2561(8)	371(6)	1948(5)	62(2)
C(3)	1368(10)	631(10)	2006(7)	87(3)
C(4)	793(8)	1636(10)	1667(6)	79(2)
C(5)	1433(8)	2405(9)	1299(5)	71(2)
C(6)	2635(6)	2205(5)	1225(4)	47(2)
C(7)	3314(8)	3074(6)	829(5)	54(2)
C(8)	4216(7)	3513(5)	-449(5)	50(2)
C(9)	4601(6)	2962(6)	-1237(5)	57(2)
C(10)	6789(7)	2153(7)	-674(5)	52(2)
C(11)	7346(5)	2995(4)	95(4)	38(1)
C(12)	8193(6)	3811(6)	-28(5)	48(2)
C(13)	8807(6)	4526(6)	692(6)	57(2)
C(14)	8574(6)	4486(5)	1545(6)	50(2)
C(15)	7729(6)	3722(5)	1690(5)	45(1)
C(16)	7108(5)	2934(5)	990(4)	42(1)
C(17)	7462(6)	-89(5)	911(5)	55(2)
C(18)	5184(8)	2535(7)	487(6)	84(3)

distance of 3.162(2) Å is shorter than that in dibridged methoxophenoxodiiron(III) complexes¹³ (3.193 Å) but slightly longer than those in $[\text{Fe}(\text{acac})_2(\text{OEt})_2]^{14}$ [3.116(1) Å] and $[\text{Fe}(3,6\text{-DBSQ})_2(\mu\text{-OMe})_2]^{15}$ [3.093(1) Å] complexes. The dimethoxo bridge is significantly asymmetric [$d(\text{Fe}-\text{O}3) = d(\text{Fe}'-\text{O}3') = 1.980(4)$ Å, $d(\text{Fe}-\text{O}3') = d(\text{Fe}'-\text{O}3) = 2.040(4)$ Å, $\Delta d = 0.06$ Å]. A similar asymmetric Fe_2O_2 core has been described

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Table 3. Bond Lengths [Å] and Bond Angles (deg) for $[\text{Fe}_2\text{C}_{34}\text{H}_{42}\text{N}_4\text{O}_6]\cdot 2\text{CH}_3\text{OH}^a$

Fe-O(2)	1.919(4)	Fe-O(1)	1.930(4)
Fe-O(3)	1.980(4)	Fe-O(3')	2.040(4)
Fe-N(1)	2.185(5)	Fe-N(2)	2.220(5)
O(1)-C(1)	1.350(7)	O(2)-C(16)	1.319(7)
O(3)-C(17)	1.427(7)	O(4)-C(18)	1.391(10)
O(2)-Fe-O(1)	94.1(2)	O(2)-Fe-O(3)	95.1(2)
O(1)-Fe-O(3)	100.1(2)	O(2)-Fe-O(3')	168.7(2)
O(1)-Fe-O(3')	94.6(2)	O(3)-Fe-O(3')	76.3(2)
O(2)-Fe-N(1)	92.4(2)	O(1)-Fe-N(1)	88.7(2)
O(3)-Fe-N(1)	168.0(2)	O(3)-Fe-N(1)	95.0(2)
O(2)-Fe-N(2)	86.0(2)	O(1)-Fe-N(2)	165.8(2)
O(3)-Fe-N(2)	94.0(2)	O(3)-Fe-N(2)	87.4(2)
N(1)-Fe-N(2)	77.1(2)	C(1)-O(1)-Fe	128.7(4)
C(16)-O(2)-Fe	135.7(4)	C(17)-O(3)-Fe	126.0(4)
C(17)-O(3)-Fe'	128.4(4)	Fe-O(3)-Fe'	103.7(2)
C(7)-N(1)-C(8)	110.9(5)	C(7)-N(1)-Fe	111.3(4)
C(8)-N(1)-Fe	107.7(4)	C(10)-N(2)-C(9)	115.0(6)
C(10)-N(2)-Fe	112.3(4)	C(9)-N(2)-Fe	111.4(4)

^a Symmetry transformations used to generate equivalent atoms: $-x + 1, -y, -z$.

by Walker and Poli.¹⁴ The asymmetry of the Fe-O-Fe-O structural unit is also evident from the difference in the external bond angles [$\text{FeO}3\text{C}17 = 126.0(4)^\circ$; $\text{Fe}'\text{O}3\text{C}17 = 128.4(4)^\circ$] at methoxo oxygens. The bridging Fe- μ -O(CH₃), the Fe-O(phenolate) [Fe-O2, 1.919(4) Å; Fe-O1, 1.930(4) Å], and the Fe-N [Fe-N1, 2.185(5) Å; Fe-N2, 2.220(5) Å] bond distances are in the ranges normally observed for iron(III)-Schiff base complexes;^{8,15-20} the Fe-N distances are close to Fe-N(tertiary amine)⁶ rather than Fe-N(azomethine)²¹ bond lengths. Both the angles at oxygen [$103.7(2)^\circ$] and those at iron [$76.3(2)^\circ$] are equal and are typical for an Fe-O-Fe-O ring.^{15-20,22} The preference of an Fe-O-Fe-O ring for the O-Fe-O angle close to 76° leads to distortions in the remaining angles in the coordination sphere from ideal octahedral ones. An increase or decrease from the ideal value of 90° occurs for the other coordination angles N2-Fe-O3' [$87.4(2)^\circ$], N1-Fe-O3' [$95.0(2)^\circ$], and O3-Fe-N2 [$94.0(2)^\circ$] and a decrease from 180° for O3-Fe-N1 [$168.0(2)^\circ$] and O2-Fe-O3' [$168.7(2)^\circ$] angles, making the coordination geometry a distorted octahedral one. The structurally long Fe- μ -O3 bond is relatively weak; this is because it is trans to the stronger and hence shorter Fe-

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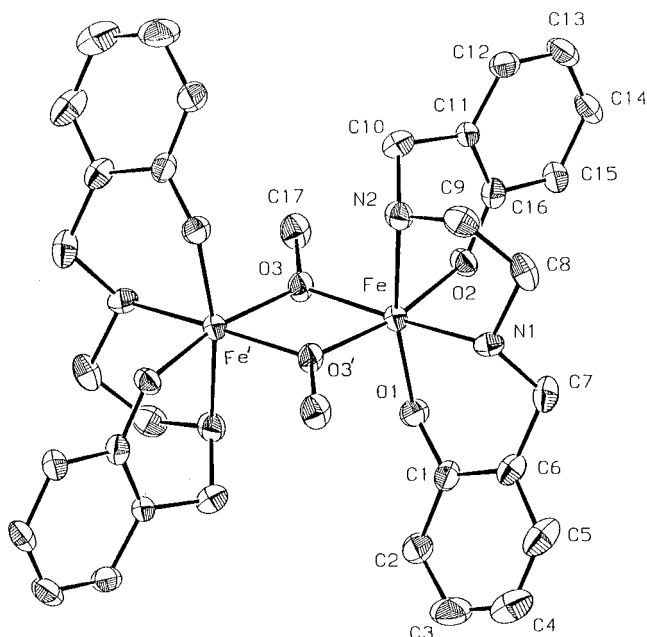


Figure 2. Thermal ellipsoid plot (30% probability ellipsoids) of the complex **1** showing the atom numbering scheme. The hydrogen atoms have been omitted for clarity.

O(phenolate) bond which mitigates the Lewis acidity of the iron center and hence decreases its affinity for the methanolate bridge. Thus, the asymmetry of the Fe–O–Fe–O bridge is not an intrinsic feature but originates from the *cis*-phenolate coordination of the tetradentate ligand.

A comparison of the structural parameters of the present asymmetric Fe₂(μ-OCH₃)₂ core with a similar Fe₂(μ-O)₂ core²³ enables us to understand the effect of increasing the electron density at the bridging atom by substituting μ-OCH₃ by the μ-O⁻ ligand. The increased repulsion between the two μ-O⁻ bridges is manifested in the decreased Fe–μ-O⁻ bond distances [1.841(4), 1.917(4) Å] and Fe–O–Fe angle [92.5(2)°] with concomitant decrease in Fe–Fe distance [2.714(2) Å]. Also this illustrates that the antiferromagnetic coupling constant for the Fe₂(μ-O)₂ core (*J*, 61 cm⁻¹) is higher than those (7 < |*J*| < 17 cm⁻¹) for Fe₂(μ-OCH₃)₂ cores^{15–20,22} similar to that in the present complex, in qualitative agreement with the predictions²⁴ of molecular orbital theory. However, it should be recognized that the higher *J* value may derive some contributions from the change in the nonbridging ligands and any accompanying changes in coordination geometries. Further, the addition of an electron into the Fe₂(μ-OCH₃)₂ core would be expected to lead to the same effect and would illustrate the participation of such cores in the oxygen activation mechanism of methane monooxygenase (MMO)²⁵ and related enzymes.²⁶

Further, the two methoxy carbon atoms deviate equally (0.286 Å) on either side of the Fe₂O₂ plane. The coordination of the bridging oxygens in the present compound differs significantly from that found for several copper(II) complexes¹⁷ and does not support a π-pathway for the spin exchange between the iron atoms.¹⁷ The strong Fe–OCH₃ interaction can be compared

to the one in Fe^{III}(TPP)–OCH₃ [1.816(2) Å]²⁷ in which the hybridization of oxygen is of the sp² type, suggesting a π-interaction between iron and oxygen.

Electronic Spectra. The electronic spectrum of the diferric complex in CH₃CN solution displays features at 506 (ε, 3860 M⁻¹ cm⁻¹), 320 (ε, 6260 M⁻¹ cm⁻¹), and 400 nm (sh, ε, 1690 M⁻¹ cm⁻¹) for the present iron(III) complex. The ligand field transitions at Fe(III) centers are expected to be spin-forbidden and hence weak. So the rather highly intense absorptions observed are most likely to arise from charge-transfer and/or intraligand transitions and the relatively weak spin–spin interaction, expected as for similar dimethoxy compounds, would lead to negligible influence on the electronic transitions.^{1a,17,28,29} The lower energy band is assigned to a charge-transfer transition from a phenolate (pπ) to half-filled dπ orbital of iron, and thus its band position falls in the range for other phenolato compounds. While the higher energy 320-nm band is associated with phenolate → Fe(III) dπ (split e_g orbital) LMCT transition,^{30,31} the 400-nm band may originate from phenolate (pπ) → Fe(III) dπ (higher energy orbital of the split t_{2g} set) LMCT transition.

EPR Spectra. The EPR spectrum of the solid complex displays two signals, one at *g* = 4.3 (peak to peak separation Δ*H*_{pp}, 120 G) and the other broad one centered at about *g* = 2.0 (Δ*H*_{pp}, 2000 G). The former feature is characteristic of high-spin magnetically noninteracting iron(III) impurity^{8,32} in an octahedral ligand field. Spin–spin coupled dimeric Fe(III) species³² would produce electronic states with a total spin *S'* of 5, 4, 3, 2, 1, and 0 with the energies of these states decreasing with *S'*. The *g* = 2.0 signal may arise from one of these states, which becomes preferentially thermally populated at 300 K but not at low temperatures. Thus, interestingly, the *g* = 2.0 signal disappears while the *g* = 4.3 signal is retained at liquid nitrogen temperature. It is also possible that the crystal contraction at low temperatures may cause line broadening leading to the disappearance.

Electrochemistry. The cyclic voltammetric response of the complex in CH₃CN solution shows a cathodic wave (*E*_{pc}, -1.130 V vs Ag/Ag⁺) at 50 mV/s scan rate but not the corresponding anodic wave. The one-electron transfer, as revealed by the magnitude of the current function, corresponds to the reduction of the Fe^{III}Fe^{III} complex to its unstable Fe^{III}Fe^{II} mixed-valence form. The latter may be relevant to that in the methane monooxygenase enzyme (MMO),²⁵ but unfortunately the chemical irreversibility even within the short time scale of cyclic voltammetry prevents its further study. The observation of the reduction at a relatively high cathodic potential (*E*_{1/2} from DPV, -1.033 V) illustrates the building up of high electron density on each iron by one methoxy and two phenolato groups. The redox wave for the second electron transfer, Fe^{III}Fe^{II} → Fe^{II}Fe^{II} could not be discerned, and it appears to be obscured by ligand reductions.

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Conclusions

In summary, we have used a tetradentate ligand to isolate a new $\text{Fe}_2(\mu\text{-O})_2$ core, the asymmetry of which is due to the trans-labilizing effect of the phenolate donor on the $\text{Fe}\text{-}\mu\text{-O}$ bond. The study of the effect of the asymmetry on the extent of anti-ferromagnetic coupling will be our future goal. Further, the core may be relevant to that present in MMO^{25} and other related enzymes²⁶ and should provide important insights into the magnetic and electronic interactions in the binuclear centers in these enzymes.

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Supporting Information Available: Complete tables (Tables S1–S6) of crystal data, bond lengths and angles, fractional atomic coordinates, and thermal parameters (7 pages). Ordering information is given on any current masthead page.

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