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A Diiron(III) Complex Containing N−N Bridges. Synthesis, Structure, and Properties

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Introduction

Recent interest in polynuclear transition metal complexes stems from the discoveries of several metalloenzymes[2] containing more than one metal ion center. The main objective is to obtain the small molecule analogs of the metal active sites in the naturally occuring systems. Polynuclear complexes are of further interest with respect to homogeneous catalysis and for magnetic, electrochemical and spectroscopic studies. Interaction between metal centers in such a complex is responsible for the change of magnetic, electrochemical, and spectral properties expected from the noninteracting metal centers. This interaction can arise due to direct metal−metal interactions or through the bridging ligands. Dinuclear iron complexes containing the Fe−O−Fe unit are relatively common[3] and studied extensively because of their varying type of magnetic interactions and occurence of this unit at the active sites of several metalloenzymes.[4] In contrast diiron cores with two atom bridge are extremely rare.[5] In this work the synthesis, structure and properties of a new dinuclear iron(III) complex containing three N−N bridges are described.

Experimental Section

Materials. Electrochemically pure dichloromethane was obtained by distillation from CaH_2 and stored over 3 Å molecular sieves. The supporting electrolyte tetraethylammonium perchlorate (TEAP) was prepared by following a reported procedure.[6] The ligand *N,N'*-bis(salicylidene)hydrazine (H_2salhn) was prepared in 95% yield by reacting hydrazine with 2 equiv of salicylaldehyde followed by recrystallization from methanol. All other chemicals and solvents used in this work were of analytical grade available commercially.

Physical Measurements. Microanalytical data (C,H,N) were obtained with a Perkin-Elmer Model 240C elemental analyzer. Variable temperature (89−300 K) magnetic susceptibilities at a field strength of 7622 G were measured by using a PAR-155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet, a dewar (Model No. 153N) from Janis Research Components, Inc., and a DRC-70C digital cryogenic thermometer/controller from Lakeshore Cryotronics, Inc. Diamagnetic correction (-381×10^{-6} cgsu for $Fe_2(Salhn)_3$) calculated from Pascal's constants[7] was used to obtain the molar paramagnetic susceptibilities. IR spectra were collected by using KBr pellets on a JASCO-5300 FT-IR spectrophotometer. Electronic spectrum was recorded by using a JASCO-7800 UV/vis spectrophotometer. EPR spectra were taken on a JEOL FE-3X spectrometer. Electrochemical experiments were performed with an EG&G PAR 370 electrochemistry system incorporating a Model 175 universal programmer, a Model 174A polarographic analyzer and a Model RE0074 X-Y recorder under dry and purified dinitrogen atmosphere. A platinum disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used for the electrochemical measurements. The potentials reported in this work are uncorrected for junction contributions.

Preparation of Fe_2(salhn)$_3$. To a methanol (10 mL) solution of 0.360 g (1.5 mmol) of H_2salhn and 0.167 g (3 mmol) of KOH a solution of $FeCl_3$ (0.162 g, 1 mmol) in methanol (5 mL) was added. Immediately the color of the mixture became deep red-brown. The solution was stirred for 2 h at room temperature in air. A dark crystalline material with little solid KCl separated. This was collected by filtration, washed with water (to remove KCl) and finally dried in vacuum over anhydrous calcium chloride. Recrystallization was performed from an acetonitrile−chloroform (1:1) solution. Yield: 0.3113 g (75%). Anal. Calcd for $Fe_2C_{42}H_{30}N_6O_6$: C, 61.04; H, 3.66; N, 10.17. Found: C, 60.86; H, 4.06; N, 9.95. Selected IR bands[8] (cm^{-1}): 1601 (s), 1572 (s), 1535 (s), 1468 (s), 1437 (s), 1366 (m), 1306 (s), 1200 (m), 1150 (w), 903 (m), 858 (w), 800 (m), 760 (s), 687 (w), 598 (s), 461 (s). Electronic spectral data[8] in $CHCl_3$ solution (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 532 (11 240), 442 (14 590), 380 (53 130)^{sh}, 331 (93 600), 305 (103 300)^{sh}, 287 (115 300), 254 (189 300).

X-ray Structure Determination. Single crystals of Fe_2(salhn)$_3$ were grown by slow evaporation of an acetronitrile−chloroform (1:1) solution. A crystal of dimensions 0.32 × 0.44 × 0.51 mm was used for the data collection on a Nicolet R3m/V single crystal diffractometer using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). Unit cell parameters were determined by the least-squares fit of 25 reflections having 2θ values in the range 5−25°. The stability of the crystal was monitored by measuring the intensities of two check reflections after every 98 reflections. The ψ-scans[9] of seven reflections with 2θ in the range 8−38° and χ within 81−87° were used for an empirical absorption correction. The compound crystallizes in the triclinic system. The structure was successfully solved in the space group $P\bar{1}$ (No. 2) by direct methods and refined by full-matrix least-squares methods and Fourier techniques. No correction for secondary extinction was applied. Atomic scattering factors were taken from ref 10. All calculations for data reduction, structure solution, and refinement were done on a MicroVAX II computer using the programs of SHELXTL-Plus.[11] Significant crystal data are summarized in Table 1. The asymmetric unit contains a molecule of Fe_2(salhn)$_3$ with one acetonitrile molecule. All non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were located on difference Fourier map and included in the structure factor calculation at idealized positions with fixed thermal parameters, but not refined. Coordinates and equivalent isotropic displacement coefficients of selected atoms are listed in Table 2.

Results and Discussion

Description of Structure. The crystal structure of Fe_2(salhn)$_3$ is shown in Figure 1. Selected bond distances and angles are listed in Table 3. Each ligand binds two metal ions via phenolate-*O* and imine-*N* atoms. The Fe- - -Fe distance is

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[1] (a) University of Hyderabad. (b) Indian Association for the Cultivation of Science.

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[8] Symbols: s, strong; m, medium; w, weak; sh, shoulder.

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Table 1. Crystallographic Data for $Fe_2(salhn)_3{\cdot}CH_3CN$

chem. formula	$Fe_2C_{44}H_{33}N_7O_6$	γ, deg	99.49(2)
fw	867.5	V, Å^3	1965.1(9)
temp, K	295	Z	2
space group	$P\bar{1}$	d_{calcd}, g cm^{-3}	1.466
a, Å	12.190(3)	μ, cm^{-1}	7.98
b, Å	12.601(4)	λ, Å	0.71073
c, Å	14.302(3)	R,[a] %	4.90
α, deg	103.90(2)	R_w,[b] %	6.27
β, deg	107.57(2)		

[a] $R = (\sum||F_o| - F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [\sigma^2(|F_o|) + 0.0001|F_o|^2]^{-1}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients[a] (Å^2 $\times$ 10^3) of Selected Atoms of $Fe_2(salhn)_3{\cdot}CH_3CN$[b]

atom	x	y	z	U(eq)
Fe(1)	915(1)	2840(1)	2125(1)	29(1)
Fe(2)	4195(1)	2845(1)	2264(1)	28(1)
O(1)	235(4)	2039(3)	2894(3)	41(2)
O(2)	4578(3)	2442(3)	1048(3)	39(2)
O(3)	−376(3)	2170(3)	819(3)	39(2)
O(4)	5423(3)	4230(3)	3022(3)	36(2)
O(5)	484(3)	4221(3)	2546(3)	36(2)
O(6)	4969(4)	1863(3)	2911(3)	42(2)
N(1)	1712(4)	1438(4)	1847(3)	31(2)
N(2)	2565(4)	1529(3)	1365(3)	30(2)
N(3)	1874(4)	3519(4)	1232(3)	29(2)
N(4)	3140(4)	3945(4)	1684(3)	31(2)
N(5)	2566(4)	3661(4)	3437(3)	32(2)
N(6)	3498(4)	3098(4)	3516(3)	28(2)
C(1)	142(5)	1037(5)	3016(4)	33(2)
C(6)	761(5)	285(5)	2650(5)	38(3)
C(7)	1517(5)	530(5)	2095(5)	35(2)
C(8)	2323(5)	793(5)	479(4)	33(2)
C(9)	3099(5)	744(5)	−100(4)	32(2)
C(14)	4185(5)	1559(4)	210(4)	29(2)
C(15)	−711(5)	2551(5)	24(4)	34(2)
C(20)	104(5)	3256(5)	−236(5)	35(2)
C(21)	1369(5)	3618(5)	331(4)	35(2)
C(22)	3598(5)	4914(5)	1624(4)	32(2)
C(23)	4844(5)	5494(5)	2078(5)	34(2)
C(28)	5691(5)	5162(4)	2789(4)	30(2)
C(29)	799(5)	4991(4)	3452(4)	30(2)
C(34)	1889(5)	5191(4)	4246(4)	30(2)
C(35)	2748(5)	4554(4)	4176(5)	34(2)
C(36)	3863(5)	2797(5)	4332(4)	37(2)
C(37)	4742(6)	2183(5)	4549(5)	39(3)
C(42)	5254(5)	1742(5)	3836(5)	35(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Numbers in parentheses are estimated standard deviations in the least significant digits.

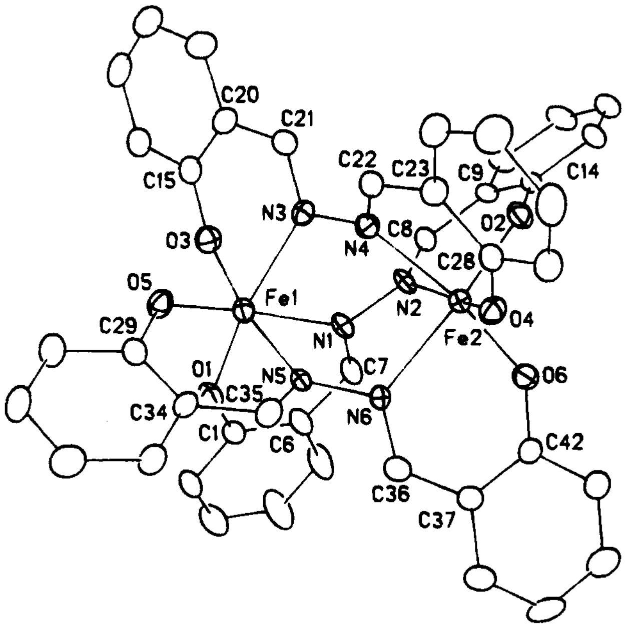

Figure 1. Structure of $Fe_2(salhn)_3$ showing the 30% probability thermal ellipsoids and atom-labeling scheme. Hydrogen atoms are omitted, and selected carbon atoms are labeled for clarity.

Table 3. Selected Bond Distances and Bond Angles for $Fe_2(salhn)_3{\cdot}CH_3CN$[a]

	Bond Distances (Å)		
Fe(1)−O(1)	1.930(5)	Fe(2)−O(2)	1.910(5)
Fe(1)−O(3)	1.925(3)	Fe(2)−O(4)	1.927(3)
Fe(1)−O(5)	1.912(4)	Fe(2)−O(6)	1.919(5)
Fe(1)−N(1)	2.164(5)	Fe(2)−N(2)	2.167(4)
Fe(1)−N(3)	2.197(6)	Fe(2)−N(4)	2.183(5)
Fe(1)−N(5)	2.178(4)	Fe(2)−N(6)	2.182(5)
	Bond Angles (deg)		
O(1)−Fe(1)−O(3)	96.9(2)	O(2)−Fe(2)−O(4)	99.1(2)
O(1)−Fe(1)−O(5)	97.7(2)	O(2)−Fe(2)−O(6)	96.4(2)
O(1)−Fe(1)−N(1)	84.4(2)	O(2)−Fe(2)−N(2)	84.5(2)
O(1)−Fe(1)−N(3)	169.6(2)	O(2)−Fe(2)−N(4)	92.1(2)
O(1)−Fe(1)−N(5)	92.6(2)	O(2)−Fe(2)−N(6)	171.0(1)
O(3)−Fe(1)−O(5)	97.8(2)	O(4)−Fe(2)−O(6)	97.8(2)
O(3)−Fe(1)−N(1)	91.8(2)	O(4)−Fe(2)−N(2)	167.6(2)
O(3)−Fe(1)−N(3)	84.8(2)	O(4)−Fe(2)−N(4)	84.4(2)
O(3)−Fe(1)−N(5)	169.7(2)	O(4)−Fe(2)−N(6)	89.6(2)
O(5)−Fe(1)−N(1)	169.9(1)	O(6)−Fe(2)−N(2)	93.5(2)
O(5)−Fe(1)−N(3)	92.2(2)	O(6)−Fe(2)−N(4)	170.7(2)
O(5)−Fe(1)−N(5)	84.7(2)	O(6)−Fe(2)−N(6)	84.2(2)
N(1)−Fe(1)−N(3)	85.3(2)	N(2)−Fe(2)−N(4)	83.6(2)
N(1)−Fe(1)−N(5)	85.3(2)	N(2)−Fe(2)−N(6)	86.6(2)
N(3)−Fe(1)−N(5)	85.1(2)	N(4)−Fe(2)−N(6)	86.9(2)

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

3.942(1) Å. The hexacoordinated metal ions have N_3O_3 coordination spheres with the salicylaldimine moiety in the facial mode. In order to accommodate two metal ions the ligands are twisted along the N−N bonds. This is clearly evident from the dihedral angle between the planes formed by the two salicylaldimine moieties of the same ligand. The extent of twisting is different for the three ligands. These are 56.8° (O1,C1,C6,C7,N1 and N2,C8,C9,C14,O2) for the first salhn^{2-}, 26.6° (O3,C15,C20,C21,N3 and N4,C22,C23,C28,O4) for the second salhn^{2-} and 44.5° (O5,C29,C34,C35,N5 and N6,C36,C37,C42,O6) for the third salhn^{2-} fragment. The atoms in parentheses define the concerned planes. All the salicylaldimine fragments are satisfactorily planar with a mean deviation in the range 0.01 to 0.05 Å. The iron atoms are displaced from these planes by 0.16 to 0.64 Å causing a fold at the O, N line of each chelate ring. This type of folding for salicylaldimine chelate ring is not uncommon.[12] The fold angles decrease with the increase of the twist angle along the N−N bond of the ligand. At the Fe1 and Fe2 centers the fold angles are 6.2, 13.1°; 25.3, 25.8°; and 20.5, 13.6° and the corresponding twist angles are 56.8, 26.6, and 44.5° for the first, second, and third salhn^{2-} respectively. Large distortions of the FeN_3O_3 octahedra are clearly evident from the bond distances and angles (Table 3). Such distortions are most probably due to the steric requirements of the dinucleating ligand. The average chelate bite angle (85.4°) is smaller than 90°. The average trans O−Fe−N angle (169.7°) deviates substantially from the ideal value of 180°. Furthermore, the average N−Fe−N angle (85.5°) is much smaller than the average O−Fe−O angle (97.6°). The smaller N−Fe−N angles and deviation of trans O−Fe−N angles from 180° indicate the pulling of the coordinated atoms on both the ferric ions to the center of the molecule. This is further indicated by the average outward deviation (0.11 Å), with respect to the

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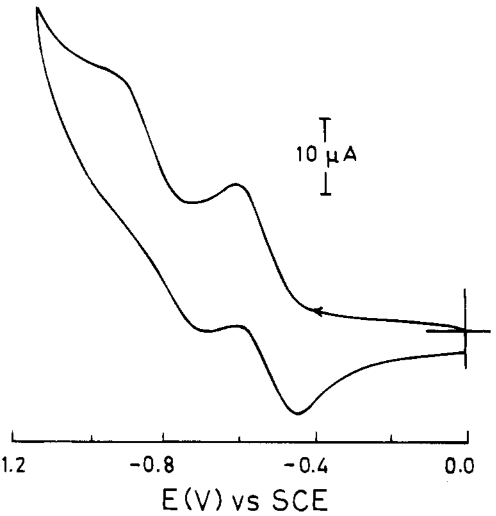

Figure 2. Cyclic voltammogram (scan rate 50 mV s^{-1}) of $Fe_2(salhn)_3$ in dichloromethane (0.1 M TEAP) at a platinum electrode (298 K).

center of the molecule, of the Fe atoms from the O_2N_2 planes (average mean deviation, 0.06 Å).

Redox Potentials. The cyclic voltammogram of $Fe_2(salhn)_3$ displays two reductions in dichloromethane solution (Figure 2). The first reduction is at $E_{1/2} = -0.52$ V ($\Delta E_p = 160$ mV)[13] and the second is at $E_{1/2} = -0.80$ V ($\Delta E_p = 200$ mV). With the increase of scan rate ΔE_p values for these reductions increase. If the scan direction is reversed after the first response ΔE_p of this couple is reduced by ~20 mV as compared to that when both the reductions are allowed. The first response is assigned to the III,III/III,II couple (eq 1) and the second is due to the III,II/II,II couple (eq 2). The one electron stoichiometry

$$[Fe^{III}_2(salhn)_3] + e^- \rightleftharpoons [Fe^{III}Fe^{II}(salhn)_3]^- \qquad (1)$$

$$[Fe^{III}Fe^{II}(salhn)_3]^- + e^- \rightleftharpoons [Fe^{II}_2(salhn)_3]^{2-} \qquad (2)$$

of each of the electrode processes was confirmed by comparing the current heights with known one-electron redox processes under identical conditions.

Spectral Properties. The infrared spectrum of the complex shows a considerable low energy shift (by 21 cm^{-1}) of the C=N stretching[14] as compared to that (1622 cm^{-1}) of the free ligand. Two overlapping bands in the visible region (532 and 442 nm) possibly due to ligand to metal charge transfer[15] are observed in the electronic spectrum of $Fe_2(salhn)_3$ in chloroform.

The molecule of $Fe_2(salhn)_3$ can have six spin states 5, 4, 3, 2, 1, and 0. Except for the lowest energy singlet state all other states can give rise to EPR signals. At room temperature the EPR spectrum of the complex in powder form shows a broad signal (peak-to-peak separation = 875 G) at $g \sim 2$. Cooling to liquid nitrogen temperature (77 K) marginally sharpens the signal. This type of broad EPR resonances for weakly coupled diiron(III) complexes have been observed previously.[16]

Magnetic Susceptibility. Variable temperature magnetic susceptibility measurements using a powdered sample of $Fe_2(salhn)_3$ were performed in the temperature range 89–300 K.

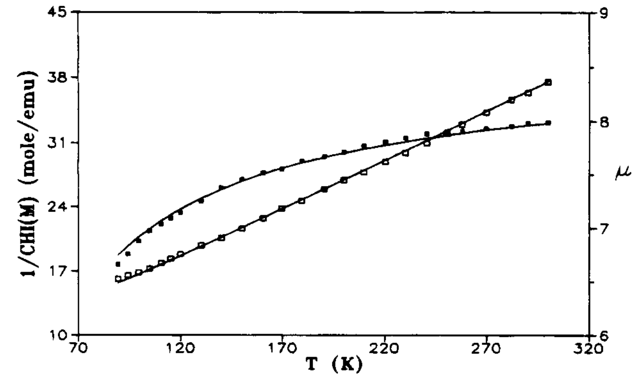

Figure 3. Inverse molar magnetic susceptibility (□) and effective magnetic moment (■) per complex as a function of temperature. The solid lines represent the quality of least-squares fit using the parameters given in the text.

The effective magnetic moment of the complex decreases gradually with temperature indicating an antiferromagnetic interaction between the two iron(III) centers (Figure 3). At 299.9 K the value of μ_{eff} (7.99 μ_B) is slightly smaller than the spin-only value (8.37 μ_B)[17] for the complex. At 89.5 K the μ_{eff} (6.66 μ_B) is decreased by 1.33 μ_B. The expression for χ_M vs T derived from the isotropic spin exchange Hamiltonian[18] $H = -2JS_1 \cdot S_2$, where $S_1 = S_2 = {}^5/_2$ for the two Fe(III) ions was used to fit the above magnetic data. The best least-squares fit was obtained (Figure 3) with J = −4.07(3) cm^{-1}, $g = 2.0$, $p = 0.92\%$, and TIP = 6.0 × 10^{-4} emu/mol, where J is the antiferromagnetic coupling constant, p is the high-spin Fe(III) impurity, and TIP is the temperature independent paramagnetism.[5f,18,19] The large Fe- - -Fe separation (3.942 Å) rules out any direct metal–metal interaction as the origin of this weak spin coupling. Thus the most likely pathway for the observed antiferromagnetic spin coupling is the superexchange via the N–N bridges.

Concluding Remarks. Very few polynuclear iron complexes containing metal ions connected by two atom bridges are known. Examples of such species are (i) trinuclear iron complexes having oximate (=N–O$^-$) as the bridging moiety,[5a–c] (ii) polymeric iron cyanide complexes with CN$^-$ ions as the bridging units,[5d] (iii) iron sulfur clusters containing the μ-S_2^{2-} group,[5e] and (iv) a few peroxo-bridged complexes.[5f] In this work we have reported a novel diferric complex, $Fe_2(salhn)_3$ containing three N–N bridges. Such a diaza-connected Fe_2 core has not been observed previously. Our current goal is to synthesize this type of N–N-bridged dinuclear complex with other metal ions having different d-electron configurations and study their magnetic and electrochemical properties in details.

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Supplementary Material Available: Tables of crystal data and structure determination summary (Table S1), atomic positional parameters (Table S2), anisotropic thermal parameters (Table S3), hydrogen atom coordinates (Table S4), intramolecular bond distances and angles (Tables S5 and S6), and magnetic data as a function of temperature (Table S7), and a fully labeled ORTEP drawing (12 pages). Ordering information is given on any current masthead page.

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(13) Symbols: E_{pa}, anodic peak potential; E_{pc}, cathodic peak potential; $E_{1/2} = (E_{pa} + E_{pc})/2$; $\Delta E_p = E_{pa} - E_{pc}$.

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(17) If both the metal centers have $S = {}^5/_2$ spin state the calculated spin-only moment is $70^{1/2} = 8.37$ μ_B.

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