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Effects of Temperature and Pressure on the Molecular and Electronic Structure of N,N′-Ethylenebis(salicylideneiminato)nitrosyliron, Fe(NO)(salen)

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The crystal and molecular structures of the two magnetically distinct forms of Fe(NO)(salen), $C_{16}H_{14}N_3O_3Fe$, have been determined by single crystal X-Ray diffraction at 23 °C and at –175 °C.

The complex crystallizes in the orthorhombic space group $Pna2_1$ with 4 molecules per unit cell. The unit cell dimensions are a = *26.377(2),* b = *8.598(5) and* c = *6.951(5) Å at 23 °C and* a = *26.18(2),* b = *8.52(1) and* c = *6.783(6) Å at –175 °C. Full-matrix least-squares refinement of the 23 °C structure based on the 840 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ gave a conventional R-factor of 0.038. The structure consists of discrete Fe(NO)(salen) molecules with tetragonal pyramidal coordination about the iron atom. The disordered nitrosyl group occupies the axial coordination site in a bent geometry (average Fe–N–O angle 147°). Full-matrix least-squares refinement of the –175 °C structure based on the 406 reflections with $F_o^2 \geqslant 2\sigma(F_o^2)$ gave a conventional R-factor of 0.087. This form of Fe(NO)(salen) also exhibits tetragonal pyramidal coordination geometry with a bent disordered nitrosyl group in the apical position. Marginally significant structural changes are observed: 1) the average Fe–N–O angle is 127°; 2) the Fe atom is 0.1 Å closer to the mean coordination plane of the salen ligand; 3) the salicylideneiminato moieties of the salen ligand are more nearly coplanar. These structural changes are consistent with a spin state of Fe(NO)(salen) from S = 3/2 to S = 1/2 upon cooling. The significant differences in the conformations of the salen ligand at the two temperatures are attributed to crystal packing. The infrared spectra of Fe(NO)(salen) at room temperature for various pressures ranging from ambient pressure up to 37 kbar are reported. The spectra suggest that Fe(NO)(salen) is converted to the S = 1/2 state at high pressure.*

Introduction

Most metal nitrosyl complexes possess strong covalent M–N bonds and consequently normally are low spin in the ground state. Earnshaw, King and Larkworthy [1] have prepared a series of monomeric mononitrosyl iron complexes based on salen, N,N′-ethylenebis(salicylideneimine), and various of its phenylene substituted derivatives which have magnetic moments between 3 and 4 B.M. at room temperature, suggestive of an S = 3/2 spin state. Most of these complexes exhibit temperature dependent magnetic moments which obey the Curie–Weiss law. However, the parent complex, Fe(NO)(salen), does not. Rather, on cooling it undergoes an abrupt magnetic change near –95 °C to a low spin form (μ_{eff} = 2.1 at –183 °C) with S = 1/2. Earnshaw, King and Larkworthy also measured the infrared spectra of these complexes and found that the ν_{NO} bands for the substituted derivatives were not altered on cooling. However, cooling Fe(NO)(salen) itself resulted in a decrease in the intensity of the ν_{NO} band at ~1710 cm^{-1} and a broadening of the strong ligand band at 1630 cm^{-1}.

It has been shown that the geometry of the $\{FeNO\}^7$ triatomic group can be controlled by the geometry adopted by the ligands around the triatomic fragment [2, 3]. Fe(NO)(salen) presents a unique opportunity to further probe the relationships between the FeNO geometry and the electronic ground states of the $\{FeNO\}^7$ group and at the same time to structurally characterize a metal nitrosyl complex with S = 3/2. The results of structural investigations of Fe(NO)(salen) at 23 °C and at –175 °C are reported herein. The results are compared to the recently determined room temperature structure of Fe(NO(TMC) [4], another $\{FeNO\}^7$ complex which has S = 3/2 at room temperature and which exhibits a temperature dependent spin state.

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Experimental

Preparation and Spectroscopy

Black crystals of Fe(NO)(salen) prepared by a modification of the method of Earnshaw, King and Larkworthy [1] were kindly furnished by Drs. O. A. Ileperuma and T. E. Nappier. Several attempts at recrystallization using various techniques and various solvent systems all failed, yielding red crystals of a compound presumed to be $[Fe(salen)]_2O$. Consequently, the crystals used for the structural studies were those obtained directly from the initial preparations. Infrared spectra were recorded, using diamond windows, at pressures from 1 bar to 37 kbar using a diamond anvil cell described previously [5].

Room Temperature Structural Study

Preliminary precession photographs (MoKα) of a crystal of approximate dimensions 0.09 X 0.10 X 0.49 mm indicated that the crystals are orthorhombic. The systematic absences of 0kl when k + l = 2n + 1, and h0l when h = 2n + 1 are consistent with the space groups $Pna2_1$ (No. 33) and Pnam, a nonstandard setting of Pnma (No. 62) which can be converted to Pnma by interchanging the *b* and *c* axes. Packing considerations make space group Pnam seem unlikely; the correct space group was shown to be $Pna2_1$ by subsequent successful solution and refinement of the structure. The unit cell parameters (at 23 ± 2 °C) determined from a least-squares refinement of the setting angles of 14 automatically centered reflections from diverse regions of reciprocal space having $20° < 2\theta < 30°$ (MoKα; $\lambda = 0.71069$ Å), are $a = 26.377(2)$, $b = 8.598(5)$ and $c = 6.951(5)$ Å. The observed density of 1.49 g/cm^3, determined by the density gradient method, agrees with the calculated density of 1.484 g/cm^3 for 4 formula units of Fe(NO)(salen) per unit cell. The crystal faces were indexed and are {1 0 0}, {0 1 0} and {0 0 1}.

The crystal used for the preliminary precession photographs was mounted on a Picker FACS-1 four-circle diffractometer and 1855 unique data from the octants hkl and $hk\bar{l}$ were collected ($\sin\theta/\lambda \leqslant 0.54$ Å^{-1}). The diffractometer utilized an incident beam monochromator equipped with a graphite crystal to obtain MoKα radiation. The take off angle was 1.7° and the reflections were collected using the θ–2θ scan technique. The scan range was 1.6° plus the dispersion correction to allow for the splitting of the MoKα lines. The scan rate was 1.0°/min, and stationary–crystal stationary–counter background counts of 10 s were taken at both ends of the scan. The scintillation counter was 31 cm from the crystal with an aperture of 4 X 4 mm. The pulse height analyzer was set to admit ~90% of the MoKα peak. Metal foil attenuators having attenuator factors of ~1.7 were inserted into the diffracted beam whenever the counting rate exceeded ~7000 counts/s. Throughout data collection three standard reflections from diverse regions of reciprocal space were monitored every 50 reflections. None of the standard reflections showed any systematic changes during the time required to collect the data.

The data were reduced to F_o^2 and $\sigma(F_o^2)$ by procedures similar to those previously described [6]. The value for p in the expression for $\sigma(F_o^2)$ was taken as 0.04. The linear absorption coefficient for the compound for MoKα radiation is 16.9 cm^{-1}. The transmission coefficients ranged from 0.87 to 0.91 and absorption corrections were not calculated.

Calculation of the normalized structure factors to be used as input to the MULTAN [7] direct methods program revealed a strong rational dependence of h + k: $E^2_{h+k=odd}/E^2_{h+k=even} = 0.23$. Initial attempts to solve the structure utilizing MULTAN and the unscaled normalized structure factors failed. The data were then rescaled so that $E^2_{average} = 1.0$ for each parity class. The structure was then solved by direct methods using the MULTAN package and the 350 reflections with $|E| \geqslant 1.06$. An E-map based upon these reflections revealed the positions of the Fe and the two O and two N atoms of the salen ligand. The y parameters of these five atoms were all close to 1.0. This pseudo-symmetry made the location of additional atoms difficult. For this reason a Patterson map was also calculated which confirmed the positions of these five atoms. In order to break the pseudo-symmetry the N atom of the nitrosyl group was introduced into the cell based on geometric considerations. The rest of the nonhydrogen atoms of the salen ligand were then located by a series of structure factor calculations, least-squares refinements and difference electron density maps. The carbon atoms of the phenylene rings were treated as rigid groups (C–C = 1.392 Å, D_{6h}–6/mm symmetry) with individual isotropic thermal parameters. The arbitrary N atom of the nitrosyl group was next removed from the structure, and its position and the position of the O atom of the nitrosyl group were located from a difference electron density map.

The strong rational dependence of h + k noted previously is due to the fact that the iron atom as well as several of the atoms of the salicylideneiminato ligand lie very close to y = 1.0. If the nitrosyl group were not present and the Fe(salen) moiety were planar then all the atoms would be on a mirror plane at y = 1.0 and the space group would be $Ccm2_1$ (nonstandard setting of $Cmc2_1$, No. 36). This would introduce systematic absences of hkl when h + k = 2n + 1. The iron atom (~15% of the electrons in the complex) is at y = 1.0, and thus cannot make any contribution to the intensities of the h + k = odd reflections. Atoms accounting for an additional ~30% of the electrons lie within 0.6 Å of y = 1.0 and thus will make at best very small contributions to the intensities of the h + k = odd reflections. This is manifested in the observation that only 22% of

TABLE I. Final Atomic Parameters for Fe(NO)(salen) 23 °C Positions.[a]

Atom	x	y	z
Fe	0.34287(5)	1.0015(3)	0.25
O(1)	0.3887(3)	0.8605(10)	0.3661(16)
O(2)	0.2846(4)	0.9300(11)	0.3908(15)
O(3A)	0.3841(8)	1.280(7)	0.371(8)
O(3B)	0.3421(15)	1.288(5)	0.435(3)
N(1)	0.3896(4)	1.0034(16)	0.0115(15)
N(2)	0.2935(5)	1.0570(14)	0.0262(17)
N(3)	0.3546(8)	1.1894(17)	0.3489(29)
C(1)	0.4348(5)	0.8129(17)	0.3191(25)
C(2)	0.4602(5)	0.7161(20)	0.4476(23)
C(3)	0.5070(7)	0.6551(18)	0.4048(28)
C(4)	0.5296(5)	0.6802(19)	0.223(3)
C(5)	0.5056(5)	0.7774(16)	0.1019(23)
C(6)	0.4579(6)	0.8465(19)	0.1394(27)
C(7)	0.4319(7)	0.9402(16)	−0.0022(19)
C(8)	0.3680(6)	1.0913(18)	−0.1474(22)
C(9)	0.3166(6)	1.0710(22)	−0.1624(20)
C(10)	0.2464(7)	1.0820(18)	0.0483(22)
C(11)	0.2176(5)	1.0665(14)	0.2195(27)
C(12)	0.1675(5)	1.1168(14)	0.229(3)
C(13)	0.1381(5)	1.1030(17)	0.388(3)
C(14)	0.1577(6)	1.0263(20)	0.5471(23)
C(15)	0.2066(5)	0.9697(18)	0.5474(18)
C(16)	0.2392(7)	0.9899(21)	0.3862(24)

[a] x, y and z are in fractional orthorhombic coordinates. The standard deviations of the least significant digits are given in parentheses.

TABLE II. Fixed Hydrogen Atom Positions for Fe(NO)-(salen) 23 °C.[a]

Atom	x	y	z
H(2)	0.4441	0.6901	0.5687
H(3)	0.5235	0.5852	0.4921
H(4)	0.5618	0.6450	0.1973
H(5)	0.5207	0.8098	−0.0209
H(7)	0.4525	0.9551	−0.1210
H(8A)	0.3848	1.0804	−0.2656
H(8B)	0.3703	1.2077	−0.1173
H(9A)	0.3131	0.9700	−0.2406
H(9B)	0.3006	1.1463	−0.2470
H(10)	0.2296	1.1258	−0.0626
H(12)	0.1555	1.1785	0.1214
H(13)	0.1042	1.1414	0.3924
H(14)	0.1359	1.0082	0.6605
H(15)	0.2190	0.9121	0.6576

[a] x, y and z are in fractional orthorhombic coordinates.

the 840 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ have h + k = odd.

Refinement of the complete structure was based on F_o, utilizing the 840 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ and minimizing the function $\Sigma w(|F_o| - |F_c|)^2$; where the weights were taken as $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors for the nonhydrogen atoms were taken from the tabulation of Cromer and Waber [8]. The effects of anomalous scattering for the iron atom were included in the calculated structure factors [9] and showed that the correct enantiomorph had been chosen ($R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ = 0.077vs 0.082). Full-matrix isotropic least-squares refinement converged with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.050$ and $R_2 = 0.052$. A difference electron density map based on this model showed the nitrosyl to be disordered and a second nitrosyl O atom was introduced into the model. The disordered nitrosyl O atoms were given fixed occupancies of 0.5. Three cycles of full-matrix least-squares refinement were carried out assuming individual isotropic atoms and including the 14 H atoms in idealized positions (C–H = 0.97 Å) as fixed contributors with isotropic thermal parameters of 8.0 Å^2. The hydrogen atom scattering factor curve was obtained from the calculation of Stewart, Davidson and Simpson [10]. Three additional cycles of full-matrix least-squares refinement during which the nonhydrogen atoms were assumed to vibrate anisotropically resulted in convergence with $R_1 = 0.038$ and $R_2 = 0.039$. The standard deviation of an observation of unit weight, defined by $[\Sigma w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, was 1.01. Here n is the number of observations (840) and m is the number of variables (216). The ratio n:m was only 3.89:1.

During the final cycle of least-squares refinement all of the parameter shifts were less than 1.1σ. An analysis of the weighting scheme showed that $w(|F_o| - |F_c|)^2$ was not dependent on $|F_o|$ or on sin θ/λ. The final atomic coordinates are given in Table I, the final H atom positions are given in Table II, selected interatomic distances and angles are given in Table III, and root-mean-square amplitudes of vibration along the principal axes for the nonhydrogen atoms are given in Table IV. The anisotropic thermal parameters (Table S1) as well as listings of $10|F_o|$ and $10|F_c|$ (Table S2) are available as supplementary material*.

Low Temperature Structural Study

A black rod-shaped crystal of approximate dimensions 0.07 X 0.13 X 0.40 mm was attached to a glass fiber with epoxy cement. The fiber was inserted into a thin-walled glass capillary and the base of the fiber fused by melting. Rubber cement was used to bind the capillary to a streamlined metal pin which had been firmly attached to a goniometer head. The mounted crystal was transferred to a Syntex P$\bar{1}$ diffractometer equipped with an LT-1 low temperature

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*See note at end of paper regarding supplementary material.

TABLE III. Selected Interatomic Distances and Angles for Fe(NO)(salen) 23 °C.[a]

Distances			
Fe–O(1)	1.892(9)	C(16)–C(15)	1.423(20)
Fe–O(2)	1.923(9)	C(1)–C(6)	1.419(18)
Fe–N(1)	2.066(10)	C(16)–C(11)	1.449(21)
Fe–N(2)	2.084(13)	C(2)–C(3)	1.372(19)
Fe–N(3)	1.783(16)	C(15)–C(14)	1.378(19)
N(3)–O(3A)	1.11(4)	C(3)–C(4)	1.412(22)
N(3)–O(3B)	1.091(22)	C(14)–C(13)	1.391(20)
O(1)–C(1)	1.324(13)	C(4)–C(5)	1.346(19)
O(2)–C(16)	1.305(17)	C(13)–C(12)	1.354(20)
N(1)–C(7)	1.245(15)	C(5)–C(6)	1.417(20)
N(2)–C(10)	1.269(18)	C(12)–C(11)	1.393(15)
N(1)–C(8)	1.455(15)	C(6)–C(7)	1.444(19)
N(2)–C(9)	1.451(17)	C(11)–C(10)	1.418(19)
C(8)–C(9)	1.370(16)	O(3A)–O(3B)[b]	1.20(3)
C(1)–C(2)	1.392(17)		
Angles			
Fe–N(3)–O(3A)	144.(5)	C(1)–C(2)–C(3)	121.5(15)
Fe–N(3)–O(3B)	150.(4)	C(16)–C(15)–C(14)	121.4(13)
O(1)–Fe–O(2)	95.1(4)	C(2)–C(3)–C(4)	121.0(14)
O(1)–Fe–N(1)	88.1(4)	C(15)–C(14)–C(13)	121.2(14)
O(1)–Fe–N(2)	149.8(5)	C(3)–C(4)–C(5)	117.1(14)
O(2)–Fe–N(2)	87.3(5)	C(14)–C(13)–C(12)	118.5(13)
O(2)–Fe–N(1)	152.6(5)	C(4)–C(5)–C(6)	124.3(15)
N(1)–Fe–N(2)	76.8(4)	C(13)–C(12)–C(11)	123.7(18)
Fe–O(1)–C(1)	132.8(7)	C(5)–C(6)–C(1)	117.2(16)
Fe–O(2)–C(16)	126.5(10)	C(12)–C(11)–C(16)	118.5(18)
Fe–N(1)–C(7)	126.4(10)	C(5)–C(6)–C(7)	122.0(12)
Fe–N(2)–C(10)	124.0(10)	C(12)–C(11)–C(10)	121.3(11)
Fe–N(1)–C(8)	112.3(7)	C(1)–C(6)–C(7)	120.6(12)
Fe–N(2)–C(9)	115.5(9)	C(16)–C(11)–C(10)	120.2(11)
O(1)–C(1)–C(2)	117.9(9)	C(6)–C(7)–N(1)	128.1(13)
O(2)–C(16)–C(15)	119.2(12)	C(11)–C(10)–N(2)	127.6(13)
O(1)–C(1)–C(6)	123.3(10)	C(7)–N(1)–C(8)	121.3(12)
O(2)–C(16)–C(11)	124.1(12)	C(10)–N(2)–C(9)	120.5(13)
C(6)–C(1)–C(2)	118.7(14)	N(1)–C(8)–C(9)	112.3(13)
C(11)–C(16)–C(15)	116.6(14)	N(2)–C(9)–C(8)	110.9(13)

[a] Distances in ångströms and angles in degrees. The standard deviations of the least significant digits are given in parentheses.
[b] Apparent distance between the disordered atoms.

TABLE IV. Root-Mean-Square Amplitudes of Vibration for Fe(NO)(salen) 23 °C.[a]

Atom	Minimum	Intermediate	Maximum
Fe	0.197(4)	0.239(3)	0.292(4)
O(1)	0.236(15)	0.252(15)	0.328(14)
O(2)	0.191(16)	0.218(15)	0.343(13)
O(3A)	0.24(4)	0.28(4)	0.67(6)
O(3B)	0.20(3)	0.25(4)	0.46(5)
N(1)	0.189(24)	0.213(17)	0.383(18)
N(2)	0.187(21)	0.204(21)	0.325(18)
N(3)	0.233(18)	0.292(26)	0.314(21)
C(1)	0.186(25)	0.249(23)	0.327(23)
C(2)	0.183(27)	0.278(23)	0.403(20)
C(3)	0.19(3)	0.307(22)	0.375(25)
C(4)	0.201(26)	0.322(25)	0.369(26)

(continued on facing page)

TABLE IV. *(continued)*

Atom	Minimum	Intermediate	Maximum
C(5)	0.217(23)	0.261(23)	0.331(24)
C(6)	0.225(26)	0.255(21)	0.309(23)
C(7)	0.214(23)	0.262(22)	0.305(21)
C(8)	0.03(12)	0.318(19)	0.464(20)
C(9)	0.152(28)	0.287(19)	0.505(24)
C(10)	0.15(3)	0.247(23)	0.320(24)
C(11)	0.191(22)	0.214(26)	0.268(27)
C(12)	0.208(28)	0.274(22)	0.313(26)
C(13)	0.226(23)	0.278(25)	0.365(21)
C(14)	0.252(22)	0.293(23)	0.333(21)
C(15)	0.202(21)	0.237(19)	0.347(22)
C(16)	0.17(4)	0.267(25)	0.30(3)

[a] Amplitudes in ångströms. The standard deviations of the least significant digits are given in parentheses.

device and oriented by standard techniques. An ω-scan showed a full-width at half maximum of ~0.3°. Upon cooling rapidly to ~−175 °C the mosaicity of the crystal increased to ~1° but polaroid oscillation pictures about *a*, *b* and *c* did not reveal any obvious change of space group. Upon warming to room temperature the mosaicity again decreased to ~0.3°. A similar increase in mosaicity occurred when the crystal was cooled to −175 °C over a three hour period. Broad (~1°) but satisfactory smooth ω-scans were obtained after annealing the crystal at −135 °C for 12 h and then slowly cooling the crystal to −175 °C over four h. The increase in mosaicity on cooling and the subsequent decrease back to the original full-width at half maximum on warming back to room temperature was observed for all crystals examined.

The unit cell parameters (at −175 ± 5 °C) determined from an unconstrained least-squares refinement of the setting angles of 11 automatically centered reflections from diverse regions of reciprocal space are $a = 26.18(2)$, $b = 8.52(1)$ and $c = 6.783(6)$ Å. A total of 795 unique data ($\sin\theta/\lambda \leqslant 0.48$ Å^{-1}) were collected from the hkl octant using an incident beam monochromator equipped with a graphite crystal to obtain MoKα radiation. Because of the mosaicity of the crystal the ω-scan technique was used. The ω step-scan (19 steps) had a width of 2.5° and variable scan rates (based on a 2 sec prescan through the peak). Stationary–crystal stationary–counter backgrounds were measured at both ends of the scan, and the ratio of scan time to total background time was 3:2. Two standard reflections monitored throughout data collection showed no systematic changes in intensity.

Intensities were calculated by the formula $I = [C - (ts/tb)(BH + BL)]SR$ where C is the total integrated peak count, ts and tb are the scan time and the total background time, BH and BL are the two background counts, and SR is the scan rate. Standard deviations were assigned by the formula $\sigma(I) = [C + (ts/tb)^2(BH + BL)]^{1/2}SR$. Lorentz and polarization corrections [11] were then applied to I and σ(I) using $Lp = \{[(1 + \cos^2 2\theta_m \cos^2 2\theta)/(1 + \cos^2 2\theta_m)] + [(1 + |\cos 2\theta_m| \cos^2 2\theta)/(1 + |\cos 2\theta_m|)]\}/(2\sin 2\theta)$ where θ_m is the Bragg angle of the monochromator crystal (6.1°) and θ is the Bragg angle of the reflection being observed.

In general as the temperature of a crystal is lowered the thermal motion of the atoms is reduced and the diffracted peaks are sharpened thus increasing the signal to noise ratio thereby increasing the number of observable data. In the crystals of the Fe(NO)(salen) complex the opposite is observed, *i.e.*, at the lower temperature the mosaicity is greater, the signal to noise ratio is lower, and fewer data are observable. The cause of the increased mosaicity at lower temperature in this case is not known. There were virtually no measurable reflections with $\sin\theta/\lambda > 0.48$ Å^{-1}. The strong rational dependence on h + k discussed above for the room temperature data also exists in the −175 °C data. Of the 407 data with $F_o^2 \geqslant 2\sigma(F_o^2)$ only 124 (30%) had h + k = odd.

Refinement based on the low temperature data was initiated using the room temperature coordinates for the Fe(salen) portion of the molecule. Least-squares refinement, a structure factor calculation, and a difference electron density map were used to locate positions for the N atom and the two half O atoms of the disordered nitrosyl group.

All refinements of the complete structure were based on F_o utilizing the 407 data with $F_o^2 \geqslant 2\sigma(F_o^2)$. The same function was minimized as before except the weights were taken as $w = 4F_o^2/[\sigma^2(F_o^2) + 0.003(F_o^2)^2]$. Several models were explored in an effort to obtain a chemically reasonable description of the structure from the −175 °C data set. The details of these models are presented elsewhere [12].

TABLE V. Final Atomic and Group Parameters for Fe(NO)(salen), −175 °C.

Atom[a]	x	y	z	B
Fe	0.34292(16)	0.9826(6)	0.25	4.12(12)
N(1)	0.3892(9)	0.984(3)	0.022(4)	3.1(6)
N(2)	0.2953(12)	1.048(3)	0.039(5)	5.8(9)
O(1)	0.3858(7)	0.8508(24)	0.395(4)	4.2(5)
O(2)	0.2866(7)	0.9162(25)	0.413(4)	4.1(6)
C(7)	0.4327(12)	0.923(4)	0.017(6)	3.8(8)
C(8)	0.3677(15)	1.068(5)	−0.155(7)	7.1(13)
C(9)	0.3200(19)	1.081(6)	−0.153(8)	11.0(17)
C(10)	0.2469(13)	1.075(4)	0.073(6)	4.7(10)
H(7)	0.4515	0.9387	−0.1030	5.0
H(8A)	0.3790	1.0224	−0.2763	7.0
H(8B)	0.3838	1.1709	−1.696	7.0
H(9A)	0.3046	1.0209	−0.2553	7.0
H(9B)	0.3097	1.1857	−0.1977	7.0
H(10)	0.2281	1.1141	−0.0319	5.0

Group[b,c]	x_c	y_c	z_c	ϕ	θ	ρ
NO(A)	0.3688(14)	1.211(4)	0.374(6)	−2.52	4.(7)	−0.07(8)
NO(B)	0.3565(24)	1.206(8)	0.396(13)	2.65	−2.51(21)	−2.54(12)
R(A)	0.4829(5)	0.7452(15)	0.3115(28)	0.00(3)	2.036(13)	−0.39(3)
R(B)	0.1895(6)	1.0349(14)	0.4187(29)	2.82(4)	−1.955(13)	0.03(4)

Group[b]	B_1	B_2	B_3	B_4	B_5	B_6
NO(A)	5.7(11)	5.5(10)				
NO(B)	5.7(11)	5.5(10)				
R(A)	5.3(9)	6.0(10)	4.7(9)	3.2(7)	5.2(9)	3.6(8)
R(B)	5.3(10)	4.6(9)	5.8(8)	3.7(8)	4.7(8)	4.2(7)

[a] x, y and z are in fractional orthorhombic coordinates. B are the isotropic atomic thermal parameters in square Angströms. The standard deviations of the least significant digits are given in parentheses. [b] x_c, y_c and z_c are the fractional orthorhombic coordinates of the group origin. The angles ϕ, θ and ρ (in radians) are the rotations necessary to bring about alignment (except for translation) of the group internal coordinate system with the fixed crystallographic coordinate system. B_i is the isotropic thermal parameter in square Angströms of atom i in a given group. The nitrogen atom is atom 1 in the nitrosyl groups. Atom 1 in the phenylene rings is attached to oxygen and atom 6 is attached to nitrogen. [c] The occupancy of group NO(A) refined to 0.57(3). The sum of the occupancies of groups NO(A) and NO(B) was constrained to be 1.0.

Hamilton R-factor ratio tests [13] on the models that refined to convergence showed them to be indistinguishable at the 95% confidence level. The "best" model chosen on the basis of the chemically reasonable nitrosyl parameters is presented below.

Two modifications were made on the original model: first the phenylene rings were treated as rigid groups (C–C = 1.392 Å, D_{6h}/6 mm symmetry) with individual atom isotropic thermal parameters to improve the observation to variable ratio; second the nitrosyl N atom was assumed to be disordered and the nitrosyl region was treated as two overlapping rigid groups (N–O = 1.15 Å) in the manner used by Ibers, *et al.* [14–16] to refine similar disordered nitrosyl groups, and by Brown and Raymond [17] to refine a disordered dioxygen group. The group origins were placed at the midpoints of the N–O vectors. The two N atoms were constrained to have the same thermal parameters and the two O atoms were constrained to have the same thermal parameters. The sum of the occupancies of the nitrosyl groups were constrained to be 1.0.

Four cycles of full-matrix least-squares refinement of this model including individual isotropic thermal parameters for all nonhydrogen atoms of the Fe(salen) moiety, hydrogen atoms as fixed contributors in idealized locations (C–H = 0.97 Å), and anomalous scattering effects for the iron atom, converged with R_1 = 0.087 and R_2 = 0.083. The standard deviation of an observation of unit weight is 1.62; the highest residual on the final difference electron density map is 0.53 e/Å^3; and the number of variables is 73 giving a ratio n:m of 5.6:1. The converged model has approximately equal thermal parameters for the nitrosyl N and O atoms (5.7 and 5.5 Å, respectively), equal Fe–N(3) bond distances

(1.80 and 1.81 Å), and similar Fe–N(3)–O(3) bond angles (122 and 132°). The ethylene C–C distance is only 1.25 Å and the thermal parameters of the C atoms are 7.1 and 11.0 Å^2. Examination of the ethylene region in difference electron density maps revealed no alternative C atom positions.

Lists of $10|F_o|$ and $10|F_c|$ are available (Table S3) as supplementary material*. The final atomic and group parameters for this model are given in Table V, the derived group atom parameters are given in Table VI, and selected interatomic distances and angles are given in Table VII.

The major programs used for the solution and refinement of this structure were local modifications of the MULTAN direct methods program [7], Ibers' NUCLS least-squares program, itself a modification of Busing, Martin and Levy's ORFLS, Zalkin's FORDAP Fourier summation program, Busing, Martin and Levy's ORFEE function and error program, Corfield's RANGER weighting analysis program, and RBANG group orientation angle calculation program. Molecular diagrams were drawn with the program ORTEP. Major calculations were performed at the University of Arizona on a CDC 6400 computer.

Description

Perspective views of the structure of the Fe(NO)(salen) molecule at 23 °C (RT) and at –175 °C (LT) are given in Fig. 1. The numbering scheme is indicated on the views in Fig. 1. The crystal structures are quite similar consisting of discrete

TABLE VI. Derived Parameters for the Group Atoms for Fe(NO)(salen), –175 °C.[a]

Group	Atom	x	y	z
NO(A)	N(3A)	0.352(3)	1.168(10)	0.37(4)
	O(3A)	0.3857(19)	1.255(8)	0.38(4)
NO(B)	N(3B)	0.369(4)	1.160(12)	0.357(18)
	O(3B)	0.344(3)	1.252(9)	0.434(12)
R(A)	C(1)	0.4340(6)	0.8011(29)	0.347(4)
	C(2)	0.4585(9)	0.7100(28)	0.487(3)
	C(3)	0.5074(9)	0.6540(21)	0.452(3)
	C(4)	0.5318(6)	0.6892(25)	0.276(4)
	C(5)	0.5074(9)	0.7804(25)	0.136(3)
	C(6)	0.4585(9)	0.8363(22)	0.171(4)
	H(2)	0.4414	0.6853	0.6105
	H(3)	0.5244	0.5902	0.5506
	H(4)	0.5660	0.6500	0.2516
	H(5)	0.5245	0.8050	0.0126
R(B)	C(11)	0.2198(8)	1.0578(24)	0.254(4)
	C(12)	0.1699(8)	1.1123(22)	0.256(3)
	C(13)	0.1396(6)	1.0894(24)	0.421(4)
	C(14)	0.1592(10)	1.0120(26)	0.584(3)
	C(15)	0.2091(10)	0.9575(23)	0.582(3)
	C(16)	0.2394(6)	0.9804(23)	0.417(4)
	H(12)	0.1562	1.1664	0.1414
	H(13)	0.1047	1.1275	0.4221
	H(14)	0.1380	0.9960	0.6995
	H(15)	0.2228	0.9034	0.6961

[a] x, y and z are in fractional orthorhombic coordinates. Estimated standard deviations (given in parentheses) are derived from those of the group parameters by NUCLS.

TABLE VII. Selected Interatomic Distances and Angles for Fe(NO)(salen), –175 °C.[a]

Distances			
Fe–O(1)	1.869(22)	N(1)–C(7)	1.26(3)
Fe–O(2)	1.929(21)	N(2)–C(10)	1.31(4)
Fe–N(1)	1.967(24)	N(1)–C(8)	1.51(4)
Fe–N(2)	1.98(3)	N(2)–C(9)	1.49(6)
Fe–N(3A)	1.80(15)	C(8)–C(9)	1.25(5)
Fe–N(3B)	1.81(11)	C(6)–C(7)	1.44(4)
N(3A)–O(3A)[b]	1.15	C(11)–C(10)	1.43(4)
N(3B)–O(3B)[b]	1.15	N(3A)–N(3B)[c]	0.46(14)
O(1)–C(1)	1.371(27)	O(3A)–O(3B)[c]	1.16(13)
O(2)–C(16)	1.352(26)		
Angles			
Fe–N(3A)–O(3A)	132.(5)	O(1)–C(1)–C(2)	115.7(13)
Fe–N(3B)–O(3B)	122.(7)	O(2)–C(16)–C(15)	118.7(14)
O(1)–Fe–O(2)	88.9(9)	O(1)–C(1)–C(6)	124.3(14)
O(1)–Fe–N(1)	92.8(10)	O(2)–C(16)–C(11)	121.2(13)
O(1)–Fe–N(2)	158.5(11)	C(5)–C(6)–C(7)	118.8(19)
O(2)–Fe–N(2)	90.9(11)	C(12)–C(11)–C(10)	116.2(17)
O(2)–Fe–N(1)	157.6(11)	C(1)–C(6)–C(7)	121.1(18)

(continued overleaf)

TABLE VII. *(continued)*

N(1)–Fe–N(2)	79.5(11)	C(16)–C(11)–C(10)	123.6(17)
Fe–O(1)–C(1)	127.8(13)	C(6)–C(7)–N(1)	128.2(23)
Fe–O(2)–C(16)	126.1(14)	C(11)–C(10)–N(2)	127.7(24)
Fe–N(1)–C(7)	125.2(24)	C(7)–N(1)–C(8)	121.2(29)
Fe–N(2)–C(10)	123.(3)	C(10)–N(2)–C(9)	123.(4)
Fe–N(1)–C(8)	113.6(19)	N(1)–C(8)–C(9)	114.(4)
Fe–N(2)–C(9)	114.6(27)	N(2)–C(9)–C(8)	115.(5)

[a] Distances in ångströms and angles in degrees. Standard deviations (given in parentheses) for the distances and angles which involve the group atoms were calculated using only variances. The estimated variances for the group atoms are those given in Table VI. [b] The nitrosyl N–O distances were fixed at 1.15 ångströms in the –175 °C model. [c] Apparent distance between the disordered atoms.

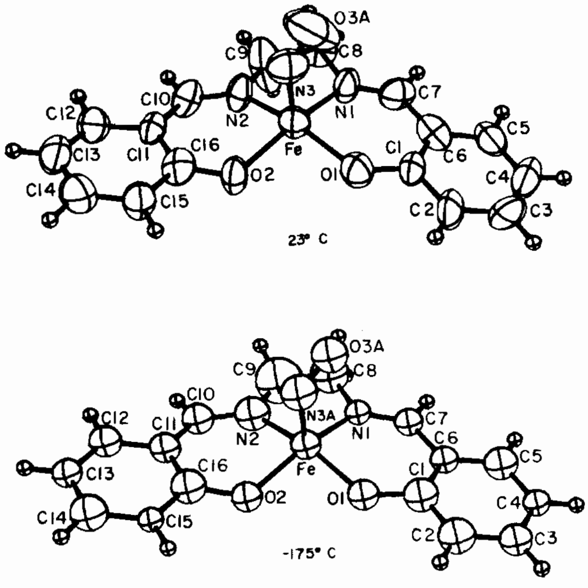

Figure 1. Perspective views and numbering schemes for Fe(NO)(salen). H atoms have arbitrary isotropic thermal parameters of 1.0 Å^2. The thermal ellipsoids are 50% probability envelopes.

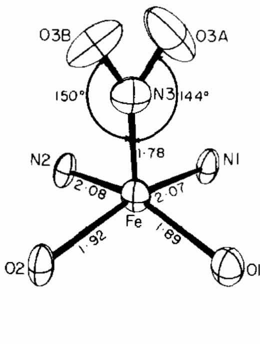

Figure 2. Perspective view of the inner coordination sphere of the RT form of Fe(NO)(salen). The N(3)–O(3) distances are 1.11 and 1.09 Å respectively. The thermal ellipsoids are 20% probability envelopes. Both positions for the disordered O atom of the nitrosyl groups are shown.

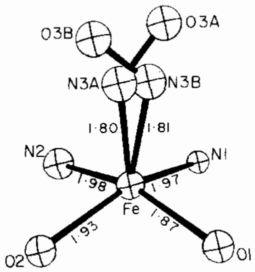

Figure 3. Perspective view of the inner coordination sphere of the LT form of Fe(NO)(salen). The Fe– N(3A)–O(3A) and Fe–N(3B)–O(3B) angles are 132 and 122° respectively. The thermal ellipsoids are 20% probability envelopes.Both positions of the disordered nitrosyl group are shown.

molecules with five-coordinate tetragonal pyramidal coordination about the Fe atoms with the nitrosyl group in the axial position. The nearest contacts to the vacant sixth coordination site are H atoms at 3.37 and 3.61 Å for the LT and the RT molecules respectively. The inner coordination sphere with bond lengths indicated is given in Fig. 2 for the RT structure and in Fig. 3 for the LT structure.

From Figs. 2 and 3 it can be seen that the $\{FeNO\}^7$ triatomic group (notation introduced by Enemark and Feltham) [18] is strongly bent as has been previously observed in several $\{FeNO\}^7$ tetraphenylporphyrinato complexes [19]. However the $\{FeNO\}^7$ triatomic groups found in $[Fe(NO)(das)_2][ClO_4]_2$ (das is *o*-phenylenebis(dimethylarsine)), in $[N(C_2H_5)_4]_2[Fe(NO)(CN)_4]$ and in Fe(NO)(TMC) are nearly linear at 173°, 177° and 178°, respectively [3, 4, 20]. Another structurally characterized $\{FeNO\}^7$ complex is $Fe(NO)(S_2CN(CH_3)_2)_2$ which has a somewhat bent (160°) $\{FeNO\}^7$ moiety [21] at room temperature and a nearly linear (170°) $\{FeNO\}^7$ moiety [22] at –80 °C. The low barrier between linear and bent geometries previously proposed [23] for $\{FeNO\}^7$ complexes could account for the wide range of Fe–N–O angles observed as well as the large thermal motions generally found for the nitrosyl groups in these complexes.

TABLE VIII. Equations of Least-squares Planes and Distances of the Individual Atoms From the Planes for Fe(NO)(salen).^{a}

(A): O(1), N(1), C(1), C(2), C(3), C(4), C(5), C(6), C(7)

Low Temperature				*Room Temperature*			
9.9514 X + 7.1167 Y + 2.7017 Z − 10.946 = 0				11.574 X + 6.9360 Y + 2.7512 Z − 11.514 = 0			
O(1)	−0.016(21)	C(4)	0.003(21)	O(1)	0.040(9)	C(4)	0.053(17)
N(1)	0.013(26)	C(5)	−0.023(22)	N(1)	0.014(13)	C(5)	−0.010(14)
C(1)	−0.012(24)	C(6)	−0.030(21)	C(1)	−0.035(15)	C(6)	−0.040(17)
C(2)	0.014(24)	C(7)	0.028(33)	C(2)	−0.011(16)	C(7)	0.000(15)
C(3)	0.022(20)			C(3)	−0.011(17)		

(B): O(2), N(2), C(10), C(11), C(12), C(13), C(14), C(15), C(16)

Low Temperature				*Room Temperature*			
8.5635 X + 7.4039 Y + 2.5246 Z − 10.332 = 0				8.4143 X + 7.5361 Y + 2.5065 Z − 10.421 = 0			
O(2)	0.050(22)	C(13)	0.009(21)	O(2)	0.038(10)	C(13)	−0.026(15)
N(2)	−0.059(30)	C(14)	0.002(22)	N(2)	−0.080(12)	C(14)	−0.012(17)
C(10)	0.072(36)	C(15)	−0.017(21)	C(10)	0.073(16)	C(15)	0.003(15)
C(11)	−0.023(21)	C(16)	−0.029(21)	C(11)	0.003(13)	C(16)	−0.020(18)
C(12)	−0.004(20)			C(12)	0.021(14)		

(C): O(1), O(2), N(1), N(2)

Low Temperature				*Room Temperature*			
5.6069 X + 7.5616 Y + 2.7742 Z − 9.6874 = 0				5.2780 X + 7.6067 Y + 2.9264 Z − 9.6941 = 0			
O(1)	−0.006(21)	N(1)	0.006(27)	O(1)	0.026(9)	N(1)	−0.028(13)
O(2)	0.006(22)	N(2)	−0.006(30)	O(2)	−0.026(10)	N(2)	0.028(12)

[a] Distances in Angströms. The equations are referred to the crystal axes and X, Y and Z are fractional orthorhombic coordinates.

In both forms of Fe(NO)(salen) the $\{FeNO\}^7$ group is disordered and is bent toward the phenylene moieites of the salen ligand. The nitrosyl bond lengths for the LT structure were fixed at 1.15 Å in the model selected to allow for disorder in the nitrogen position. In the RT structure the nitrosyl nitrogen atom may also be slightly disordered as indicated by the observed N–O distances of 1.11 and 1.09 Å. Examination of the thermal ellipsoid for N(3) in Figs. 1 and 2 shows that it is slightly elongated in the direction expected for this type of disorder; however, the magnitude of this elongation is less than the magnitudes of the elongation of many of the other atoms in the structure (see Fig. 1 and Table IV).

Examination of the FeNO parameters indicates that the FeNO group is more strongly bent in the LT structure than in the RT structure. However, the Fe–N–O angle is especially sensitive to the disorder model chosen to describe N(3). Moreover the average Fe–N(3)–O(3) angles of 127° (LT) and 147° (RT) differ by only ~3σ, and hence are marginally significant. The Fe–NO distances of 1.78 Å in the RT structure and 1.80 Å in the LT structure are slightly longer than the distances reported previously for $\{FeNO\}^7$ complexes [2, 3, 19–22]. They are, however, essentially the same as the 1.81 Å found in Co(NO)(salen) [6] and the 1.74 Å found in Fe(NO)(TMC) [4]. The refined occupation factors for the nitrosyl groups in the LT structure are 0.57 for NO(A) and 0.43 for NO(B).

The decrease of ~0.1 Å in the distance of the Fe atom to the N atoms of the salen ligand between the RT and LT forms is consistent with a change in spin state from S = 3/2 to S = 1/2, but the errors are such that this structural difference is barely significant. The distance from the Fe atom to the mean plane of the coordinating N and O atoms of the salen ligand also decreases ~0.1 Å from 0.47 to 0.36 Å, consistent with spin-pairing. The distances from the Fe atom to the O atoms of the salen ligand, however, range from 1.87 to 1.93 Å and do not differ significantly. The angles about the Fe atom are normal for salen complexes.

The observed distances and angles within the salen ligand are similar to those in other metal salen complexes which have been structurally characterized [24] except for the abnormally short C(8)–C(9) distance of 1.37 Å in the RT structure and 1.25 Å in the LT structure. These short distances as well as large thermal parameters for C(8) and C(9) suggest the possibility of conformational disorder, but a

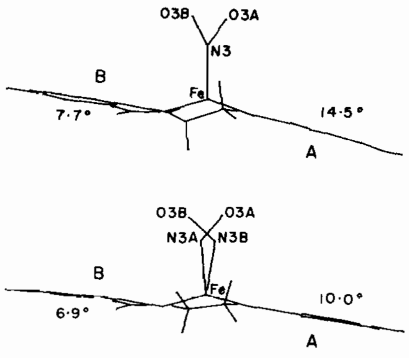

Figure 4. Line drawings of Fe(NO)(salen). The view orientation is parallel to the salen coordination plane. The top molecule is the RT form and the bottom molecule is the LT form. The angle between planes *A* and *B* is 8.2° in the RT form and 3.9° in the LT form.

TABLE IX. Important Nonbonded Contacts to the Atoms of Planes *A* and *B* in Fe(NO)(salen).[a]

Contacts to	on atom	from atom	a–a[b] 23 °C	a–a[b] −175 °C
Top of Plane *A*	c			
Top of Plane *B*	N(2)	C(15)	3.55	3.50
	C(10)	O(2)	3.29	3.22
	C(10)	C(15)	3.55	3.45
	C(10)	C(16)	3.70	3.63
	C(12)	O(1)	3.60	3.50
	C(12)	O(2)		3.66
	C(13)	C(6)	3.72	3.73
	C(13)	C(7)	3.52	3.48
	C(13)	N(1)	3.62	3.51
	C(15)	C(10)		3.61
Bottom of Plane *A*	O(1)	C(12)	3.60	3.50
	C(6)	C(13)	3.72	3.73
	C(7)	C(13)	3.52	3.48
	N(1)	C(13)	3.62	3.51
Bottom of Plane *B*	C(10)	C(15)		3.61
	C(15)	C(10)	3.55	3.45
	C(15)	N(2)	3.55	3.50
	C(16)	C(10)	3.70	3.63
	O(2)	C(10)	3.29	3.22
	O(2)	C(12)		3.66

[a] Contacts are tabulated only for the nonhydrogen atoms. Distances are in ångströms. [b] Interatomic distances. [c] The closest contact on top of plane *A* is 3.80 Å.

search of difference electron density maps did not yield alternative positions for these C atoms. The unreaslistic C–C distances may be an artifact of the pseudo C-centered unit cell which causes most reflections with $h + k \neq 2n$ to be weak or unobserved (*vide supra*).

Line drawings of the molecule viewed parallel to the best weighted least-squares plane through the coordinating atoms of each salen ligand are given in Fig. 4. The conformation of the salen ligand is conveniently discussed in terms of three planes [5, 24]. Place *C* is the best plane through the four coordinating atoms of the salen ligand. Planes *A* and *B* are the best planes through the two salicylideneiminato moieties. Plane *A* is adjacent to C(8); plane B is adjacent to C(9). The equations for these planes along with the atoms constituting each of them are given in Table VIII. Both forms exhibit a stepped conformation [5, 24] with the RT form displaying a greater deviation from overall planarity of the salen ligand. The interplanar angles are given in Fig. 4. The difference in the conformations at the two temperatures is that plane *A* has moved up about 4.4° relative to planes *B* and *C* on going from 23 °C to −175 °C.

A plausible explanation for the conformational difference is provided by the packing diagrams and the nonbonded intermolecular contacts. Fig. 5 shows stereopacking diagrams oriented perpendicular to the *ab* plane (Fig. 5a) and perpendicular to the *ac* plane (Fig. 5b), and Table IX gives nonbonded interactions to planes *A* and *B*. The contacts listed in Table IX can be readily observed in the packing diagrams in Fig. 5. The important point here is that there are *no* contacts on the top side of plane *A* that are less than Van der Waals distances [estimated to be ∼3.45 Å plane to plane from the Co(NO)(salen) structure [6] and from Pauling's [25] tabulation of Van der Waals radii which gives the half thickness of an aromatic ring to be 1.7 Å]. However, there are contacts on the

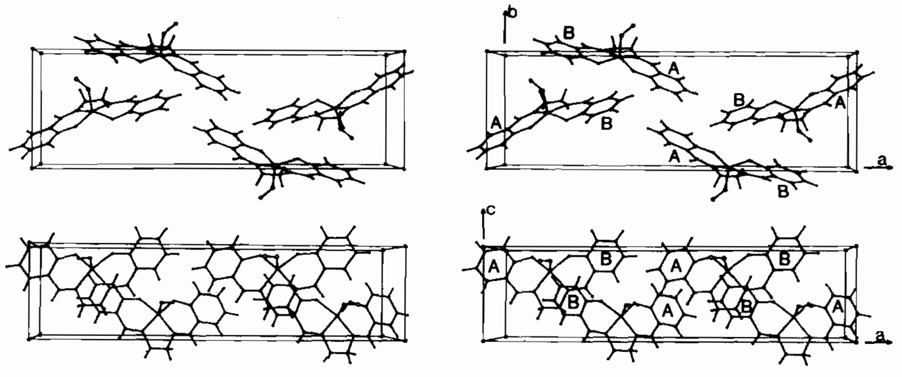

Figure 5. Stereoviews of the packing of Fe(NO)(salen); (a) Perpendicular to the *ab* plane and (b) perpendicular to the *ac* plane.

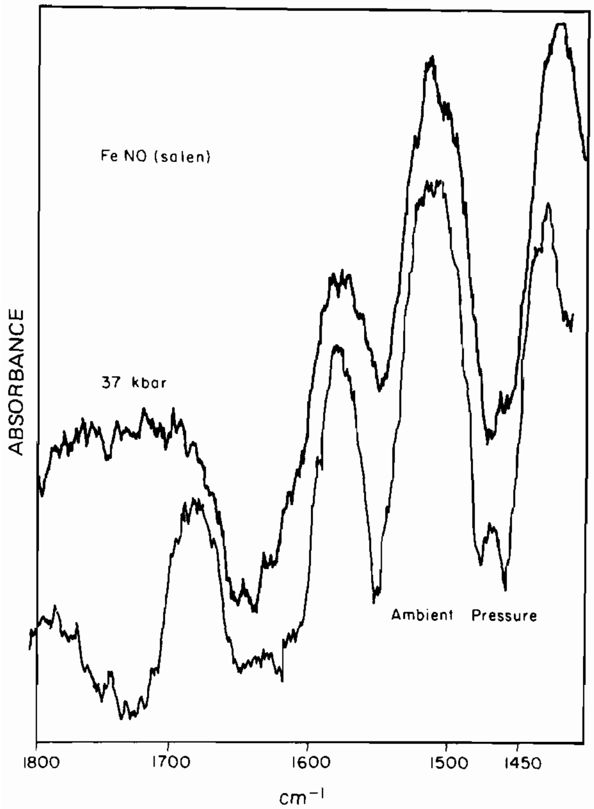

Figure 6. Infrared spectrum of solid Fe(NO)(salen) at ambient pressure (lower curve) and at 21 kbar (upper curve). Experiment made in DAC with Type II diamond windows.

bottom of plane *A* such as C(13) under C(6), C(7) and O(1) with an atom to plane contact distance of 3.45 Å in the RT structure and 3.38 Å in the LT structure, and an interaction between the top edge of plane *B* on one molecule [in the region of C(15), C(16) and O(2)] and the bottom edge of plane *B* on the adjacent molecule [in the region of N(2), C(10), C(11) and C(12)] with atom to plane contact distances of 2.5 to 3.2 Å at both temperatures. Thus, since plane *B* has appproximately equal nonbonded contacts on both the top and bottom while plane *A* has nonbonded contacts only on the bottom, one would expect that any conformational change brought about by lattice contraction on cooling would show up predominantly in the upward movement of plane *A* as observed. Calculation of the angles between planes *A*, *B* and *C* and the unit cell faces verifies that plane *A* has moved while planes *B* and *C* have remained in essentially the same orientation.

In summary, lowering the temperature of crystals of Fe(NO)(salen) from 23 °C to –175 °C results in three changes in the molecular parameters which decrease the molecular volume: 1) a smaller Fe–N(3)–O(3) angle; 2) a smaller displacement of the iron atom from the salen coordination plane; 3) a closer approach to coplanarity of the salicylidene-iminato moieties of the salen ligand. These structural changes are also consistent with a change of the spin state of Fe(NO)(salen) upon cooling from S = 3/2 to S = 1/2.

External pressure can also decrease molecular volume [26] and it was thought that conversion of Fe(NO)(salen) from the S = 3/2 form to the S = 1/2 form should occur upon applying external pressure at ambient temperature. The pressure dependence of the infrared spectrum of Fe(NO)(salen) provides a convenient spectroscopic probe of this possibility because ν_{NO} is distinctly different for the two spin states (1710 cm^{-1} for S = 3/2 and ~1610 cm^{-1} for S = 1/2). Infrared spectra were obtained for various pressures ranging from ambient pressure up to 37 kbar. The spectra for the ν_{NO} region of Fe(NO)(salen) at ambient pressure and at 21 kbar are given in Fig. 6. The appearance of the band at 1610 cm^{-1} is accompanied by the disappearance of the band at 1710 cm^{-1}. At 37 kbar the band at 1710 cm^{-1} is absent, but the band at 1610 cm^{-1} is obscured by the intense salen ligand band at 1630 cm^{-1}. Upon removing the pressure the band at 1610 cm^{-1} disappears and the 1710 cm^{-1} band reappears. These infrared results clearly show that solid Fe(NO)(salen) can be converted to the S = 1/2 spin state by applying external pressure at ambient temperature.

The Mössbauer spectrum of Fe(NO)(salen) has been investigated in several laboratories [4, 27, 28]. Temperature dependent Mössbauer studies [4, 27] are consistent with Fe(NO)(salen) being a two state, S = 3/2, S = 1/2 system.

Summary

Two ligand systems, salen and TMC, are now known to give well-characterized {FeNO}^{7} complexes which exhibit an S = 3/2 spin state at room temperature and which show spin-state changes upon cooling. The present work on Fe(NO)(salen) provides the first structural characterization of {FeNO}^{7} in both spin states while the structure of Fe(NO)(TMC) with S = 3/2 has been determined at room temperature [4]. In spite of the crystallographic difficulties presented by Fe(NO)(salen) it is quite obvious that it is structurally distinct from Fe(NO)(TMC). Fe(NO)(salen) has essentially tetragonal pyramidal coordination geometry at both temperatures and a strongly bent FeNO group, whereas the coordination geometry of Fe(NO)(TMC) at room temperature is distorted toward a trigonal bipyramid, and the FeNO group is essentially linear. The spectroscopic properties of the two complexes also differ significantly. The NO stretch of Fe(NO)(salen) decreases from 1710 cm^{-1} to ~1630 cm^{-1} upon cooling or under pressure. The NO stretch of Fe(NO)(TMC) is unusually high (1840

cm^{-1}) and broadens only slightly upon cooling to ~−230 °C [4].

Thus, Fe(NO)(salen) and Fe(NO)(TMC) must have different electronic structures in both the $S = 1/2$ and the $S = 3/2$ spin states. These recent results suggest that there are even more electronic structures possible for $\{FeNO\}^7$ complexes than were previously considered [2, 3]. A more detailed analysis of the electronic structures of $\{FeNO\}^7$ complexes in light of current information is deferred to a future paper.

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Supplementary Material Available

A listing of the anisotropic thermal parameters (Table S1) for the 23 °C structure as well as listings of $10\,|F_o|$ and $10\,|F_c|$ for the 23 °C structure (Table S2) and the −175 °C structure (Table S3) are available from the Editor as supplementary material (11 pages).

References

1 A. Earnshaw, E. A. King and L. F. Larkworthy, *J. Chem. Soc. A*, 2459 (1969).

2 J. H. Enemark and R. D. Feltham, *Coord. Chem. Revs.*, *13*, 339 (1974).

3 J. H. Enemark, R. D. Feltham, B. T. Huie, P. L. Johnson and K. B. Swedo, *J. Am. Chem. Soc.*, *99*, 3285 (1977).

4 K. D. Hodges, R. G. Wollman, S. L. Kessel, D. N. Hendrickson, D. G. Van Derveer, and E. K. Barefield, submitted for publication; TMC is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

5 J. R. Ferraro and L. J. Basile, *Appl. Spectrosc.*, *28*, 505 (1974).

6 K. J. Haller and J. H. Enemark, *Acta Cryst.*, *B34*, 102 (1978).

7 G. Germain, P. Main and M. M. Woolfson, *Acta Cryst.*, *A27*, 368 (1971).

8 D. T. Cromer and J. T. Waber, *Acta Cryst.*, *18*, 104 (1965).

9 D. T. Cromer, *Acta Cryst.*, *18*, 17 (1965).

10 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, *42*, 3175 (1965).

11 K. A. Kerr and J. P. Ashmore, *Acta Cryst.*, *A30*, 176 (1974).

12 K. J. Haller, *Ph.D. Thesis*, The University of Arizona (1978).

13 W. C. Hamilton, "Statistics in Physical Sciences", Ronald Press, New York, N.Y., pp. 157–162 (1964).

14 D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, *10*, 1035 (1970).

15 C. S. Pratt, B. A. Coyle and J. A. Ibers, *J. Chem. Soc. A*, 2146 (1971).

16 J. A. Ibers, *Acta Cryst.*, *B27*, 250 (1971).

17 L. D. Brown and K. N. Raymond, *Inorg. Chem.*, *14*, 2595 (1975).

18 J. H. Enemark and R. D. Feltham, *J. Am. Chem. Soc.*, *96*, 5002 (1974).

19 W. R. Scheidt, *Accts. of Chem. Res.*, *10*, 339 (1977).

20 J. Schmidt, H. Kühr, W. L. Dorn, and J. Kopf, *Inorg. Nucl. Chem. Letters*, *10*, 55 (1974).

21 G. R. Davies, R. H. B. Mais and P. G. Owston, *Chem. Comm.*, 81 (1968).

22 G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais and P. G. Owston, *J. Chem. Soc. A*, 1275 (1970).

23 M. Quinby-Hunt and R. D. Feltham, *Inorg. Chem.*, *17*, 2515 (1978).

24 M. Calligaris, G. Nardin and L. Randaccio, *Coord. Chem. Rev.*, *7*, 385 (1972).

25 L. Pauling, "The Nature of the Chemical Bond", 3rd Ed., Cornell University Press, Ithaca, New York, p. 260 (1960).

26 J. R. Ferraro and G. J. Long, *Acc. Chem. Res.*, *8*, 171 (1975).

27 H. H. Wickman, personal communication.

28 H. Mosback and K. G. Poulsen, *Acta Chem. Scand.*, *25*, 2421 (1971).