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Synthesis and Structure of $Fe(L'H)(NO)_2$, a Tetracoordinate Complex Having a Twelve-Membered Chelate Ring, and Its Conversion to Pentacoordinate $FeL'(NO)$ through Formal Loss of "HNO" ($L' = {}^-SCH_2CH_2NMeCH_2CH_2CH_2NMeCH_2CH_2S^-$)

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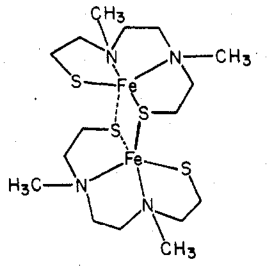
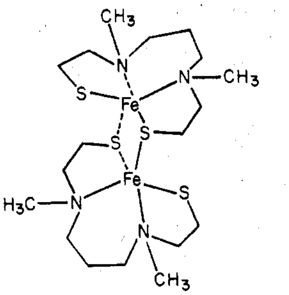
The reaction of $(FeL')_2$, where L' is the dianion of *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine, with $NOPF_6$ in dichloromethane gave, after chromatography on alumina, a small crop of olive green crystals. X-ray diffraction studies revealed the presence of two crystalline forms, one of which (**1**) contained $Fe(L'H)(NO)_2$, the other (**2**) being a 1:1 mixture of $FeL'(NO)$ and $Fe(L'H)(NO)_2$. A pure sample of $Fe(L'H)(NO)_2$ was subsequently obtained in the reaction of $[Fe(NO)_2Br_2]^-$ with $L'H_2$. The molecule $Fe(L'H)(NO)_2$ has pseudotetrahedral iron coordination geometry comprised of two linear nitrosyl ligands and two sulfur atom donors of the potentially tetradentate ligand $L'H$. Average molecular dimensions are as follows: Fe–N, 1.67 (1) Å; Fe–S, 2.272 (6) Å; S–Fe–S, 109.2 (1)°; N–Fe–N, 118.2 (5)°; S–Fe–N, 107 (4)°. An unusual feature of the structure is that the two nitrogen atoms of the ligand are not coordinated to the iron atom, resulting in a 12-membered chelate ring. One of these $L'H$ nitrogens is protonated (N–H = 0.88 Å) and intramolecularly hydrogen bonded to the other nitrogen atom (N···H = 2.10 Å; N–H···N = 140°). The resulting six-membered H–N–C–C–C–N ring, including the hydrogen bond, has the chair conformation. The geometry of $FeL'(NO)$ is that of a square-based pyramid with the base of the pyramid containing two sulfur (Fe–S = 2.22 (2) Å) and two nitrogen (Fe–N = 2.09 (1) Å) atoms of the now tetradentate L' ligand and the apex of the pyramid occupied by a bent nitrosyl ligand (Fe–N = 1.697 (9) Å; Fe–N–O = 155.2 (9)°). Both $Fe(L'H)(NO)_2$ and $FeL'(NO)$ are 17-electron paramagnetic species. Temperature-dependent electron spin resonance studies show that in $FeL'(NO)$ there is hyperfine coupling of the odd electron to the nitrogen atom of the nitrosyl ligand (A = 12 G) while in $Fe(L'H)(NO)_2$ no such coupling is observed. The transformation of $Fe(L'H)(NO)_2$ to $FeL'(NO)$ through formal loss of "HNO" was observed in solution by infrared spectroscopy.

The physical properties and chemical reactions of the sulfur-bridged dimeric iron(II) compounds $(FeL)_2$ and $(FeL')_2$,



$(FeL)_2$

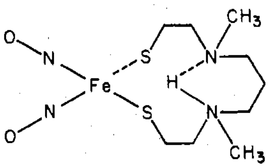


$(FeL')_2$

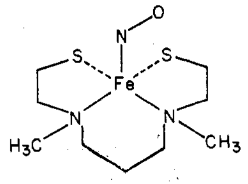
where L and L' are potentially tetradentate N_2S_2 ligands, have been previously reported.[1-5] The reaction of $(FeL)_2$ with nitrosonium (NO^+) salts produced the binuclear complex $[(FeL)_2NO]^+$, which contains a bridging nitrosyl ligand.[4] Also obtained was mononuclear FeL(NO), although the best synthesis of this compound is in the reaction of $(FeL)_2$ with nitric oxide.[5]

Parallel studies of the chemistry of $(FeL')_2$ with nitrosonium salts did not generate a nitrosyl-bridged complex. Chromatography of the reaction mixture of $(FeL')_2$ with $NOPF_6$ on aluminum oxide gave a green band, shown to be $FeL'(NO)$, and an olive green-brown band that yielded two types of crystals upon workup.[5,6] Elemental analyses of this mixture best fit the formula "$FeL'(NO)_2$", but the presence of three nitrosyl stretching bands in the infrared spectrum at 1735 (s), 1700 (s, br), and 1645 (s, br) cm^{-1} suggested that the material was something more complicated.

As described here, single-crystal X-ray diffraction studies of the two crystalline forms showed one (**1**) to be the novel compound $Fe(L'H)(NO)_2$ and the other (**2**) to be a 1:1 mixture of $Fe(L'H)(NO)_2$ and $FeL'(NO)$. Since the synthesis



$Fe(L'H)(NO)_2$



$FeL'(NO)$

of these compounds was serendipitous, difficult to reproduce, and in low yield, a new preparative route to $Fe(L'H)(NO)_2$ was devised. As a consequence, we were able to study its properties and present our findings in this paper.

Experimental Procedure and Results

All work, unless otherwise specified, was performed under a nitrogen atmosphere. The ligand $L'H_2$ was prepared as described previously.[2] The compound $[(Ph_3P)_2N][Fe(NO)_2Br_2]$ and its precursor $[(Ph_3P)_2N][Fe(CO)_3(NO)]$ were prepared by a literature procedure.[7] Other chemicals were commercially available, reagent grade materials, used without further purification. The chromatography material used was "Baker analyzed" reagent acid-washed aluminum oxide. Microchemical analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Synthesis of $Fe(C_9H_{21}N_2S_2)(NO)_2$, $Fe(L'H)(NO)_2$ (1). There are several alternative ways of generating $Fe(L'H)(NO)_2$.[6] The method described here gives the best yield and greatest purity of the compound. A 0.45-g (5.5×10^{-4} mol) portion of $[(Ph_3P)_2N][Fe(NO)_2Br_2]$ was combined with 0.15 mL (6.8×10^{-4} mol) of $L'H_2$ in approximately 75 mL of dichloromethane. The reaction mixture was stirred for about 30 min at 0 °C after which time the solution was concentrated and chromatographed on acid-washed aluminum oxide. The preparation

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(1) Hu, W. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1974**, *96*, 2366.
(2) Karlin, K. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 6951.
(3) Ginsberg, A. P.; Lines, M. E.; Karlin, K. D.; Lippard, S. J.; DiSalvo, F. J. *J. Am. Chem. Soc.* **1976**, *98*, 6958.
(4) (a) Karlin, K. D.; Lewis, D. L.; Rabinowitz, H. N.; Lippard, S. J. *J. Am. Chem. Soc.* **1974**, *96*, 6519. (b) Rabinowitz, H. N.; Karlin, K. D.; Lippard, S. J. *Ibid.* **1977**, *99*, 1420.
(5) Karlin, K. D.; Rabinowitz, H. N.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1977**, *16*, 3262.
(6) Karlin, K. D. Ph.D. Dissertation, Columbia University, 1975.
(7) Connelly, N. G.; Gardner, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1525.

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of the chromatography column influences the type of products obtained. To obtain exclusively Fe(L′H)(NO_2), we packed the 2.5 cm × 40 cm column with a freshly opened bottle of alumina using reagent grade anhydrous methanol. The column was then washed with a 1:1 mixture of methanol and dichloromethane and finally with dichloromethane. The reaction mixture was then passed through the column. Fe(L′H)$(NO)_2$ eluted as an olive green band which was collected and reduced to dryness under vacuum. Crystals of Fe(L′H)$(NO)_2$ were grown at 0 °C from a concentrated dichloromethane solution onto which diethyl ether was carefully layered. It was found unnecessary to do the chromatography under a nitrogen atmosphere. Crystallizations were performed under nitrogen to retard decomposition.

The course of the reaction of $[Fe(NO)_2Br_2]^-$ with L′H_2 may be followed by solution infrared spectroscopy which showed rapid disappearance of the two NO stretching frequencies due to $[Fe(NO)_2Br_2]^-$ (1780, 1710 cm^{-1}) and the appearance of the two NO frequencies of Fe(L′H)$(NO)_2$ (1740, 1695 cm^{-1}). On occasion the yield of Fe(L′H)$(NO)_2$ could be quite high (77%), but the amount of material isolated was usually much smaller owing to its propensity to form the one-to-one mixture of Fe(L′H)$(NO)_2$ and FeL′(NO) (**2**) during recrystallization. Consequently there was never enough material for an elemental analysis. With the excellent refinement of the Fe(L′H)$(NO)_2$ crystal structure (vide infra), we believe the complex to be sufficiently well characterized. IR (Nujol mull, KBr plates): 1740 (s), 1695 (s), 1305, 1295, 1275, 1265, 1200 (s, br, mult), 1070, 1065, 1045 (s, br, mult), 1000, 980, 960, 935, 840 (br, mult), 800 (br, mult), 775, 750, 725 (s), 695 (s) cm^{-1}.

Synthesis of the 1:1 Mixture (2) of Fe($C_9H_{21}N_2S_2$)$(NO)_2$ and Fe($C_9H_{20}N_2S_2$)NO, Fe(L′H)$(NO)_2$·FeL′(NO). Crystals of this material can be obtained by passing the reaction mixture containing Fe(L′H)$(NO)_2$, described above, through acid-washed aluminum oxide which had been stored without special precautions on the laboratory shelf and thereby, presumably, absorbing water. Elution of the sample with dichloromethane causes broadening of the band and a progressive color change from the olive green of Fe(L′H)$(NO)_2$ to the bright green of FeL′(NO). A concentrated dichloromethane solution of the mixture of compounds layered with diethyl ether and kept at 0 °C yields needles of the one-to-one mixture of complexes. The cocrystallized species was also obtained on occasion from solutions of Fe(L′H)$(NO)_2$ which, over a period of time, change to mixtures of the mono- and dinitrosyl complexes. IR (Nujol mull, NaCl plates): 1740 (s), 1695 (s), 1645 (s), 1305, 1272, 1256, 1229, 1211, 1186, 1157, 1142, 1122, 1098, 1057, 1043, 1025, 994, 970, 952, 947, 934, 912, 861, 790, 767, 754, 729 (br, mult) cm^{-1}. Anal. Calcd for the one-to-one mixture of Fe(L′H)$(NO)_2$ and FeL′(NO), $C_{18}H_{41}N_7S_4O_3Fe_2$: C, 33.60; H, 6.42; N, 15.24; S, 19.93. Found: C, 33.66; H, 6.46; N, 15.16; S, 19.76.

Collection and Reduction of X-ray Data. Fe(L′H)(NO)$_2$ (1). The crystal used for the structure determination was an irregularly shaped seven-faced prism with approximate orthogonal dimensions 0.20 mm × 0.25 mm × 0.32 mm. Preliminary precession and Weissenberg photographs (λ 1.5418 Å) showed the crystal to have $2/m$ Laue symmetry, and the systematic absences $h0l$ when $l \neq 2n$ indicated the space group to be either $P2/c$ (C_{2h}^4, No. 13) or its noncentrosymmetric equivalent Pc (C_s^2, No. 7).[8] The quality of the data crystal was checked by taking open-counter ω scans of several strong low-angle reflections. The average width at half-height of these peaks was 0.12°. Details of the data collection and reduction are given in Table I.

Fe(L′H)(NO)$_2$·FeL′(NO) (2). A platelike crystal bounded by the faces (100) and ($\bar{1}$00), 0.066 mm apart, (001) and (00$\bar{1}$), 0.363 mm apart, and (010) and (0$\bar{1}$0), 0.396 mm apart, was used in the diffraction study. The crystal, mounted approximately along [010], was shown to have Laue symmetry $2/m$ from preliminary precession and Weissenberg photographs (λ 1.5418 Å). Systematic absences $h0l$ when $l \neq 2n$ and $0k0$ when $k \neq 2n$ uniquely determined the space group as $P2_1/c$ (C_{2h}^5, No. 14).[8] Open-counter ω scans of several strong low-angle reflections had average half-height widths of 0.12°. Details of the data collection and reduction appear in Table I.

Structure Solution and Refinement. Compound 1. The structure of Fe(L′H)$(NO)_2$ was determined by the heavy-atom method. A Patterson map showed the space group to be Pc and was solved for the positions of the iron and sulfur atoms. Subsequent difference Fourier maps revealed the positions of all the remaining atoms including hydrogen. All nonhydrogen atoms were refined anisotropically, and hydrogen atoms were successfully refined with individual isotropic temperature factors. Neutral atom scattering factors for the nonhydrogen atoms and corrections for the anomalous dispersion effects for the iron and sulfur atoms were obtained from ref 9. Scattering

Table I. Experimental Details of the X-ray Diffraction Study of Fe(L′H)$(NO)_2$ (1) and Fe(L′H)$(NO)_2$·FeL′(NO) (2)[a]

	Fe(L′H)$(NO)_2$[b]	Fe(L′H)$(NO)_2$·FeL′(NO)
(A) Crystal Parameters at 23 °C[c]		
a, Å	8.611 (3)	15.572 (9)
b, Å	7.112 (2)	13.996 (8)
c, Å	12.616 (4)	13.677 (6)
β, deg	103.22 (2)	104.80 (3)
V, $Å^3$	752.13	2881.95
mol wt	337	643
cryst system	monoclinic	monoclinic
space group	Pn[d]	$P2_1/c$
Z	2	4
ρ(calcd), g cm^{-3}	1.489	1.482
ρ(obsd), g cm^{-3}	1.47 (1)[e]	1.45 (1)[f]
(B) Measurement of Intensity Data		
instrument	Picker FACS-I-DOS diffractometer	
radiation	Mo Kα ($λ_{α_1}$ 0.7093 Å), graphite monochromatized	
takeoff angle, deg	1.7	1.8
detector aperture, mm^2	4.5 × 4.5	6.3 × 6.3
crystal–detector dist, cm	33	
scan technique	coupled θ(cryst)–2θ(counter)	
scan range, deg	1.5 (symmetric, plus $Kα_1$–$Kα_2$ dispersion)	
scan rate	1° min^{-1} in 2θ	
max 2θ, deg	55	
bkgd measurements	stationary crystal, stationary counter; 20-s counts at each end of 2θ scan range	
stds[g]	three reflctns (1$\bar{3}$6), ($\bar{4}$32), and (2$\bar{3}$2) measd every 97 data reflctns	three reflctns (30$\bar{4}$), ($\bar{4}\bar{1}$0), and ($\bar{1}\bar{2}$2) measd every 47 data reflctns
no. of reflctns collected	2291 reflctns [$2θ \leqslant 30°$ (±h, +k, ±l), $30 < 2θ \leqslant 55°$ (+h, +k, ±l)]	6431 reflctns [$2θ \leqslant 30°$ (±h, +k, ±l), $30 < 2θ \leqslant 55°$ (+h, +k, ±l)]
(C) Treatment of Intensity Data		
reduction to preliminary F_o^2 and $σ(F_o^2)$	correction for background, attenuators and Lorentz–polarization of monochromatized X radiation in the usual manner[h]	
ε[i]	0.04	0.05
μ, cm^{-1}	12.6	12.0
transmission factors	estimated range 0.7–0.8[j]	0.669–0.923
averaging		$R_{av} = 0.038$[k]
scaling	not done; final scale factor was 4.697 (7)	Wilson's method[l]
obsd unique data [$F_o^2 > 2σ(F_o^2)$]	1645	2322

[a] For a list of computer programs used in this work see: Lerner, E. I.; Lippard, S. J. *Inorg. Chem.* 1977, *16*, 1546, Table I, footnote *c*. [b] Unit cell used in final refinement. The unit cell used for the data collection, reduction, and structure solution is described in the text. [c] From a least-squares fit to the setting angles of 12 reflections. [d] A nonstandard setting of space group Pc (C_s^2, No. 7) having the general equivalent positions (x, y, z) and ($^1/_2 + x$, $-y$, $^1/_2 + z$). [e] By suspension in a mixture of CCl_4 and hexane. [f] By suspension in aqueous NaI. [g] Showed only random, statistical fluctuations. [h] Gill, J. T.; Lippard, S. J. *Inorg. Chem.* 1975, *14*, 751. [i] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Ibid.* 1967, *6*, 197. [j] Absorption correction not applied. [k] $R_{av} = (\Sigma_{i=1}^{N}\Sigma_{j=1}^{n}|\bar{F}_i^2 - F_{ij}^2|)/\Sigma_{i=1}^{N}\bar{F}_i^2$, where N is the number of reflections measured more than once and n is the number of observations of the Nth reflection. [l] Wilson, A. J. C. *Nature (London)* 1942, *150*, 151.

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(8) "International Tables for X-ray Crystallography", 2nd ed.; Kynoch Press: Birmingham, England, 1965; Vol. I, pp 85, 97, 99.

Table II. Final Positional Parameters for the Atoms of $Fe(L'H)(NO)_2$ (1)[a]

atom	*x*	*y*	*z*
Fe	0.25	0.85088 (5)	0.25
S(1)	0.24778 (12)	0.53304 (9)	0.22951 (6)
S(2)	0.35984 (10)	0.98409 (9)	0.12119 (7)
O(1)	−0.0569 (3)	1.0144 (5)	0.2193 (3)
O(2)	0.4261 (4)	0.9200 (5)	0.4644 (2)
N(1)	0.2016 (3)	0.5863 (3)	−0.03026 (17)
N(2)	0.5330 (3)	0.6545 (3)	0.02928 (19)
N(3)	0.0644 (3)	0.9390 (4)	0.2232 (2)
N(4)	0.3663 (3)	0.8849 (4)	0.3750 (2)
C(1)	0.0757 (4)	0.4758 (5)	0.1224 (3)
C(2)	0.0577 (3)	0.5885 (5)	0.0174 (2)
C(3)	0.2511 (4)	0.3908 (4)	−0.0529 (2)
C(4)	0.4152 (4)	0.3785 (4)	−0.0768 (3)
C(5)	0.5468 (4)	0.4507 (4)	0.0157 (3)
C(6)	0.6036 (3)	0.7156 (4)	0.1402 (2)
C(7)	0.5707 (4)	0.9210 (4)	0.1598 (3)
C(8)	0.1704 (5)	0.7081 (5)	−0.1289 (3)
C(9)	0.6018 (5)	0.7581 (5)	−0.0495 (3)
H1C(1)	−0.021 (5)	0.504 (6)	0.144 (3)
H2C(1)	0.078 (4)	0.341 (5)	0.110 (3)
H1C(2)	−0.026 (6)	0.546 (7)	−0.041 (4)
H2C(2)	0.039 (4)	0.718 (5)	0.029 (3)
H1C(3)	0.252 (4)	0.321 (5)	0.017 (3)
H2C(3)	0.170 (5)	0.348 (5)	−0.110 (4)
H1C(4)	0.432 (4)	0.254 (5)	−0.090 (3)
H2C(4)	0.415 (4)	0.426 (5)	−0.152 (3)
H1C(5)	0.537 (5)	0.379 (6)	0.085 (4)
H2C(5)	0.656 (5)	0.407 (6)	0.006 (4)
H1C(6)	0.552 (4)	0.639 (5)	0.188 (3)
H2C(6)	0.730 (4)	0.695 (5)	0.160 (3)
H1C(7)	0.626 (5)	1.005 (6)	0.114 (4)
H2C(7)	0.611 (5)	0.946 (5)	0.231 (4)
H1C(8)	0.079 (6)	0.688 (6)	−0.176 (4)
H2C(8)	0.157 (5)	0.835 (5)	−0.115 (3)
H3C(8)	0.258 (6)	0.707 (6)	−0.161 (4)
H1C(9)	0.563 (5)	0.898 (6)	−0.064 (4)
H2C(9)	0.713 (7)	0.754 (8)	−0.030 (4)
H3C(9)	0.567 (5)	0.702 (6)	−0.122 (4)
H	0.284 (4)	0.639 (5)	0.015 (3)

[a] Atoms are labeled as shown in Figure 1. Hydrogen atoms are labeled according to the carbon atoms to which they are attached; that labeled H is bound to N(1). Standard deviations, in parentheses, occur in the last significant digit for each parameter.

factors for the hydrogen atoms were those of Stewart et al.[10]

For minimization of possible correlation problems due to a large β angle, the space group was changed from *Pc* [$a = 8.611$ (3) Å, $b = 7.112$ (2) Å, $c = 13.551$ (4) Å, $\beta = 115.00$ (2)°] to *Pn* by using the transformation matrix ($\bar{1}00$; $0\bar{1}0$; 101). The final full-matrix least-squares refinment, carried out in *Pn*, converged at $R_1 = 0.019$ and $R_2 = 0.024$.[11] The "goodness of fit" parameter $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ was 0.956 for NO = 1645 observations and NV = 245 variables. Inspection of the function $\sum w\Delta^2$ for groups of reflections ordered according to $|F_o|$ and $(\sin\theta)/\lambda$ showed satisfactory consistency, and the weighting scheme was therefore considered to be appropriate.[12] A final-difference Fourier map showed no peak greater than 0.20 e Å^{-3}. In the final cycle of refinement no parameter shifted by more than 0.024 of its estimated standard deviation. Since *Pn* lacks a center of symmetry, refinement of the alternative, inverted structure was carried out, leading to final values of 0.026 and 0.033 for R_1 and R_2, respectively. The original refinement was therefore taken to be correct. This assignment was also checked by comparison of Friedel pairs for several hundred low-angle reflections.

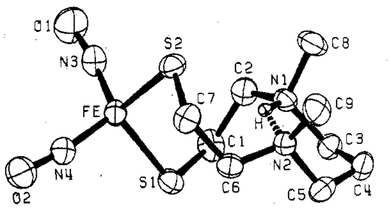

Figure 1. Structure of $Fe(L'H)(NO)_2$ in **1** showing the atom labeling scheme and 40% probability thermal ellipsoids.

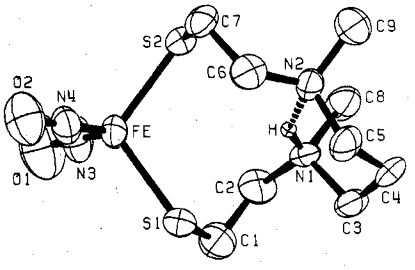

Figure 2. Structure of $Fe(L'H)(NO)_2$ in **2** showing the atom labeling scheme and 40% probability thermal ellipsoids.

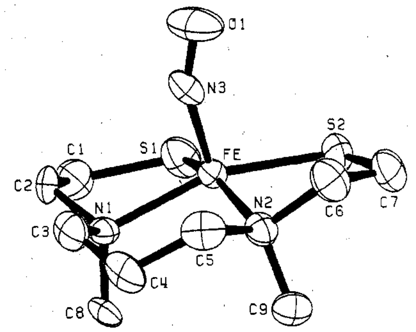

Figure 3. Structure of FeL'(NO) in **2** showing the atom labeling scheme and 40% probability thermal ellipsoids.

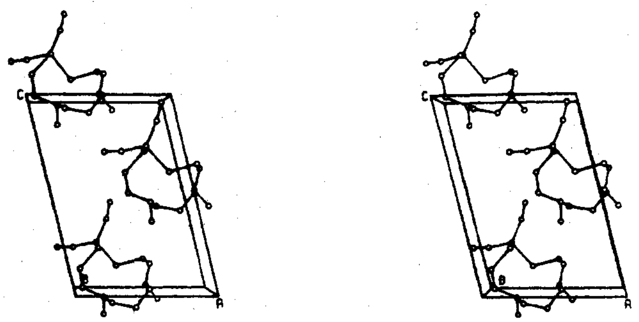

Figure 4. Stereo drawing of the unit cell contents of $Fe(L'H)(NO)_2$, **1**.

Compound 2. The structure of the 1:1 mixture of $Fe(L'H)(NO)_2$ and FeL'(NO) was solved in an analogous manner using Patterson and Fourier maps. Refinement[11] converged at $R_1 = 0.069$ and $R_2 = 0.061$. The standard deviation of an observation of unit weight was 1.29, and a check of the weighting scheme showed no unusual variations in the function $\sum w\Delta^2$.[12] A total of 311 variable parameters was used to fit 2322 data having $F_o^2 > 2\sigma(F_o^2)$. Nonhydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and included in the refinement as invariants with isotropic thermal parameters fixed at 4.0 Å^2. On a final difference Fourier map the largest peak was 0.60 e Å^{-3}. In the final cycle of refinement, no parameter shifted by more than 0.006 of its estimated standard deviation.

Atomic positional parameters, along with their standard deviations as derived from the inverse matrix of the final cycle of least-squares refinement, are given in Tables II and III for **1** and **2**, respectively. Tables IV and V list interatomic distances and angles for Fe-

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(9) Scattering factors for neutral nonhydrogen atoms were taken from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72 ff. Anomalous scattering factors were those of: Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

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

(11) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$. In the least-squares refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized.

(12) Cruickshank, D. W. J. In "Computing Methods of Crystallography"; Rollet, J. S., Ed.; Pergamon Press: Elmsford, N.Y., 1965; pp 112–115.

Table III. Final Positional Parameters for the Atoms of $Fe(L'H)(NO)_2 \cdot FeL'(NO)$ (2)[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
	$Fe(L'H)(NO)_2$				FeL'(NO)		
Fe	−0.41411 (11)	0.18512 (11)	0.08516 (13)	Fe	0.14057 (9)	0.29271 (10)	0.29138 (10)
S(1)	−0.4790 (2)	0.3276 (2)	0.0325 (3)	S(1)	0.0674 (2)	0.1597 (2)	0.2276 (2)
S(2)	−0.26412 (19)	0.20498 (20)	0.1357 (2)	S(2)	0.2479 (2)	0.24188 (20)	0.2256 (2)
O(1)	−0.4754 (8)	0.1147 (9)	0.2462 (8)	O(1)	0.0823 (6)	0.4269 (6)	0.1391 (6)
O(2)	−0.4592 (7)	0.0578 (7)	−0.0806 (7)	N(1)	0.0563 (5)	0.2954 (5)	0.3876 (5)
N(1)	−0.3164 (6)	0.4409 (6)	0.1667 (7)	N(2)	0.2393 (5)	0.3745 (5)	0.3879 (6)
N(2)	−0.2338 (6)	0.3890 (6)	0.0127 (7)	N(3)	0.0934 (6)	0.3814 (6)	0.2109 (7)
N(3)	−0.4451 (8)	0.1498 (7)	0.1857 (8)	C(1)	−0.0309 (7)	0.1685 (9)	0.2778 (8)
N(4)	−0.4391 (7)	0.1159 (7)	−0.0176 (8)	C(2)	−0.0320 (7)	0.2645 (8)	0.3235 (9)
C(1)	−0.4743 (9)	0.3931 (9)	0.1483 (11)	C(3)	0.0466 (8)	0.3924 (8)	0.4274 (8)
C(2)	−0.3838 (8)	0.4076 (8)	0.2176 (9)	C(4)	0.1334 (9)	0.4342 (7)	0.4894 (8)
C(3)	−0.3447 (8)	0.5293 (7)	0.1032 (9)	C(5)	0.2005 (8)	0.4586 (7)	0.4291 (8)
C(4)	−0.2840 (8)	0.5519 (7)	0.0348 (10)	C(6)	0.2958 (8)	0.4114 (8)	0.3234 (9)
C(5)	−0.2808 (8)	0.4729 (8)	−0.0393 (9)	C(7)	0.3325 (8)	0.3326 (9)	0.2729 (9)
C(6)	−0.2595 (8)	0.3014 (9)	−0.0443 (8)	C(8)	0.0810 (7)	0.2264 (8)	0.4732 (7)
C(7)	−0.2292 (7)	0.2108 (7)	0.0180 (8)	C(9)	0.2972 (7)	0.3201 (7)	0.4715 (7)
C(8)	−0.2309 (8)	0.4552 (8)	0.2460 (8)	H1C(1)	−0.083	0.160	0.225
C(9)	−0.1372 (9)	0.4017 (9)	0.0378 (10)	H2C(1)	−0.029	0.121	0.328
H1C(1)	−0.498	0.455	0.129	H1C(2)	−0.073	0.263	0.365
H2C(1)	−0.509	0.360	0.184	H2C(2)	−0.051	0.309	0.271
H1C(2)	−0.363	0.349	0.251	H1C(3)	0.025	0.434	0.372
H2C(2)	−0.387	0.454	0.268	H2C(3)	0.007	0.390	0.469
H1C(3)	−0.403	0.520	0.062	H1C(4)	0.160	0.388	0.540
H2C(3)	−0.344	0.582	0.147	H2C(4)	0.121	0.490	0.522
H1C(4)	−0.225	0.562	0.076	H1C(5)	0.170	0.498	0.374
H2C(4)	−0.304	0.609	−0.002	H2C(5)	0.247	0.494	0.472
H1C(5)	−0.251	0.496	−0.087	H1C(6)	0.343	0.447	0.364
H2C(5)	−0.340	0.455	−0.073	H2C(6)	0.261	0.451	0.272
H1C(6)	−0.234	0.302	−0.100	H1C(7)	0.382	0.304	0.321
H2C(6)	−0.322	0.300	−0.066	H2C(7)	0.353	0.357	0.219
H1C(7)	−0.166	0.208	0.032	H1C(8)	0.087	0.165	0.448
H2C(7)	−0.254	0.158	−0.024	H2C(8)	0.036	0.227	0.508
H1C(8)	−0.236	0.505	0.290	H3C(8)	0.136	0.246	0.517
H2C(8)	−0.215	0.397	0.284	H1C(9)	0.321	0.267	0.445
H3C(8)	−0.184	0.470	0.214	H2C(9)	0.343	0.359	0.508
H1C(9)	−0.109	0.347	0.071	H3C(9)	0.263	0.297	0.515
H2C(9)	−0.122	0.456	0.081				
H3C(9)	−0.120	0.413	−0.023				
H	−0.298 (7)	0.401 (8)	0.128 (8)				

[a] Atoms are labeled as shown in Figures 2 and 3. See footnote *a*, Table II.

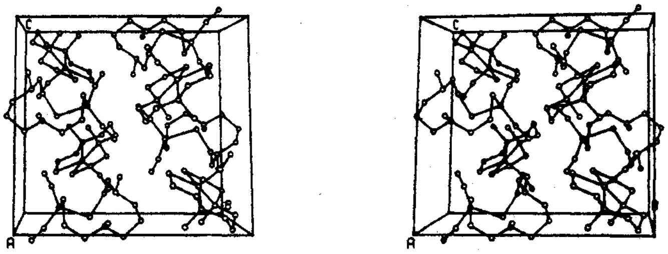

Figure 5. Stereo drawing of the unit cell contents of the 1:1 mixture of $Fe(L'H)(NO)_2$ and FeL'(NO), **2**.

$(L'H)(NO)_2$ in **1** and **2**, respectively. The geometry of FeL'(NO) in **2** is provided in Table VI. Listings of observed and calculated structure factor amplitudes, thermal parameters, root-mean-square amplitudes of thermal vibration for atoms refined anisotropically, and hydrogen atom geometry are provided as supplementary material. Views of the geometry of $Fe(L'H)(NO)_2$ in **1** and **2** are shown in Figures 1 and 2, respectively. The structure of FeL'(NO) in **2** is shown in Figure 3. Unit-cell packing diagrams of **1** and **2** are provided as Figures 4 and 5, respectively.

Electron Spin Resonance Studies. Electron spin resonance spectra were recorded by using a Varian E-line X band spectrometer operating in the 9.134–9.149 GHz range at a modulating frequency of 100 kHz. The samples used to record the spectra were degassed and sealed under vacuum. Crystals of **2** were dissolved to a concentration of about 1.2×10^{-2} M in dry acetonitrile. Compound **1** was dissolved in dichloromethane to a concentration of about 1.4×10^{-2} M. Spectra of the cocrystallized compounds (**2**) were taken over a temperature range of 6–263 K. The temperature was controlled with an Air Products LTD-3-110 liquid-helium cryostat and the temperature

Table IV. Interatomic Distances (Å) and Angles (Deg) for $Fe(L'H)(NO)_2$ in **1**[a]

	Distances		
Fe–S(1)	2.2748 (10)	N(1)–C(3)	1.501 (3)
Fe–S(2)	2.2663 (9)	N(1)–C(8)	1.490 (4)
Fe· · ·N(1)	3.942 (2)	N(2)–C(5)	1.467 (4)
Fe· · ·N(2)	4.330 (2)	N(2)–C(6)	1.458 (4)
Fe–N(3)	1.678 (3)	N(2)–C(9)	1.467 (4)
Fe–N(4)	1.681 (3)	C(1)–C(2)	1.525 (5)
S(1)–C(1)	1.809 (3)	C(3)–C(4)	1.514 (5)
S(2)–C(7)	1.825 (3)	C(4)–C(5)	1.519 (5)
O(1)–N(3)	1.165 (4)	C(6)–C(7)	1.519 (5)
O(2)–N(4)	1.156 (4)	N(1)–H	0.88 (4)
N(1)–C(2)	1.497 (4)	N(2)–H	2.12 (4)
	Angles		
S(1)–Fe–S(2)	109.15 (3)	C(5)–N(2)–C(6)	112.3 (2)
S(1)–Fe–N(3)	111.46 (9)	C(5)–N(2)–C(9)	111.2 (2)
S(1)–Fe–N(4)	103.75 (9)	C(6)–N(2)–C(9)	110.9 (3)
S(2)–Fe–N(3)	103.52 (9)	Fe–N(3)–O(1)	169.8 (3)
S(2)–Fe–N(4)	110.83 (10)	Fe–N(4)–O(2)	169.8 (3)
N(3)–Fe–N(4)	118.09 (12)	S(1)–C(1)–C(2)	115.7 (2)
Fe–S(1)–C(1)	107.0 (1)	N(1)–C(2)–C(1)	114.5 (2)
Fe–S(2)–C(7)	105.0 (1)	N(1)–C(3)–C(4)	114.2 (2)
C(2)–N(1)–C(3)	112.5 (2)	C(3)–C(4)–C(5)	113.2 (2)
C(2)–N(1)–C(8)	108.8 (2)	N(2)–C(5)–C(4)	111.0 (3)
C(3)–N(1)–C(8)	112.6 (2)	N(2)–C(6)–C(7)	113.0 (2)
H–N(1)–C(2)	111 (2)	S(2)–C(7)–C(6)	113.8 (2)
H–N(1)–C(3)	107 (2)	N(1)–H–N(2)	136 (3)
H–N(1)–C(8)	105 (2)		

[a] Atoms are labeled as shown in Figure 1. Standard deviations, in parentheses, occur in the last significant digit for each parameter. Distances are not corrected for thermal motion.

Table V. Interatomic Distances (Å) and Angles (Deg) for $Fe(L'H)(NO)_2$ in **2**[a]

	Distances		
Fe-S(1)	2.268 (4)	N(1)-C(3)	1.51 (1)
Fe-S(2)	2.277 (4)	N(1)-C(8)	1.50 (1)
Fe· · ·N(1)	3.939 (9)	N(2)-C(5)	1.47 (1)
Fe· · ·N(2)	4.294 (9)	N(2)-C(6)	1.45 (1)
Fe-N(3)	1.64 (1)	N(2)-C(9)	1.46 (1)
Fe-N(4)	1.67 (1)	C(1)-C(2)	1.50 (2)
S(1)-C(1)	1.81 (1)	C(3)-C(4)	1.52 (1)
S(2)-C(7)	1.83 (1)	C(4)-C(5)	1.51 (1)
O(1)-N(3)	1.16 (1)	C(6)-C(7)	1.53 (1)
O(2)-N(4)	1.17 (1)	N(1)-H	0.87 (10)
N(1)-C(2)	1.48 (1)	N(2)-H	2.08 (11)
	Angles		
S(1)-Fe-S(2)	109.2 (1)	C(5)-N(2)-C(6)	112.4 (9)
S(1)-Fe-N(3)	109.1 (4)	C(5)-N(2)-C(9)	111.8 (9)
S(1)-Fe-N(4)	104.7 (3)	C(6)-N(2)-C(9)	110.7 (9)
S(2)-Fe-N(3)	106.3 (4)	Fe-N(3)-O(1)	169.1 (11)
S(2)-Fe-N(4)	109.1 (4)	Fe-N(4)-O(2)	170.5 (10)
N(3)-Fe-N(4)	118.3 (5)	S(1)-C(1)-C(2)	116.3 (8)
Fe-S(1)-C(1)	104.6 (4)	N(1)-C(2)-C(1)	114.4 (10)
Fe-S(2)-C(7)	104.5 (4)	N(1)-C(3)-C(4)	112.7 (9)
C(2)-N(1)-C(3)	113.1 (9)	C(3)-C(4)-C(5)	113.1 (9)
C(2)-N(1)-C(8)	107.9 (9)	N(2)-C(5)-C(4)	111.0 (9)
C(3)-N(1)-C(8)	112.5 (9)	N(2)-C(6)-C(7)	113.4 (9)
H-N(1)-C(2)	118 (7)	S(2)-C(7)-C(6)	114.1 (7)
H-N(1)-C(3)	106 (7)	N(1)-H-N(2)	144 (10)
H-N(1)-C(8)	99 (8)		

[a] Atoms are labeled as shown in Figure 2. See footnote *a*, Table IV.

Table VI. Interatomic Distances (Å) and Angles (Deg) for for FeL'(NO) in **2**[a]

	Distances		
Fe-S(1)	2.240 (3)	N(1)-C(3)	1.49 (1)
Fe-S(2)	2.209 (3)	N(1)-C(8)	1.49 (1)
Fe-N(1)	2.082 (7)	N(2)-C(5)	1.50 (1)
Fe-N(2)	2.093 (8)	N(2)-C(6)	1.49 (1)
Fe-N(3)	1.697 (9)	N(2)-C(9)	1.47 (1)
S(1)-C(1)	1.84 (1)	C(1)-C(2)	1.48 (1)
S(2)-C(7)	1.82 (1)	C(3)-C(4)	1.52 (2)
O(1)-N(3)	1.146 (9)	C(4)-C(5)	1.53 (1)
N(1)-C(2)	1.49 (1)	C(6)-C(7)	1.49 (1)
	Angles		
S(1)-Fe-S(2)	86.4 (1)	C(2)-N(1)-C(8)	106.7 (8)
S(1)-Fe-N(1)	85.5 (2)	C(3)-N(1)-C(8)	109.5 (7)
S(1)-Fe-N(2)	156.8 (2)	Fe-N(2)-C(5)	111.4 (6)
S(1)-Fe-N(3)	105.2 (3)	Fe-N(2)-C(6)	105.4 (6)
S(2)-Fe-N(1)	158.1 (2)	Fe-N(2)-C(9)	114.3 (6)
S(2)-Fe-N(2)	85.5 (2)	C(5)-N(2)-C(6)	107.8 (8)
S(2)-Fe-N(3)	102.7 (3)	C(5)-N(2)-C(9)	109.9 (8)
N(1)-Fe-N(2)	94.1 (3)	C(6)-N(2)-C(9)	107.6 (8)
N(1)-Fe-N(3)	99.1 (3)	Fe-N(3)-O(1)	155.2 (9)
N(2)-Fe-N(3)	97.8 (4)	S(1)-C(1)-C(2)	108.5 (8)
Fe-S(1)-C(1)	100.9 (4)	N(1)-C(2)-C(1)	113.6 (9)
Fe-S(2)-C(7)	100.6 (4)	N(1)-C(3)-C(4)	113.5 (8)
Fe-N(1)-C(2)	105.0 (6)	C(3)-C(4)-C(5)	114.8 (9)
Fe-N(1)-C(3)	112.8 (6)	N(2)-C(5)-C(4)	115.2 (8)
Fe-N(1)-C(8)	114.0 (6)	N(2)-C(6)-C(7)	111.8 (8)
C(2)-N(1)-C(3)	108.3 (8)	S(2)-C(7)-C(6)	110.5 (8)

[a] Atoms are labeled as shown in Figure 3. See footnote *a*, Table IV.

recorded from the instrument control panel. The spectra of **1** were taken at liquid-nitrogen and at ambient temperatures.

The electron spin resonance signal of $Fe(L'H)(NO)_2$ is a singlet with $g_{iso} = 2.028$ in both **1** and **2**. No hyperfine coupling was observed. The spectrum of FeL'(NO) in **2** is a triplet at 198 K, the melting point of the sample, with g_{iso} and $A_{iso}(^{14}N)$ being 2.041 and 12.0 G, respectively.

Discussion

Structure and ESR Properties of $Fe(L'H)(NO)_2$ and FeL'(NO). The structure of $Fe(L'H)(NO)_2$ is essentially the same regardless of whether it is crystallized alone (**1**) or in a 1:1 mixture with FeL'(NO) (**2**), as revealed by inspection of Tables IV and V and Figures 1 and 2. The iron atom is pseudotetrahedrally coordinated. The average Fe–S, Fe–N, and N–O bond lengths of 2.272 (6), 1.67 (1), and 1.163 (10) Å, respectively, compare quite favorably with the corresponding values of 2.265, 1.665, and 1.17 Å for the compound $[(C_2H_5S)Fe(NO)_2]_2$, Roussin's red ethyl ester,[13] which has a strikingly similar coordination geometry. In $Fe(L'H)(NO)_2$ the largest angle at the iron atom is that subtended by the two nitrosyl ligands, 118.2 (5)°. This deviation from the tetrahedral value is comparatively small and is consistent with observations for first-row transition-metal dinitrosyl complexes; by contrast, dinitrosyl complexes of second- and third-row transition-metal complexes exhibit larger (139–158°) N–Fe–N angles.[14]

The most unusual geometric feature of $Fe(L'H)(NO)_2$ is the 12-membered chelate ring formed by coordination of only the two sulfur atoms of the potentially tetradentate N_2S_2 ligand. The other two (nitrogen) atoms participate in a six-membered, hydrogen-bonded H–N–C–C–C–N ring (Figures 1 and 2; Tables IV and V). The average distance between the iron and the chelate ring nitrogen atoms is 4.13 Å. Examples of large chelate rings containing potentially coordinating nitrogen atoms are known but are few in number. In these examples the nitrogens can be protonated, as in the case of $Mo_2O_4(L'H)_2$,[15] where L' is the same ligand as used here, or unprotonated as seen in the structure of $[Ph_2PCH_2N(Me)CH_2CH_2N(Me)CH_2PPh_2]Mo(CO)_4$.[16] In $Fe(L'H)(NO)_2$ the stability of the large chelate ring may be due in part to the stability of the H–N–C–C–C–N ring which dihedral angle calculations[17] show to be in a low-energy chair conformation. Other features of the geometry of $Fe(L'H)(NO)_2$ in **1** and **2** are unexceptional and may be explored by consulting Tables IV and V and Figures 1 and 2.

The structure of FeL'(NO) is similar to that reported previously for FeL(NO)[5] but with a few notable differences. The geometry of FeL'(NO) better approximates that of a square-based pyramid, as expected for a less sterically constrained[1,5] molecule. A best planes calculation through the N_2S_2 donor atoms of the L' ligand reveals departures of –0.015 Å for atoms S1 and N2 and +0.015 Å for S2 and N1 from the mean plane through the four atoms. The iron atom sits 0.414 Å above the plane. Another structural difference is that in FeL(NO) the two methyl groups are directed toward the axial nitrosyl ligand while in FeL'(NO) (Figure 3) they point away from it. The relative orientations of these methyl groups presumably reflect the thermodynamically most favorable conformation since equilibrium can be achieved kinetically through intermediates in which the nitrogen atoms of the L' ligand are not coordinated, viz., $Fe(L'H)(NO)_2$. The formerly puzzling observation[4] that, in the reaction of $(FeL)_2$ with nitrosonium ion to form $[(FeL)_2NO]^+$, the two methyl groups start out on the same side of the plane defined by N–Fe–N but end up on opposite sides now has a logical interpretation. Somewhere along the reaction pathway the iron–nitrogen bonds are probably broken, facilitating rotation of the methyl groups.

The average Fe–S, Fe–N, N–O, and intraligand bond lengths in FeL'(NO) (Table VI) are, within statistical limits,

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(13) Thomas, J. T.; Robertson, J. H.; Cox, E. G. *Acta Crystallogr.* **1958**, *11*, 599.

(14) See the discussion in: Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2610.

(15) Kim, N.; Kim, S.; Vella, P. A.; Zubieta, J. A. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 457.

(16) Grim, S. O.; Matienzo, L. J.; Shah, D. P.; Statler, J. A.; Stewart, J. M. *J. Chem. Soc., Chem. Commun.* **1975**, 928.

(17) Baltusis, L. M. Ph.D. Dissertation, Columbia University, 1979.

identical with those reported previously for FeL(NO).[5] Only the angular parameters differ owing to the steric constraints of the five-membered ethylenediamine chelate ring in FeL(NO). The Fe-N-O angle of 155.2° in FeL′(NO) compares favorably with the average value of 156.8° in FeL(NO). Thus FeL′(NO) provides another example[5] of a partially bent, ordered metal nitrosyl complex at room temperature.

Both Fe(L′H)$(NO)_2$ and FeL′(NO) are paramagnetic, 17-electron species that exhibit electron spin resonance spectra. The results obtained for Fe(L′H)$(NO)_2$ in **1** fit in very nicely with those reported for the compounds $[Fe(NO)_2X_2]^-$ where X = Cl, Br, and I.[7] These dihalodinitrosyliron anions have g_{iso} values of 2.033, 2.049, and 2.072, respectively, and show no hyperfine coupling to the nitrosyl groups. The g_{iso} value measured for Fe(L′H)$(NO)_2$ is 2.028. In the 1:1 cocrystallized mixture of Fe(L′H)$(NO)_2$ and FeL′(NO), **2**, there was no observed magnetic interaction between the two iron centers, the closest iron-iron distance being 6.9 Å (see Figure 5). The ESR spectrum of **2** is the sum of the spectra of two species. The values for g_{iso} and A_{iso} observed for FeL′(NO) are the same as previously reported for this compound alone.[5]

Synthesis and Stability of Fe(L′H)$(NO)_2$ and Its Conversion to FeL′(NO) through Formal Loss of "HNO". Although small amounts of **1** and **2** were obtained in the reaction of $(FeL')_2$ with $NOPF_6$, the best synthesis is the substitution reaction of $[Fe(NO)_2Br_2]^-$ with $L'H_2$. In the solid state, both compounds are relatively stable and the X-ray studies were performed with the crystals exposed to the air. In solution, however, infrared spectral studies show that Fe(L′H)$(NO)_2$ transforms to FeL′(NO) upon standing for several days or during chromatography over aluminum oxide which had absorbed water. It is reasonable that, with loss of the proton, the ligand nitrogen atoms would coordinate readily to the central iron atom forming one six-membered ring and two five-membered rings. This change in the coordination number of the iron results in reduction of the nitrosyl ligands. Formally, one of them leaves as "HNO" although the fate of the lost nitrosyl group is unknown. The remaining, coordinated nitrosyl group exhibits a decreased Fe-N-O angle, hyperfine coupling of the odd electron to the nitrosyl nitrogen nucleus, and a decrease in the NO stretching frequency in the infrared spectrum from 1740 and 1695 cm^{-1} in Fe(L′H)$(NO)_2$ to 1645 cm^{-1} in FeL′(NO). These results are reminiscent of the changes observed upon coordinating a sixth ligand to $[Fe(das)_2NO]^{2+}$.[18]

The conversion of Fe(L′H)$(NO)_2$ to FeL′(NO) and "HNO" may be viewed as a coupled proton-electron-transfer reaction. The process is mechanistically similar to that proposed for the reduction of substrates by molybdenum enzymes[19] except that the proton is donated by a ligand in the process of becoming coordinated rather than one already attached to the metal atom. The reaction of coordinated nitric oxide with acid to form HNO has been observed previously.[20]

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Registry No. 1, 73940-64-4; FeL′(NO), 64175-41-3; $[(Ph_3P)_2N][Fe(NO)_2Br_2]$, 61003-12-1.

Supplementary Material Available: Tables S1-S8 listing respectively final structure factor amplitudes, final atomic thermal parameters, root-mean-square amplitudes of thermal vibration, and hydrogen atom geometry for **1** and **2** (35 pages). Ordering information is given on any current masthead page.

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(18) Enemark, J. H.; Feltham, R. D.; Huie, B. T.; Johnson, P. L.; Swedo, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3285 and references therein.
(19) Stiefel, E. I. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 988.
(20) Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1979**, *18*, 336 and references cited therein.

Contribution from the Departments of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1 Canada, and Leicester University, Leicester, LE1 7RH England

Fluorine-19 and Xenon-129 NMR Studies of the $XeF_2 \cdot nWOF_4$ and $XeF_2 \cdot nMoOF_4$ (n = 1-4) Adducts: Examples of Nonlabile Xenon-Fluorine-Metal Bridges in Solution

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Xenon difluoride adducts with the weak fluoride ion acceptor species WOF_4 and $MoOF_4$ have been prepared and shown to possess the stoichiometries $XeF_2 \cdot MOF_4$ and $XeF_2 \cdot 2MOF_4$ (M = Mo or W). Fluorine-19 NMR spectroscopy has been used to study their solution structures in BrF_5 and SO_2ClF solvents. Equilibria involving higher chain length species, $XeF_2 \cdot nMOF_4$ (n = 1-4), have been observed at low temperatures in SO_2ClF solution. The structures have been shown to contain XeF···M bridges which are nonlabile on the NMR time scale at low temperatures. Isomerization between oxygen- and fluorine-bridged XeF groups, which has not previously been observed in noble-gas chemistry, has been observed in the tungsten adducts $XeF_2 \cdot nWOF_4$ (n = 2 and 3). The solvolytic behavior of $XeF_2 \cdot MOF_4$ adducts has also been studied, leading to the discovery of a new class of fluorosulfate-bridged species FXeO(F)S(=O)$OMOF_4$. Corroborating ^{129}Xe NMR data are discussed. The relative degree of covalent character in the terminal Xe-F bonds of the adduct species, as well as the relative fluoride ion acceptor strengths of $MoOF_4$ and WOF_4 and their polymeric chains, has been assessed on the basis of the observed ^{19}F and ^{129}Xe NMR complexation shifts. It has been concluded that WOF_4 and its polymers are stronger fluoride ion acceptors relative to XeF_2 than their $MoOF_4$ analogues.

Introduction

Many adducts between XeF_2 and the metal pentafluorides are known.[2] These have frequently been formulated as $XeF^+MF_6^-$, $XeF^+M_2F_{11}^-$, and $Xe_2F_3^+MF_6^-$ salts. From X-ray crystallographic and vibrational spectroscopic studies, it is clear, however, that a significant degree of covalent bonding between the anion and the cation must be present in the XeF^+ compounds, and, consequently, it is not entirely accurate to formulate these species as ionic compounds.[3] Several prior ^{19}F NMR investigations, which have dealt with solution studies

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(2) N. Bartlett and F. O., Sladky, "Comprehensive Inorganic Chemistry", A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973, Vol. 1, Chapter 6.
(3) R. J. Gillespie and B. Landa, *Inorg. Chem.*, **12**, 1383 (1973).

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