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Synthesis and Characterization of the Pentacoordinate Mononitrosyliron Complexes $Fe(NO)[SCH_2CH_2N(CH_3)(CH_2)_nN(CH_3)CH_2CH_2S]$, $n = 2, 3$

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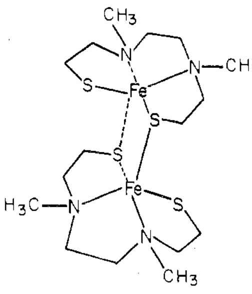
Received May 2, 1977 AIC70303R

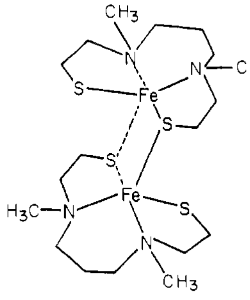
Addition of nitronium ion, nitrosonium ion, or nitric oxide to $(FeL)_2$ or $(FeL')_2$, where L and L′ are the tetradentate N_2S_2 donor ligands derived from *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)ethylenediamine (LH_2) and *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine ($L'H_2$), respectively, affords the crystalline green complexes FeL(NO) and FeL′(NO), respectively. A single-crystal x-ray diffraction study of FeL(NO) revealed a pentacoordinate structure in which the nitrosyl ligand occupies the apical position of a distorted square pyramid. The Fe–N–O angles in two crystallographically independent molecules are 155.2 (5) and 158.4 (5)°. The corresponding distances are Fe–N = 1.693 (5) and 1.702 (5) Å and N–O = 1.170 (6) and 1.130 (6) Å, respectively. Crystal data are as follows: orthorhombic space group $Pca2_1$; $a = 13.890$ (2), $b = 11.939$ (2), $c = 15.198$ (3) Å; ρ(obsd) = 1.529 (5) and ρ(calcd) = 1.540 g cm^{-3} for mol wt 292.2; $V = 2520$ (4) Å^3; $Z = 8$. Temperature-dependent magnetic susceptibility studies (to 80 K) show both FeL(NO) and FeL′(NO) to have $S = {}^1/_2$ ground states. Electron spin resonance, Mössbauer, and electronic spectral data are presented and shown to be consistent with results for other isoelectronic, sulfur-containing iron nitrosyl complexes.

Introduction

We have recently reported the synthesis and described the physical and chemical properties of the iron(II) complexes $(FeL)_2$ and $(FeL')_2$.[1-4] During the preparation of $[(FeL)_2NO]^+$ from $(FeL)_2$ and nitrosonium (NO^+) salts,[4] a green monomeric complex having the composition FeL(NO) was isolated. Here we describe the synthesis and characterization of this complex and its analogue FeL′(NO). These results are of interest because they reveal some further reactions of $(FeL)_2$ and $(FeL')_2$ and because the structure of FeL(NO), determined by x-ray diffraction, is one of the few known cases of a partially bent, ordered metal nitrosyl complex at room temperature.



$(FeL)_2$



$(FeL')_2$

Experimental Section

Materials and methods are as reported previously,[1] with the following additions. Nitric oxide was purchased from Matheson and passed through a dry ice–acetone trap prior to use to remove water and higher oxide impurities.[5] Electron spin resonance experiments were carried out using a Varian E-line ESR spectrometer at a modulation frequency of 100 kHz. Samples were made up on a vacuum line. Solvents were distilled into the solid samples in quartz tubes and then sealed under vacuum. Low-temperature spectra were taken employing a Varian variable-temperature controller, which was calibrated using an iron–constantan thermocouple. The *g* values were calibrated by comparison with the spectrum of strong pitch (a Varian standard, $g = 2.0028$)[6] and are accurate to ±0.005.

Synthesis of Compounds. $Fe(C_8H_{18}N_2S_2)(NO)$, FeL(NO). (a) Twenty-five milliliters of dichloromethane was added to a mixture of 1.048 g (2 mmol) of $(FeL)_2$ and 0.764 g (4 mmol) of NO_2PF_6, and the mixture was stirred overnight. The resulting solution was then chromatographed under a nitrogen atmosphere on alumina (Merck, acid washed (9 × 1.5 in.)) using dichloromethane as the eluent. The distinct green band was collected under nitrogen and reduced in volume under vacuum. Twice the volume of diethyl ether was added to the green solution which was then placed in a freezer overnight. The green crystals obtained were filtered, washed with ether, and dried under vacuum. Recrystallization from dichloromethane–ether yielded 150 mg of product (13%, based on iron). FeL(NO) decomposes slowly in air in both the solution and solid states; it should be stored under nitrogen.

A comparable yield of FeL(NO) can be achieved using $NOPF_6$ in a 2:1 ratio of FeL:NO^+ in dichloromethane, the same ratio used in the synthesis of $[(FeL)_2NO]PF_6$.[4] The reaction mixture was quickly (about 1 h) chromatographed in the air. After collection of the green band from the column, the product was isolated as described above and recrystallized under nitrogen.

(b) In a three-necked 100-mL round-bottomed flask was suspended 730 mg (1.4 mmol) of $(FeL)_2$ in 50 mL of methanol. The three inlets were all equipped with gas stopcocks, one to a N_2 line, one to the NO source, and one to a bubbler as a pressure escape vent. Nitric oxide was released into the flask in small spurts as the suspension of $(FeL)_2$ was stirred vigorously with heating (50 °C). The process was continued until the point where nearly all the brown $(FeL)_2$ had reacted forming a green solution. Excess NO should be avoided as an insoluble brown residue forms, particularly near the NO gas inlet. The green solution was filtered, 2 volumes of ether were added, and the solution was allowed to stand in the freezer overnight. The crude product was filtered, washed with ether, and dried under vacuum. Recrystallization from CH_2Cl_2–Et_2O yielded 320 mg of green crystals (39%).

Anal. Calcd for $FeC_8H_{18}N_3OS_2$: C, 32.88; H, 6.21; N, 14.38; S, 21.94. Found: C, 32.84; H, 6.12; N, 14.25; S, 21.87.

Electronic spectrum (acetonitrile solution, molar extinction coefficient in parentheses): 243 (16 300), 302 (5620), 339 (5620), 402 (sh, 2200), 653 (525) nm.

IR: Nujol, CsI, 1650 (s, br), 1310 (w), 1290, 1260, 1230 (sh), 1225, 1203, 1195, 1173 (w), 1152 (w), 1091 (w), 1058, 1033, 1020, 1000, 990, 941 (sh), 932, 911 (w), 891, 840 (w, br), 800 (w, br), 772, 743, 720, 672, 563, 540 (w), 504 (w), 465, 420 (w), 400 (w), 370, 355 cm^{-1}; methanol solution, 1690 cm^{-1} (s, br); methylene chloride solution, 1665 cm^{-1} (s, br, asymmetric multiplet).

MS, 50 V: most intense peak *m/e* 145 (100%), 524 (0.5), 262 (78), 234 (13), 216 (17), 201 (26), 188 (47), 173 (31), 172 (30), 163 (21), 131 (28), 120 (29), 102 (36), 99 (48), 89 (22).

$Fe(C_9H_{20}N_2S_2)NO$, FeL′(NO). (a) Fifty milliliters of dichloromethane was added to a mixture of 2.2 g (4 mmol) of $(FeL')_2$ and 1.40 g (8 mmol) of $NOPF_6$, and the mixture was stirred overnight. The brown solution obtained was chromatographed on alumina (Merck, acid washed) in the air. The green band was collected and placed under a nitrogen atmosphere, in which all subsequent work took place. The volume of the solution was reduced, 2 volumes of ether were added, and the resulting solution was allowed to stand in a freezer overnight. The solid obtained was filtered, washed with ether, and dried under vacuum. Recrystallizations from acetone–ether, methylene chloride–ether, and methanol–ether yielded 100 mg of green solid (4%, based on iron). (b) FeL′(NO) can also be prepared by allowing nitric oxide to react with $(FeL')_2$ in methanol in a manner analogous to that described above for FeL(NO). Upon completion of the NO addition and filtering the reaction mixture, some dichloromethane (20 mL) was added to dissolve the green precipitate obtained. FeL′(NO) is not very soluble in methanol. Recrystallization from MeOH–CH_2Cl_2–Et_2O afforded about a 40% yield of green microcrystalline material.

Anal. Calcd for $C_9H_{20}N_3OS_2Fe$: C, 35.30; H, 6.58; N, 13.72; S, 20.94. Found: C, 35.28; H, 6.29; N, 13.61; S, 20.86.

Electronic spectrum (acetonitrile solution, molar extinction coefficient in parentheses): 242 (13 500), 297 (6800), 343 (4720), 428 (sh, 1090), 638 (460) nm.

IR: Nujol, KBr, 1630 (s, br, mult), 1313, 1290, 1248, 1202, 1193 (sh), 1135, 1098, 1085 (sh), 1048 (w), 1035 (sh), 1020, 990, 978 (w, sh), 960, 935, 905, 888 (w, sh), 855 (w), 778, 745, 665 (w), 545 (w, br), 500 (w, sh), 485, 465 (w, sh), 435 (w), 375 cm^{-1}; methylene chloride solution, 1638 cm^{-1} (s, br, mult).

Table I. Experimental Details of the X-Ray Diffraction Study of FeL(NO)

(A) Crystal Parameters at 23 °C[a]

$a = 13.890\ (2)$ Å	Space group $Pca2_1$
$b = 11.939\ (2)$ Å	$Z = 8$
$c = 15.198\ (3)$ Å	ρ(calcd) = 1.540 g cm^{-3}
$V = 2520\ (4)$ Å^3	ρ(obsd)[b] = 1.529 (5) g cm^{-3}
	Mol wt = 292.2

(B) Measurement of Intensity Data

Instrument: Picker FACS-I-DOS diffractometer
Radiation: Mo Kα ($\lambda_{\alpha 1}$ 0.7093 Å), graphite monochromatized
Takeoff angle: 2.0°
Detector aperature: 3 × 3 mm
Crystal–detector distance: 33 cm
Scan technique: coupled θ(crystal)–2θ(counter)
Scan range: 1.75° (symmetric, plus $K\alpha_1$–$K\alpha_2$ dispersion)
Scan rate: 1.0°/min
Maximum 2θ: 55°
Background measurements: stationary crystal, stationary counter; 20-s counts at each end of 2θ scan range.
Standards: three reflections, (153), (512), and (306), measured every 100 data, showed only random, statistical fluctuations.
No. of reflections collected: 3467 including equivalent forms

(C) Treatment of Intensity Data[c]

Reduction to preliminary F_o^2 and $\sigma(F_o^2)$: correction for background, attenuators, and Lorentz–polarization of monochromatized x radiation in the usual manner;[d] $\epsilon = 0.05$[e]
Absorption correction: $\mu = 15.2\ cm^{-1}$; transmission factors varied between 0.785 and 0.869
Averaging: over equivalent forms with an agreement factor R_{av}[f] = 0.033
Scaling: Wilson's method[g]
Obsd data: 3289 unique reflections of which 2557 having $F_o^2 > 2\sigma(F_o^2)$ were used in the refinement

[a] From a least-squares fit to the setting angles of 12 reflections. [b] By suspension in carbon tetrachloride and heptane mixtures. [c] Programs for an IBM 360/91 computer used in this work include ORABS, the local version of the absorption correction program by D. J. Wehe, W. R. Busing, and H. A. Levy, adapted to FACS-I geometry; XDATA, the Brookhaven Wilson plot and scaling program; FOURIER, the Dellaca and Robinson modification of the Zalkin Fourier program FORDAP; CUGLS, the local version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS) modified by Ibers and Doedens for rigid-body refinement; ORFFE, the Busing–Martin–Levy molecular geometry and error function program; and ORTEP II, the Johnson thermal ellipsoid plotting program; in addition to various local data processing programs. [d] J. T. Gill and S. J. Lippard, *Inorg. Chem.*, 14, 751 (1975). [e] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *ibid.*, 6, 197 (1967). [f] $R_{av} = \Sigma_{i=1}^{N}\Sigma_{j=1}^{n}|\bar{F}_i^2 - F_{ij}^2|/\Sigma_{i=1}^{N}\bar{F}_i^2$, where N is the number of reflections measured more than once and n is the number of observations of the ith reflection. [g] A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

MS, 50 V: most intense peak *m/e* 215 (100%), 276 (54), 214 (55), 202 (56), 188 (63), 187 (77), 154 (93), 145 (53), 131 (44), 113 (72), 102 (61), 97 (44), 58 (47).

Collection and Reduction of X-Ray Data. Green crystals of FeL(NO) were obtained as described above. Preliminary photographs taken on precession and Weissenberg cameras showed the crystal to belong to the orthorbombic system. The extinctions *h0l*, $h = 2n + 1$, and *0kl*, $l = 2n + 1$, are characteristic of the space groups C_{2v}^5-$Pca2_1$ and D_{2h}^{11}-$Pcam$.[7] The crystal used for data collection was a bifrustum of approximate dimensions 0.13 mm between the (010) and $(0\bar{1}0)$ faces, 0.20 mm between $(1\bar{1}0)$ and $(\bar{1}10)$, 0.20 mm between (110) and $(\bar{1}\bar{1}0)$, 0.14 mm between (011) and $(0\bar{1}\bar{1})$, and 0.14 mm between $(01\bar{1})$ and $(0\bar{1}1)$. Details of the data collection and reduction are given in Table I.

Determination and Refinement of the Structure. $Pca2_1$ was shown to be the correct space group when the Patterson map revealed the presence of two crystallographically independent iron atoms. Two complete FeL(NO) molecules therefore comprise the asymmetric unit. The remaining nonhydrogen atoms were located on subsequent difference Fourier maps. The isotropic model refined to values of 0.079 and 0.096 for the discrepancy factors R_1 and R_2, respectively.[8,9a]

Anomalous dispersion corrections[9b] were then applied to the scattering factors for the iron and sulfur atoms, the isotropic thermal parameters were converted to anisotropic form, and the weighting scheme was introduced. Structure factor calculations and difference Fourier maps revealed the locations of the 36 hydrogen atoms. The positional parameters of these atoms were included in the least-squares refinement in which the independent FeL(NO) molecules were refined on alternate cycles. Since transforming the z coordinates of all atoms to $-z$ produced a statistically less satisfactory refinement ($R_2 = 0.043$ compared to 0.040 for all reflections having $F > 3\sigma(F)$), the polarity as originally chosen was assumed to be correct. In the final least-squares refinement the hydrogen atoms had their positions fixed at the values obtained from the previous least-squares cycles and were assigned isotropic B values set at one greater than the final isotropic parameters of the carbon atoms to which they are attached. Refinement of 270 parameters converged at $R_1 = 0.036$ and $R_2 = 0.043$. In the final least-squares cycle, no parameter varied by more than 0.1 of its estimated standard deviation. Inspection of the function $\sum w\Delta^2$ for reflections ordered according to $|F_0|$ and $((\sin\theta)/\lambda)$ showed satisfactory consistency and the error in an observation of unit weight, $[\sum w\Delta^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, was 1.079. The weighting scheme was therefore considered to be adequate.[10] A final difference Fourier map showed no peaks higher than 0.425 e/Å^3.

Results and Discussion

Synthesis and Spectral Properties of FeL(NO) and FeL′(NO). These green monomeric complexes can be obtained by several means. Reaction of $(\mathrm{FeL})_2$ or $(\mathrm{FeL'})_2$ with $\mathrm{NO^+}$ or $\mathrm{NO_2^+}$, followed by chromatography, affords crystalline material in low yield (approximately 10%). A higher yield (~40%) can be achieved by direct addition of gaseous nitric oxide to a solution or suspension of $(\mathrm{FeL})_2$ or $(\mathrm{FeL'})_2$ in a suitable solvent. In addition, FeL(NO) can be generated by reduction of $[(\mathrm{FeL})_2\mathrm{NO}]^+$ with sodium borohydride, a reaction that also produces $(\mathrm{FeL})_2$.[4a,11] This method was not found to be of synthetic utility, however, since it was extremely difficult to isolate FeL(NO) from the reaction mixture.

The complexes are soluble in a variety of polar organic solvents such as acetone, dichloromethane, acetonitrile, and methanol. Both these solutions and the solids are air sensitive. The infrared spectra exhibit an intense band in the range 1630–1690 cm^{-1}, depending upon the solvent, that is assigned to the N–O stretching frequency. The breadth and asymmetry of this band could be the result of different conformational isomers involving either the Fe–N–O bond axes and/or puckering of the ligand chelate rings. The electronic spectrum of FeL(NO) in acetonitrile is similar to those of $\mathrm{Fe(NO)(S_2CNMe_2)_2}$[12] and $\mathrm{Fe(NO)[S_2C_2(CN)_2]_2}$.[13] The bands observed probably correspond to charge-transfer transitions involving the π^* orbitals of the nitrosyl ligand.[12]

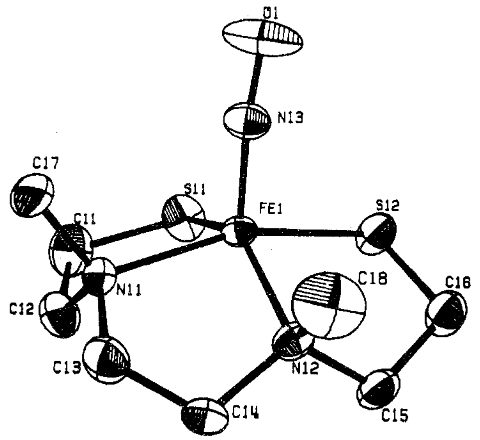


Figure 1. Structure of FeL(NO), molecule 1, showing the 40% probability thermal ellipsoids and omitting hydrogen atoms.

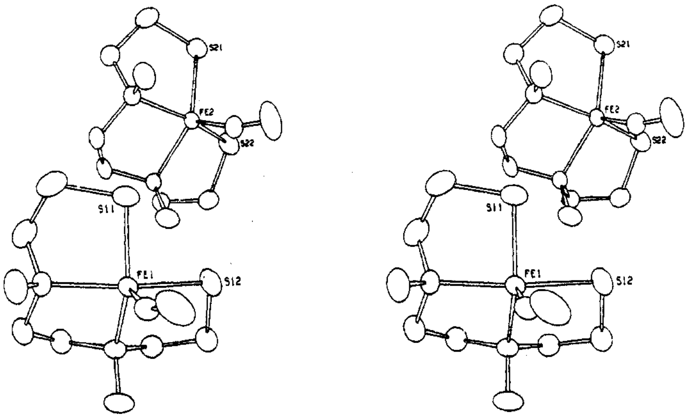


Figure 2. Stereoview of the two molecules comprising the asymmetric unit of FeL(NO).

The compounds FeL(NO) and FeL′(NO) are paramagnetic, having a doublet ground state. The effective room temperature magnetic moments are 1.85 and 1.80 μ_B, respectively. The temperature dependence of the magnetic susceptibility of FeL(NO) was measured by the Faraday method over the range $80 < T < 300$ K. The complex obeys a Curie–Weiss law ($\chi = C/(T + \Theta)$) with $\Theta \sim 21°$. The electron spin resonance spectrum of FeL(NO) in acetonitrile at −40 °C exhibits a triplet due to the hyperfine splitting of the unpaired electron with the nitrogen atom of the nitrosyl ligand. The isotropic g value is 2.043 and the nitrogen hyperfine coupling constant, $A_{\mathrm{iso}}(^{14}\mathrm{N})$, is 12.0 G. The molecule FeL′(NO) exhibits a nearly identical ESR spectrum with $g_{\mathrm{iso}} = 2.041$ and $A_{\mathrm{iso}}(^{14}\mathrm{N}) = 12.0$ G at −39 °C in acetonitrile. These ESR spectra are comparable to those observed in related bis(dithiocarbamato)nitrosyliron compounds[14,15] as well as in related bis(dithiolene)iron nitrosyl dianions.[13,16] The g and A(N) values in these compounds are quite similar to those of FeL(NO) and FeL′(NO), implying similar electronic structures. The triplet spectrum is consistent with the presence of the unpaired electron in the iron d_{z^2} orbital where direct interaction with the nitrosyl nitrogen atom occurs. This assignment was demonstrated previously in a single-crystal ESR spectral study of $\mathrm{Fe(NO)[S_2CNMe_2]_2}$.[15c] The absence of further hyperfine splitting from the nitrogen atoms of L or L′ is also consistent with there being little unpaired electron spin density in the xy plane.

A Mössbauer effect spectrum of FeL(NO) recorded at room temperature consists of a single, quadrupole split doublet. The isomer shift has a value of 0.01 mm/s vs. iron metal and the quadrupole splitting is 1.07 mm/s. These values may be compared with those for isoelectronic iron–sulfur nitrosyl complexes. The isomer shift and quadrupole splitting for $\mathrm{Fe(NO)[S_2CNMe_2]_2}$ at room temperature are 0.28 and 0.89 mm/s,[17] respectively, while the corresponding values for $\mathrm{Fe(NO)/S_2C_2(CN)_2]^{2-}}$ at 77 K are 0.31 mm/s (corrected to iron metal as the standard) and 0.97 mm/s.[18]

Crystal Structure of FeL(NO). Table II lists the final positional and thermal parameters for all nonhydrogen atoms. Hydrogen atom positional parameters are supplied as Table S1.[19] The root-mean-square thermal amplitudes for anisotropically refined atoms, the final observed and calculated structure factor amplitudes, and interatomic distances and angles involving hydrogen atoms are available as Tables S2–S4, respectively.[19] Figure 1 shows the structure of one of the two crystallographically independent molecules. In the following discussion comparisons will be made with this molecule only. As may be seen from the interatomic bond distances and angles summarized in Tables III and IV, geometric differences between the two crystallographically independent molecules are small in most cases. Figure 2 displays a stereoview of the two molecules as they pack in one asymmetric unit.

Table II. Final Positional and Thermal Parameters of the Atoms in FeL(NO)[a,b]

Atom	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe1	−0.02696 (5)	0.06018 (6)	0. (0)	2.83 (3)	3.73 (4)	2.76 (3)	0.19 (4)	−0.31 (3)	−0.09 (4)
Fe2	0.19450 (5)	0.46811 (6)	0.23859 (7)	2.37 (3)	3.93 (4)	2.72 (3)	−0.02 (3)	0.14 (3)	−0.17 (4)
S11	0.04163 (13)	0.06786 (17)	0.13184 (12)	5.24 (9)	10.94 (17)	3.32 (8)	−0.50 (11)	−1.11 (7)	−0.39 (9)
S12	0.09839 (10)	0.15883 (14)	−0.05299 (14)	3.21 (7)	7.55 (13)	6.12 (10)	−0.32 (8)	−0.22 (7)	2.42 (9)
S21	0.27155 (11)	0.51628 (14)	0.36127 (12)	4.36 (8)	7.67 (13)	3.66 (7)	−1.32 (8)	−0.70 (7)	−0.53 (8)
S22	0.23998 (12)	0.63331 (13)	0.18079 (14)	4.18 (8)	6.36 (11)	6.14 (10)	−1.25 (8)	−0.61 (8)	2.11 (9)
O1	0.0506 (4)	−0.1398 (4)	−0.0649 (4)	6.3 (3)	8.6 (4)	9.4 (4)	3.0 (3)	−2.2 (3)	−5.0 (4)
O2	0.3328 (3)	0.3364 (5)	0.1557 (5)	4.4 (3)	10.8 (5)	11.8 (5)	1.3 (3)	2.2 (3)	−5.0 (4)
N11	−0.1550 (3)	0.0246 (4)	0.0654 (3)	3.4 (2)	4.8 (3)	3.7 (2)	−0.2 (2)	0.62 (20)	0.5 (2)
N12	−0.1128 (3)	0.1568 (3)	−0.0816 (3)	3.8 (2)	4.4 (3)	2.9 (2)	0.5 (2)	−0.64 (19)	0.1 (2)
N13	0.0003 (3)	−0.0647 (4)	−0.0465 (3)	3.8 (2)	5.0 (4)	3.5 (2)	0.6 (2)	−0.37 (20)	−1.0 (2)
N21	0.1160 (3)	0.3569 (4)	0.3157 (3)	3.3 (2)	4.6 (3)	3.1 (2)	−0.4 (2)	0.15 (18)	0.4 (2)
N22	0.0668 (3)	0.4878 (4)	0.1692 (3)	2.6 (2)	5.8 (3)	2.8 (2)	−0.2 (2)	0.25 (18)	0.0 (2)
N23	0.2649 (3)	0.3778 (4)	0.1805 (3)	3.6 (2)	4.6 (3)	3.8 (2)	−0.3 (2)	0.5 (2)	−0.3 (2)
C11	−0.0611 (6)	0.0378 (7)	0.2016 (5)	8.9 (6)	9.9 (7)	3.5 (3)	−0.3 (5)	−0.1 (4)	0.9 (4)
C12	−0.1506 (5)	0.0744 (6)	0.1552 (5)	6.5 (4)	8.4 (6)	3.9 (3)	1.1 (4)	1.8 (3)	0.2 (4)
C13	−0.2347 (4)	0.0788 (5)	0.0137 (5)	3.0 (3)	8.3 (5)	5.3 (4)	0.7 (3)	0.0 (3)	1.4 (4)
C14	−0.2011 (4)	0.1827 (5)	−0.0282 (4)	3.4 (3)	6.6 (5)	4.5 (3)	1.5 (3)	0.1 (3)	0.4 (3)
C15	−0.0638 (4)	0.2637 (5)	−0.1069 (4)	4.7 (3)	5.6 (4)	4.1 (3)	0.3 (3)	−0.2 (3)	1.3 (3)
C16	0.0371 (4)	0.2391 (6)	−0.1371 (5)	4.3 (3)	7.9 (5)	4.7 (3)	−0.2 (3)	−0.2 (3)	2.2 (4)
C17	−0.1731 (5)	−0.0976 (6)	0.0727 (6)	4.7 (3)	5.9 (5)	7.1 (5)	−0.9 (3)	1.1 (3)	1.1 (4)
C18	−0.1411 (5)	0.0968 (6)	−0.1636 (5)	6.3 (4)	8.0 (5)	3.7 (3)	0.4 (4)	−1.7 (3)	−1.0 (3)
C21	0.2102 (5)	0.4285 (6)	0.4413 (4)	6.7 (4)	10.3 (6)	2.3 (3)	−0.7 (4)	−0.1 (3)	−0.6 (4)
C22	0.1111 (4)	0.4001 (6)	0.4076 (4)	4.6 (3)	8.5 (5)	3.0 (3)	−0.9 (4)	0.3 (3)	−0.4 (3)
C23	0.0166 (4)	0.3486 (5)	0.2770 (4)	2.9 (3)	6.7 (5)	4.1 (3)	−1.0 (3)	0.6 (2)	0.6 (3)
C24	−0.0087 (3)	0.4576 (5)	0.2332 (5)	2.1 (2)	7.5 (4)	4.3 (3)	0.1 (3)	0.4 (2)	−0.2 (3)
C25	0.0531 (4)	0.6049 (5)	0.1379 (4)	3.5 (3)	6.7 (5)	3.4 (3)	0.5 (3)	−0.0 (2)	0.9 (3)
C26	0.1442 (5)	0.6501 (5)	0.1000 (5)	5.3 (4)	7.3 (5)	4.2 (3)	0.3 (4)	−0.2 (3)	1.9 (3)
C27	0.1591 (4)	0.2434 (5)	0.3180 (5)	4.1 (3)	4.4 (4)	6.0 (4)	0.2 (3)	0.5 (3)	0.4 (3)
C28	0.0630 (5)	0.4111 (6)	0.0915 (5)	4.9 (4)	10.6 (7)	3.9 (3)	−0.5 (4)	−0.8 (3)	−2.5 (4)

[a] Atoms are labeled as indicated in Figure 1. The two crystallographically independent molecules are designated Fe1, S11, S12, O1, N11, etc., and Fe2, S21, S22, O2, N21, etc. [b] Numbers in parentheses are errors in the last significant digit(s). [c] The anisotropic temperature factors are 10^3. The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Interatomic Distances (Å) in FeL(NO)[a]

Molecule 1		Molecule 2	
Fe1–S11	2.221 (19)	Fe2–S21	2.226 (18)
Fe1–S12	2.251 (17)	Fe2–S22	2.250 (17)
Fe1–N11	2.082 (5)	Fe2–N21	2.080 (4)
Fe1–N12	2.071 (4)	Fe2–N22	2.076 (4)
Fe1–N13	1.693 (5)	Fe2–N23	1.702 (5)
N13–O1	1.170 (6)	N23–O2	1.130 (6)
S11–C11	1.813 (9)	S21–C21	1.817 (7)
S12–C16	1.811 (7)	S22–C26	1.822 (7)
N11–C12	1.489 (9)	N21–C22	1.489 (8)
N11–C13	1.504 (8)	N21–C23	1.504 (7)
N11–C17	1.485 (8)	N21–C27	1.483 (8)
N12–C14	1.504 (7)	N22–C24	1.475 (8)
N12–C15	1.496 (7)	N22–C25	1.489 (7)
N12–C18	1.491 (8)	N22–C28	1.496 (8)
C11–C12	1.494 (11)	C21–C22	1.507 (9)
C13–C14	1.471 (9)	C23–C24	1.503 (9)
C15–C16	1.504 (8)	C25–C26	1.492 (9)

[a] See footnotes *a* and *b*, Table II. Values are not corrected for thermal motion.

Table IV. Interbond Angles (deg) for FeL(NO)[a]

Molecule 1		Molecule 2	
S11–Fe1–S12	88.24 (7)	S21–Fe2–S22	88.02 (7)
S11–Fe1–N11	86.78 (14)	S21–Fe2–N21	86.85 (14)
S11–Fe1–N12	139.83 (15)	S21–Fe2–N22	143.78 (14)
S11–Fe1–N13	108.48 (18)	S21–Fe2–N23	108.79 (18)
S12–Fe1–N11	159.81 (16)	S22–Fe2–N21	157.95 (14)
S12–Fe1–N12	86.53 (13)	S22–Fe2–N22	86.69 (13)
S12–Fe1–N13	97.96 (18)	S22–Fe2–N23	101.04 (17)
N11–Fe1–N12	84.72 (18)	N21–Fe2–N22	84.86 (17)
N11–Fe1–N13	102.2 (2)	N21–Fe2–N23	100.91 (19)
N12–Fe1–N13	111.7 (2)	N22–Fe2–N23	107.4 (2)
Fe1–N13–O1	155.2 (5)	Fe2–N23–O2	158.4 (5)
Fe1–S11–C11	100.5 (3)	Fe2–S21–C21	100.7 (2)
Fe1–S12–C16	99.5 (2)	Fe2–S22–C26	98.9 (2)
Fe1–N11–C12	108.7 (4)	Fe2–N21–C22	109.3 (3)
Fe1–N11–C13	107.0 (3)	Fe2–N21–C23	107.6 (3)
Fe1–N11–C17	112.4 (4)	Fe2–N21–C27	112.6 (3)
C12–N11–C13	109.7 (5)	C22–N21–C23	110.4 (5)
C12–N11–C17	109.4 (5)	C22–N21–C27	108.2 (5)
C13–N11–C17	109.6 (5)	C23–N21–C27	108.7 (4)
Fe1–N12–C14	105.1 (3)	Fe2–N22–C24	104.2 (4)
Fe1–N12–C15	111.6 (3)	Fe2–N22–C25	112.2 (3)
Fe1–N12–C18	112.6 (4)	Fe2–N22–C28	111.2 (4)
C14–N12–C15	109.5 (4)	C24–N22–C25	110.4 (4)
C14–N12–C18	109.6 (5)	C24–N22–C28	110.2 (5)
C15–N12–C18	108.4 (5)	C25–N22–C28	108.5 (5)
S11–C11–C12	108.7 (5)	S21–C21–C22	109.3 (5)
N11–C12–C11	110.5 (6)	N21–C22–C21	110.8 (5)
N11–C13–C14	110.8 (5)	N21–C23–C24	109.3 (4)
N12–C14–C13	108.6 (5)	N22–C24–C23	109.7 (4)
N12–C15–C16	109.6 (5)	N22–C25–C26	110.7 (5)
S12–C16–C15	109.0 (5)	S22–C26–C25	108.6 (4)

[a] See footnote *a*, Table III.

The molecule FeL(NO) is a pentacoordinate monomer having approximately square-pyramidal coordination geometry. The four (N_2S_2) donor atoms from the ligand L comprise the basal plane, and the apical position is occupied by the nitrogen atom of the nitrosyl ligand. The iron atom sits 0.55 Å above the best least-squares plane formed by the N_2S_2 donor atoms. Atoms S11 and N12 (Figure 1) lie 0.17 and 0.18 Å, respectively, below this plane while atoms S12 and N11 lie 0.17 and 0.18 Å, respectively, above the plane. These deviations are those expected for distortion of a square-pyramidal (SP) structure toward that of a trigonal bipyramid (TBP) in which the unique axis would be defined by N11–Fe1–S12. The observed structure is closer to that of a square pyramid, using the δ' angle criterion proposed by Muetterties and Guggenberger (Table V).[20] An independent analysis of the FeL(NO) structure was performed by Haymore.[21] All 25 possible idealized geometries, generated by permuting the donor atoms among the apices of the SP and TBP, were explored for both crystallographically independent molecules.

Table V. Analysis of Edge Dihedral Angles (deg) in FeL(NO)[a]

Structure	$\delta e_1'$	$\delta e_2'$	$\delta e_3'$
FeL(NO) molecule 1	66.1	61.0	19.1
FeL(NO) molecule 2	67.5	64.7	13.7
Idealized square pyramid	75.7	75.7	0
Idealized trigonal bipyramid	53.1	53.1	53.1

[a] See ref 20 for definition of terms and discussion.

Table VI. Comparison of Isoelectronic Pentacoordinate Iron Nitrosyl Complexes[a]

Compd	ν_{NO}, cm^{-1}	Geometry	Fe–N, Å	Fe–N–O, deg	Ref
Fe(TPP)(NO)	1700	TP, apical NO	1.717	149.2	*b, c*
FeL(NO)	1650	TP, apical NO	1.693	155.2	This study
			1.702	158.4	
$Fe[S_2CNMe]_2(NO)$	1735	TP, apical NO	1.705	160	*d, e*
			1.705	173.3	*f*
$Fe[S_2C_2(CN)_2]_2(NO)^{2-}$	1645	TP, apical NO	1.56	168	*g, h*
			1.58	165	*i*
$Fe[S_2CNEt_2]_2(NO)$	1673	TP, apical NO	1.69	174	*j, k*
$Fe(das)_2(NO)^{2+}$	1760	TP, apical NO	1.655	172.8	*l*

[a] Abbreviations: TPP, α,β,γ,δ-tetraphenylporphinato; TP, tetragonal prism; Me, methyl; Et, ethyl; das, *o*-phenylenebis(dimethylarsine). [b] B. B. Wayland and L. W. Olson, *J. Am. Chem. Soc.*, **96**, 6037 (1974). [c] Reference 23c. [d] H. B. Gray, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, 84, 3404 (1962). [e] Reference 23a; data taken at room temperature. [f] G. R. Davies, J. A. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1275 (1970); data taken at −80 °C. [g] J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. J. Winscom, *J. Am. Chem. Soc.*, 89, 6082 (1967). [h] A. I. M. Rae, *Chem. Commun.*, 1245 (1967). [i] Structure redetermined; results quoted in ref 26. [j] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 7, 32 (1958). [k] M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Commun.*, 583 (1967). [l] T. E. Nappier, R. D. Feltham, J. H. Enemark, A. Kruse, and M. Cooke, *Inorg. Chem.*, **14**, 806 (1975); J. H. Enemark, R. D. Feltham, B. T. Huie, P. L. Johnson, and K. B. Swedo, *J. Am. Chem. Soc.*, 99, 3285 (1977).

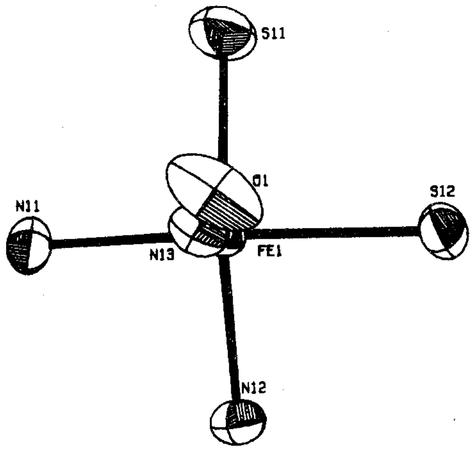


Figure 3. Coordination geometry of FeL(NO), top view, showing the direction of bending of the nitrosyl ligand (40% probability thermal ellipsoids).

Differences between the observed and idealized structures were computed and analyzed statistically. The results showed the square-based pyramid with NO as the axial ligand to be the best idealized geometry. For both molecules, the second best fit was the corresponding trigonal bipyramid with N1 and S2 axial.

The average iron–sulfur bond length is 2.237 Å and the mean Fe–N(amine) distance is 2.077 Å. These values are considerably shorter than those found in $(FeL)_2$[2] (av Fe–S, 2.41 Å; av Fe–N, 2.23 Å), consistent with the presence of low-spin iron found in the magnetic susceptibility study of FeL(NO). The Fe–S and Fe–N bond lengths in FeL(NO) are comparable to the values observed for $[(FeL)_2NO]PF_6$·acetone.[4] Other geometric features of the FeL(NO) structure, listed in Tables III and IV, are unexceptional.

The ligand conformation in both crystallographically independent molecules of FeL(NO) is the same as found previously for $(FeL)_2$,[2] with both *N*-methyl groups on the same side of the N1–Fe–N2 plane. The methyl groups are directed toward the axial nitrosyl ligand. As evident from Figures 2 and 3, the nitrosyl bends (Fe–N3–O1 angles of 155.2 and 158.4°) over the basal plane in a direction between the two sulfur atoms of the ligand L, thereby minimizing nonbonded steric interactions with the *N*-methyl groups. Bending at N3 implies formal charge transfer from the metal to the nitrosyl group which decreases the extent of π bonding with iron. The resulting Fe–N3 distance (av 1.698 Å) is longer than corresponding values for linearly coordinated iron nitrosyl groups[22] and comparable to those observed for partly bent iron nitrosyl complexes.[23] Table VI compares the N–O stretching frequencies and geometries of several isoelectronic, pentacoordinate iron nitrosyl compounds. The structure and bonding in transition metal nitrosyl complexes have been extensively discussed,[14,24-30] and the present results fit nicely into the existing conceptual frameworks.

Acknowledgment. This work was supported by NIH Grant No. GM 16449 from the National Institutes of General Medical Sciences. We thank Professor C.-S. Wu for assistance in obtaining the Mössbauer spectra.

Registry No. FeL(NO), 64175-42-4; FeL′(NO), 64175-41-3; $(FeL)_2$, 52699-83-9; $(FeL')_2$, 52699-84-0; NO_2PF_6, 19200-21-6; $NOPF_6$, 16921-91-8; NO, 10102-43-9.

Supplementary Material Available: Tables S1–S4 listing, respectively, the final positional and thermal parameters of the hydrogen atoms, the root-mean-square amplitudes of vibration for anisotropically refined atoms, structure factor amplitudes, and geometry involving hydrogen atoms for the FeL(NO) structure (21 pages). Ordering information is given on any current masthead page.

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(8) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = 4F_o^2/\sigma^2(F_o)$. In the least-squares refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized.
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Molecules with an M_4X_4 Core. 9.[1-8] Crystal Structure and Molecular Geometry of Tetrameric (Methyldiphenylphosphine)copper(I) Iodide, $[(PMePh_2)CuI]_4$

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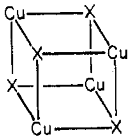
Received May 5, 1977 AIC70313S

The tetrameric species (methyldiphenylphosphine)copper(I) iodide, $[(PMePh_2)CuI]_4$, has been synthesized and investigated via a full three-dimensional x-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $C2/c$ [C_{2h}^6; No. 15] with $a = 25.704\ (5)$ Å, $b = 11.971\ (2)$ Å, $c = 19.631\ (4)$ Å, $\beta = 110.70\ (1)°$, $V = 5651\ (4)$ Å^3, ρ(obsd) = 1.83 (3) g cm^{-3}, and ρ(calcd) = 1.84 g cm^{-3} for molecular weight = 1562.67 and $Z = 4$. Diffraction data were collected with a Picker FACS-1 four-circle automated diffractometer using Nb-filtered Mo Kα radiation. The structure was solved by symbolic addition and refined via a combination of difference-Fourier and least-squares techniques. The resulting discrepancy indices are $R_F = 5.1\%$ and $R_{wF} = 4.4\%$ for 3701 independent reflections with $2\theta \le 45°$. The $[(PMePh_2)CuI]_4$ molecule lies on a site of crystallographic C_2 symmetry, the Cu_4I_4 core consisting of a "cubane-like" skeleton of alternating copper(I) and iodide ions. Copper···copper distances range from 2.8395 (13) to 3.0095 (13) Å (average = 2.9300 Å), iodine···iodine contacts range from 4.2973 (12) to 4.4883 (8) Å (average = 4.4061 Å), and copper–iodine bond lengths range from 2.6108 (11) to 2.7591 (11) Å (average = 2.6982 Å). These results are discussed in relation to previous studies on $[(PEt_3)CuI]_4$ (which has a regular "cubane-like" Cu_4I_4 core of precise T_d symmetry) and $[(PPh_3)CuI]_4$ (which has a "step-like" core of crystallographic C_i symmetry).

Introduction

We have recently completed x-ray structural analyses of three complete series of tetrameric phosphinecopper(I) and phosphinesilver(I) halides, viz., $[(PPh_3)CuX]_4$ (X = Cl,[1] Br,[2] I[4]), $[(PEt_3)CuX]_4$ (X = Cl,[5] Br,[5] I[3]), and $[(PEt_3)AgX]_4$ (X = Cl,[8] Br,[8] I[7]). Related studies of the species $[(PPh_3)AgX]_4$ (X = Cl,[9] Br,[10] I[11]) have been carried out by Teo and Calabrese. It is established that for copper, the familiar and ubiquitous "cubane" structure (I) is destabilized relative to the "step" structure (II) when large halogen atoms (X) are accompanied by bulky ligands on the metal atom.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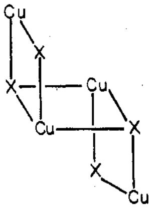
II

The species $[(PPh_3)CuI]_4$ has previously been shown to possess a "step structure",[4] whereas $[(PEt_3)CuI]_4$ has a "cubane structure".[3] We now report the results of a structural study on a copper(I) iodide complex of a trisubstituted phosphine ligand of intermediate bulk, i.e., the species $[(PMePh_2)CuI]_4$.

Experimental Section

Synthesis of $[(PMePh_2)CuI]_4$. Approximately 3 mL of $PMePh_2$ (ca. 3 g, 14 mmol) was injected into a slurry of CuI (4.3 g, 22.5 mmol) in toluene (50 mL) under a positive pressure of nitrogen. The solution was stirred for 24 h at 80–90 °C and excess CuI removed by filtration. Cooling of the filtrate yielded crystals of $[(PMePh_2)CuI]_4$ which were collected and recrystallized from toluene. Anal. Calcd for $C_{52}H_{52}Cu_4I_4P_4$: C, 39.97; H, 3.35; Cu, 16.26; I, 32.48; P, 7.93. Found (Galbraith Laboratories, Knoxville, Tenn.): C, 40.03; H, 3.25; Cu, 16.12; I, 32.57; P, 7.79.

Collection of X-Ray Diffraction Data. The crystal selected for the structural analysis *approximated* to a block extended in the [010] direction and with pointed ends. The crystal was bounded by nine discernible faces [(100), ($\bar{1}$00), (001), (00$\bar{1}$), and ($\bar{1}$01) defining the sides, ($\bar{1}$11) and (11$\bar{1}$) defining one end, and (1$\bar{3}\bar{2}$) and (0$\bar{1}$1) defining the other end]. The approximate dimensions of the crystal were 0.50 × 0.23 × 0.22 mm. The crystal was inserted into a thin-walled capillary, which was flushed with nitrogen, flame sealed, fixed with beeswax into a brass pin, and set in a eucentric goniometer head.

Preliminary Weissenberg, rotation, precession, and cone-axis photographs provided preliminary unit cell parameters, indicated C_{2h} ($2/m$) Laue symmetry, and revealed the systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. Possible space groups for the monoclinic crystal are the centrosymmetric space group $C2/c$ [C_{2h}^6; No. 15] and the noncentrosymmetric space group Cc [C_s^4; No. 9].

Based upon unit cell and density measurements (see Table I), there are four tetrameric molecules in the unit cell. In the absence of gross disorder, the crystallographic asymmetric unit is therefore half of the molecule in space group $C2/c$ or one entire tetrameric unit in space group Cc. The space group $C2/c$ allows the tetrameric unit to possess either an inversion center (possible for the "step" structure) or a C_2 axis (possible for a "cubane-like" geometry).

Data collection was carried out at the University of Illinois at Chicago Circle. The crystal was mounted on a Picker FACS-1 four-circle automated diffractometer, was accurately centered, and was aligned with b^* coincident with the instrumental ϕ axis. X-ray diffraction data were collected as described previously;[12] details of the present study are listed in Table I.

The effects of absorption were investigated by measuring (via θ–2θ scans) the 040 reflection ($2\theta = 13.61°$) at $\chi = 90°$ and at 10° intervals of ϕ from 0 to 350°. The observed variation was ~6%. While we had intended to make an absorption correction, the crystal was unfortunately lost during the move of our research group from Chicago

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