(8) J. L. Dye and V. A. Nicely, *J. Chem. Educ.*, **48**, 443 (1971).
(9) W. C. Krueger and L. M. Pschigoda, *Anal. Chem.*, **43**, 675 (1971). *d*-10-Camphorsulfonic acid appears to be a suitable standard for CD calibration since it is readily purified and gives a sharp CD maximum in the near-uv. However, there is not at this time, agreement as to the absolute circular dichroism of this compound. Therefore, the value used to calibrate the instrument in this study is given here to facilitate accurate comparison of CD data.
(10) E. L. Buhle, A. M. Moore, and F. G. Wiseloge, *J. Am. Chem. Soc.*, **65**, 29 (1943).
(11) J. H. Billman and L. C. Dorman, *J. Org. Chem.*, **27**, 2419 (1962).
(12) E. J. Billo, *Inorg. Nucl. Chem. Lett.*, **11**, 491 (1975).
(13) D. Hopgood and R. J. Angelici, *J. Am. Chem. Soc.*, **90**, 2508 (1968).
(14) C. J. Hawkins and C. L. Wong, *Aust. J. Chem.*, **23**, 2237 (1970).
(15) Since the spectra were similar for all the amino acids studied, comparison of $\Delta\epsilon$ values gives a good estimate of the relative rotatory strengths.
(16) T. Murakami, T. Nozawa, and M. Hatano, *Bull. Chem. Soc. Jpn.*, **46**, 2456 (1973).
(17) S. Kirschner and K. H. Pearson, *Inorg. Chem.*, **5**, 1614 (1966).
(18) D. C. Bhatnagar and S. Kirschner, *Inorg. Chem.*, **3**, 1256 (1964).
(19) T. Murakami, T. Nozawa, and M. Hatano, *J. Am. Chem. Soc.*, **92**, 5768 (1970).
(20) E. W. Wilson, Jr., M. H. Kasperian, and R. B. Martin, *J. Am. Chem. Soc.*, **92**, 5365 (1970).
(21) R. J. Sundberg and R. B. Martin, *Chem. Rev.*, **74**, 471 (1974).
(22) A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc. A*, 1905 (1968).
(23) T. Yasui, *Bull. Chem. Soc. Jpn.*, **38**, 1746 (1965).
(24) T. Yasui, J. Hidaka, and J. Shimura, *J. Am. Chem. Soc.*, **87**, 2762 (1965).
(25) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).
(26) C. W. Maricondi and B. E. Douglas, *Inorg. Chem.*, **11**, 668 (1972); C. W. Maricondi and C. Maricondi, *ibid.*, **12**, 1524 (1973); W. T. Jordan and B. E. Douglas, *Ibid.*, **12**, 403 (1973); W. T. Jordan and J. I. Legg, *ibid.*, **13**, 955 (1974).
(27) J. W. Allison and R. J. Angelici, *Inorg. Chem.*, **10**, 2233 (1971).

Sulfur-Bridged Binuclear Iron(II) Complexes. Effect of Ligand Constraints on Their Physical Properties; Reactions with Carbon Monoxide and Alkyl Isocyanides

Kenneth D. Karlin and Stephen J. Lippard*

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027.

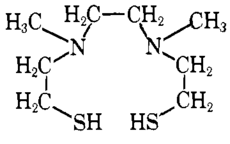
Received January 26, 1976

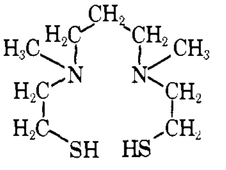
Abstract: The synthesis of the sulfur-bridged iron(II) complexes $(FeL)_2$ and $(FeL')_2$ is described. Differences in the steric constraints of the tetradentate N_2S_2 donor ligands *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine (LH_2) and *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine ($L'H_2$) are reflected in the physical properties of the complexes. Magnetic and Mössbauer studies over a temperature range show both $(FeL)_2$ and $(FeL')_2$ to contain high spin iron(II) ($S = 2$) atoms which are antiferromagnetically coupled leading to an overall $S = 0$ ground state. The extent of coupling is substantially greater in $(FeL)_2$, however, which has a more constrained geometry and a shorter nonbonded iron-iron distance. The reversible reaction of $(FeL)_2$ with carbon monoxide to give crystalline $FeL(CO)_2$ is described. Analogous chemistry with alkyl isocyanides leads to $FeL(CNR)_2$, $R = CH_3$ or $t\text{-}C_4H_9$. Under the same conditions, $(FeL')_2$ does not react with these ligands. The similarity between the physical and chemical properties of $(FeL)_2$ and $[Fe(cys)_2]_n$, cys $= {}^-SCH_2CH(NH_3{}^+)(CO_2{}^-)$, is noted.

There has been much recent interest in the synthesis and characterization of iron-sulfur complexes.[1,2] The attention given to this area by coordination chemists stems largely from the recognition of redox active iron-sulfur cores in a wide variety of proteins.[3-7] Many of these proteins embody nFe-nS* units that release hydrogen sulfide upon mild acidification. Analogues of the iron-sulfur protein cores for $n = 2$ and $n = 4$ have been prepared and well characterized.[2] Other iron-sulfur proteins are known or thought to contain $Fe\text{-}SCH_2R$ linkages, in which the thiolate donor ligand is cysteine.[3,4] Iron cysteinate complexes have been studied, but definitive structural information is lacking.[8-13]

The studies described in the present series of papers[14-16] were undertaken with the objectives of (1) synthesizing iron sulfur complexes in which the sulfur donor ligand is saturated (i.e., $R\text{-}CH_2\text{-}S^-$) and with no additional stabilizing π acid ligands such as CO, $C_5H_5^-$, or a porphyrin ring; (2) producing high spin iron centers and, in the case of sulfur-bridged compounds, evaluating the magnetic exchange between the iron atoms; and (3) examining the effects of ligand constraints on the physical properties and chemical reactions of the iron complexes. The rationale underlying these objectives is described in part elsewhere.[1]

To achieve these aims, the ligands LH_2 and $L'H_2$ were synthesized. Geometric considerations suggested that high-spin complexes of L would be much more strained than those of L', an expectation verified by subsequent x-ray structural investigations of iron and zinc complexes of these ligands.[17,18] In particular, the long iron-nitrogen bond lengths (2.2-2.35 Å) in high spin iron complexes of L produce angular strain in the five-membered ethylenediamine chelate ring of $(FeL)_2$ that is relieved in the analogous six-membered 1,3-propanediamine chelate ring of $(FeL')_2$ (Figure 1).[18]


LH_2


$L'H_2$

In the present paper we describe an improved synthesis of the ligands and their iron(II) complexes, magnetic and Mössbauer data that fix the oxidation and spin states, and reactions with carbon monoxide and alkyl isocyanides. Three subsequent papers report the results of a detailed magnetic analysis of $(FeL)_2$ and $(FeL')_2$,[14] the oxidative addition reaction of nitrosonium ion with $(FeL)_2$ and $(CoL)_2$ and the x-ray crystal structures of the products,[15] and the synthesis of mononuclear iron nitrosyl complexes together with the molecular structure determination of $FeL(NO)$.[16]

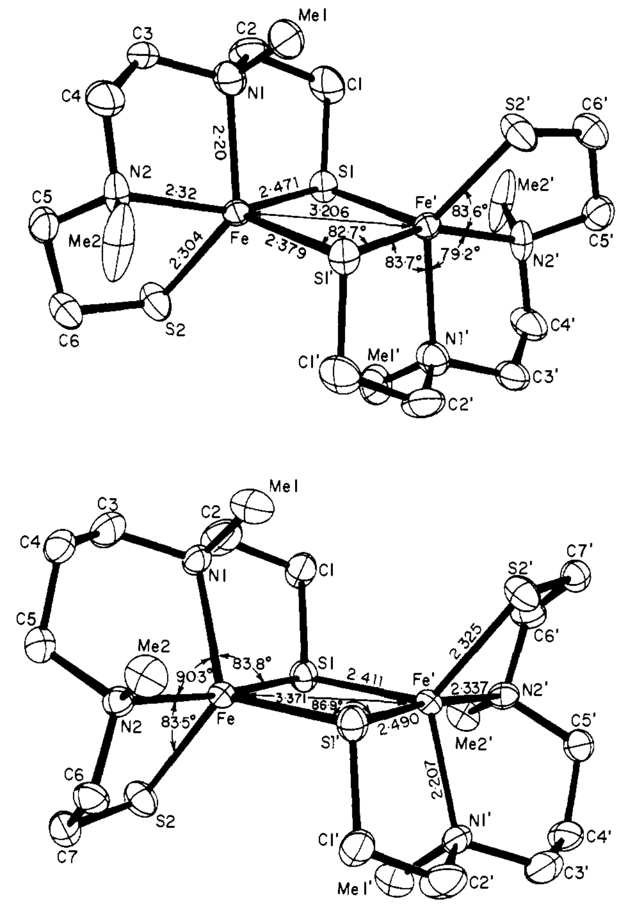


Figure 1. Structures of $(FeL)_2$ (top) and $(FeL')_2$ (bottom) as determined by x-ray diffraction. The primed and unprimed atoms are related by a crystallographic center of symmetry. Bond distances are in Å units. Full details are given in ref 18.

Experimental Procedure

Material and Methods. All compounds were prepared from commercially available starting materials used without further purification. Passage of CO through alkaline pyrogallol to remove oxygen impurities[8,19] had no effect on spectral properties of the carbonyl derivative of $(FeL)_2$. Methyl isocyanide[20] and *tert*-butyl isocyanide[21] were prepared by literature methods, and freshly distilled before use.

The synthesis and handling of all iron complexes and their solutions were carried out under inert atmosphere using either prepurified nitrogen or argon. Freshly opened, deaerated reagent grade solvents were used without further purification except for acetonitrile which was distilled from calcium hydride prior to use.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points were obtained by packing standard capillaries in a drybox and sealing them off under nitrogen with melted paraffin. The values reported are uncorrected.

The magnetic susceptibilities of the compounds (50–100 mg samples) were measured by the Faraday method over the temperature range $80 < T < 400$ K. The calibrant was $Hg[Co(NCS)_4]$.[22-24] Each sample was run at three field strengths in the range 6–10 kOe, and the results were averaged to give the final value. Diamagnetic corrections were computed using tabulated constants.[25]

Mössbauer spectra were recorded and analyzed in two laboratories. Room temperature spectra for all compounds, and at 87 K for $(FeL)_2$, were measured by members of the research group of Professor C. S. Wu, Department of Physics, Columbia University. Other measurements at lower temperature, as well as magnetically perturbed Mössbauer experiments, were performed and analyzed by Dr. George Lang, at Harwell, England. Details of the experimental methods employed can be found in publications by these workers.[26,27]

Proton nuclear magnetic resonance spectra were recorded on a Varian Associates A-60A spectrometer. Tetramethylsilane (Me_4Si) was added as an internal chemical shift calibrant, and all shifts are reported in parts per million downfield from Me_4Si (δ). Solution electronic spectra were recorded with a Cary 17 or Cary 14 spectrophotometer using 1-cm matched quartz cells. Visible and near-ir spectra of solids were also taken on these instruments by impregnating Nujol mulls of the solids on filter paper. Filter paper saturated with Nujol was used in the reference beam in these cases. Infrared spectra of solids were recorded on Nujol mulls between alkali-halide disks. Solution samples were taken in 0.1-mm pathlength NaCl cells. Polystyrene was used as the calibrant. Mass spectra were recorded by electron impact (EI) on a Finnigan 3300 mass spectrometer, utilizing a Finnigan 6000 data system. Reported spectra give *m/e* values for the most abundant ions.

Synthesis of Ligands. *N,N'*-Dimethyl-*N,N'*-bis(2-mercaptoethyl)-ethylenediamine (LH_2). Ethylene sulfide (33.5 g, 0.56 mol) in 10–20 ml of benzene was added dropwise to a warm, but not refluxing, solution of *N,N'*-dimethylethylenediamine (24.5 g, 0.28 mol) in 100 ml of benzene. The heat was removed and the solution stirred overnight. The resulting solution was washed twice with 5 ml of water, and then thoroughly dried over $MgSO_4$. Filtration and removal of the benzene by rotary evaporation (followed by vacuum to remove last traces of solvent) yielded 50.7 g (87%) of pure LH_2, as judged by proton NMR and TLC (one component on silica with methanol as the eluent). Further proof that the ligand synthesized is as formulated comes from the x-ray structures of metal complexes containing L.[15-18,28]

***N,N'*-Dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine ($L'H_2$).** Comparable yields of $L'H_2$ are obtained in the same manner as that for LH_2, where *N,N'*-dimethyl-1,3-propanediamine is substituted for *N,N'*-dimethylethylenediamine in the same molar quantity.

The syntheses of LH_2 and $L'H_2$ carried out under a nitrogen atmosphere generally gave better products. The ligands could be stored for months at room temperature under a blanket of nitrogen, which prevents air oxidation. (*Caution: The ligands have been found to cause severe allergic reactions (dermatitis and blistering), and physical contact with the compounds or their vapors should be avoided.*)

NMR: LH_2, $CDCl_3$, δ 1.83 (s, 2 H), 2.25 (s, 6 H), 2.42–2.75 (complex multiplet, 12 H); $L'H_2$, $CDCl_3$, δ 1.59 (quintet, $J = 8$ Hz, 2 H), 1.88 (s, 2 H), 2.20 (s, 6 H), 2.29–2.76 (complex multiplet 12 H) (s = singlet).

Synthesis of Iron Complexes. $[Fe(C_8H_{18}N_2S_2)]_2$, $(FeL)_2$. (a) The disulfide of ligand L was prepared by bubbling air through the neat liquid over molecular sieves (Linde no. 4A). The slightly yellow oil obtained was taken up in toluene and filtered, after which the solvent was removed. Oxidation was judged to be complete on the basis of infrared (disappearance of the S–H stretching vibration at about 2500 cm^{-1}) and NMR (disappearance of the sulfhydryl proton absorption) spectra.

Iron pentacarbonyl (2.3 g, 0.012 mol) was added to 2.4 g (0.012 mol) of ligand (L)-disulfide in 50 ml of toluene. The solution was refluxed overnight, then allowed to cool. The resulting precipitate was filtered, washed with benzene and pentane, and dried under vacuum; yield 0.40 g (13%).

Anal. Calcd for $C_8H_{18}N_2S_2Fe$: C, 36.63; H, 6.92; N, 10.68; S, 24.48. Found: C, 36.57; H, 7.17; N, 10.56; S, 24.22.

When the above reaction was run in dimethylformamide or benzene, a deep burgandy color was observed upon cooling of the reaction mixture. This color is presumed to be due to the dicarbonyl derivative of $(FeL)_2$ (vide infra); however, attempts to isolate the dicarbonyl complex from these reaction mixtures were unsuccessful. Concentration of these solutions by slow evaporation in a stream of nitrogen affords $(FeL)_2$, but no $FeL(CO)_2$.

(b) A filtered solution of ferric acetylacetonate (7.1 g, 0.02 mol) in 100 ml of toluene was added quickly to a solution of LH_2 (21 g, 0.1 mol) in 300 ml of toluene. The solution was mixed only briefly, then allowed to stand overnight. The resulting microcrystalline precipitate was filtered, washed thoroughly with toluene and ether, and dried in vacuo. The yield was 4.96 g (95%, based on Fe).

Anal. Found: C, 36.64; H, 6.78; N, 10.56; S, 24.09.

Ir: 1342, 1309, 1296, 1272, 1265(sh), 1238, 1217(w), 1210, 1197, 1158, 1142, 1131(w), 1102, 1078, 1046, 1030, 1018, 960(w), 946(w), 942, 922, 884, 765, 740, 673 (mult), 578, 524, 515, 465(br), 430 cm^{-1}.

MS: 50 V; most intense peak, *m/e* 262 (100%), parent peak *m/e* 524 (4), 326 (7), 234 (19), 216 (22), 201 (17), 188 (24), 145 (34), 102 (15), 99 (17).

$[Fe(C_9H_{20}N_2S_2)]_2$, $(FeL')_2$. (a) The synthesis of $(FeL')_2$ using

$Fe(CO)_5$ is analogous to that of $(FeL)_2$ described above. The yields are very poor, about 1%.

(b) Synthesis via thiol reduction of $Fe(acac)_3$ is the preferable route, as described above for $(FeL)_2$. High yields (>90%) of crystalline $(FeL')_2$ are attained; mp >200 °C.

Anal. Calcd for $C_9H_{20}N_2S_2Fe$: C, 39.13; H, 7.29; N, 10.14; S, 23.22. Found: C, 39.14; H, 6.91; N, 9.99; S, 23.08.

Ir: 1328, 1305, 1291, 1271, 1252 (w), 1229 (mult), 1219 (w), 1197, 1150, 1140, 1130, 1110, 1068 (sh), 1060, 1039 (mult), 1009 (w), 991, 979, 966, 942 (mult), 920, 894 (w), 868 (w), 832 (2), 782 (w, sh), 772, 730, 672, 550, 520 (w), 506, 469, 438 (mult) cm^{-1}.

MS: 50 V; most intense peak *m/e* 276 (100%), parent peak *m/e* 524 (1), 491 (3), 431 (2), 248 (19), 215 (58), 202 (38), 187 (36), 154 (45), 145 (26), 131 (23), 113 (28), 91 (37), 70 (38), 58 (26).

$Fe(C_8H_{18}N_2S_2)(CO)_2$, $FeL(CO)_2$. Seventy-five milliliters of deaerated dichloromethane was added to $(FeL)_2$ (3.20 g, 6.1 mmol). Carbon monoxide was *immediately* bubbled vigorously through the solution with warming (35–40 °C) until it was deep red. Addition of 75 ml of THF along with heating and CO bubbling was carried out quickly until the total volume was reduced to about 75 ml. The solution was filtered and 200 ml of petroleum ether was added under a CO blanket, and the solution placed at −15 °C overnight. Filtration under nitrogen atmosphere and drying in vacuo yielded 3.37 g (87% yield) of red, air stable microcrystals; >110 °C dec. The compound $FeL(CO)_2$ can also be synthesized by stirring a suspension of $(FeL)_2$ in dry THF under a blanket of carbon monoxide, followed by slow addition of petroleum ether saturated with CO at 0 °C to form microcrystals.[29]

Solid $FeL(CO)_2$ can be stored in the air in a desiccator. However, solutions of $FeL(CO)_2$ are very oxygen sensitive and they decompose to a brown insoluble precipitate. In the absence of oxygen, solutions of $FeL(CO)_2$ gradually decompose to $(FeL)_2$. $FeL(CO)_2$ also decomposes *slowly* in dichloromethane to an intractable oil. Prolonged exposure to CH_2Cl_2 should therefore be avoided during synthesis. As described above, this may be accomplished by working quickly or by using only THF.

Anal. Calcd for $C_{10}H_{18}N_2O_2S_2Fe$: C, 37.74; H, 5.70; N, 8.80; S, 20.15. Found: C, 37.91; H, 5.68; N, 8.85; S, 20.10.

Ir (Nujol mull, CsI): 2005 (s, br), 1940 (s, br), 1920 (w), 1428, 1403, 1377, 1365 (sh), 1342 (w), 1302, 1292, 1274 (w), 1263 (w), 1232, 1216, 1196, 1145 (w), 1124 (w), 1098 (w), 1058 (sh), 1050 (sh), 1043, 1035, 1025, 1015, 1010, 999 (w), 980 (w), 949, 930, 920 (w), 910 (w), 882 (w), 865 (w), 762, 735, 684, 661, 612, 580, 543, 531, 502 (w), 475 (w), 458 (w), 430, 410, 360, 270 cm^{-1}.

Ir (ν_{CO} region, CH_3CN solution): 2020 (s), 1960 (s), 1930 (vw, sh) cm^{-1}.

NMR: $CDCl_3$, δ 2.2–2.6 (multiplet, 6 H), δ 2.7–3.2 (multiplet, 12 H).

MS: 20 V, most intense peak *m/e* 262 (100%); parent peak *m/e* 318 (11); 290 (7), 234 (36), 216 (19), 201 (13), 188 (27), 145 (16).

$Fe(C_8H_{18}N_2S_2)(CH_3NC)_2$, $FeL(CH_3NC)_2$. Approximately 1 ml (large excess) of freshly prepared methyl isocyanide in 40 ml of benzene was added to 380 mg (0.73 mmol) of $(FeL)_2$. The mixture was stirred with warming (~50 °C) until the solution appeared purple, then stirring at room temperature was continued overnight. The precipitate obtained was filtered, washed with ether and dried in vacuo. The yield was 380 mg (76% based on Fe) of purple microcrystalline powder. $FeL(CH_3NC)_2$ is very air sensitive and should be stored under an inert atmosphere.

Anal. Calcd for $C_{12}H_{24}N_4S_2Fe$: C, 41.86; H, 7.03; N, 16.27; S, 18.62. Found: C, 41.08, H, 6.95; N, 15.89, S, 18.32.

Gravimetric measurements: 11.0 mg sample; 95 °C, vacuum, weight loss is 2.7 mg = 24.6%. Expected weight loss for $FeL(CH_3NC)_2$ is 23.8%; CH_3NC bands lost from ir spectrum.

Ir (Nujol mull, CsI): 2130 (s, br), 1980 (s, br), 1930 (w), 1407, 1302, 1291, 1278 (w), 1268 (w), 1229, 1212, 1192, 1143 (w), 1126 (w), 1100 (w), 1057, 1050, 1035, 1025, 1018, 998 (w), 970 (w), 960 (w), 944 (mult), 920, 905 (w), 899 (w), 875 (w), 860 (mult, w), 750, 728, 680, 611 (w), 590 (w, sh), 576 (w), 540 (w), 532 (w), 510, 483 (w, sh), 470, 450 (w), 417 (w), 395 (w), 340, 300 (w), 288 (w), 278 (w), 255 (w, mult) cm^{-1}.

Ir (ν_{CN} region, $CHCl_3$ solution): 2150 (s), 2110 (s), 1970 (w) cm^{-1}.

NMR: $CDCl_3$, δ 2.1–2.5 (mult, 6 H), 2.6–3.1 (mult, 12 H), 3.48 (s, 6 H).

MS: 70 V, as the temperature is raised large quantities of *m/e* 41 ($CNCH_3$) are observed with very little *m/e* 262 (FeL). At higher temperatures more *m/e* 262 is observed. No peak greater than *m/e* 262 was observed. At a point where total ion current for *m/e* 262 is maximum, the major peaks are: 262 (12), 234 (3), 216 (3), 201 (2), 188 (6), 145 (14), 102 (13), 99 (18), 70 (26), 56 (28), 42 (100).

$Fe(C_8H_{18}N_2S_2)(t\text{-}C_4H_9NC)_2$, $FeL(t\text{-BuNC})_2$. A solution of *tert*-butyl isocyanide (425 mg, 5.12 mmol) in 30 ml of tetrahydrofuran was added to solid $(FeL)_2$ (672 mg, 1.28 mmol). The solution was stirred with warming until dissolution of solid occurred and then stirring at room temperature was continued overnight. The resulting purple-red solution was filtered and the solvent was removed under vacuum. The solid remaining was further dried under vacuum yielding 735 mg (67% yield based on Fe) of purple crystalline precipitate. The solid is quite air sensitive and should be stored under an inert atmosphere.

Anal. Calcd for $C_{18}H_{36}N_4S_2Fe$: C, 50.46; H, 8.47; N, 13.08; S, 14.97. Found: C, 48.46; H, 8.26; N, 12.50; S, 14.59.

C, H, and N analyses are consistently low, and it is believed this is because some *t*-BuNC is lost before analysis. *t*-BuNC can be removed from $FeL(t\text{-BuNC})_2$ quantitatively by heating under vacuum.

Gravimetric measurements: 45.1 mg sample; 110 °C, vacuum; weight loss 17.6 mg = 39.0% loss. Expected weight loss for $FeL(t\text{-BuNC})_2$ is 38.8%. The *t*-BuNC absorptions were lost from the ir spectrum (depending on the conditions employed, *t*-BuNC was not always removable. Use of a sublimation apparatus (50 °C) equipped with a dry ice-acetone condenser worked quite well leaving a light brown precipitate having an ir spectrum identical to that of $(FeL)_2$).

Ir: 2100–2000 (broad, strong mult), 1363, 1305 (w), 1295 (w), 1279 (w), 1260 (w), 1228, 1203 (br, mult), 1134 (w), 1102 (w), 1059, 1051, 1040, 1029, 1001 (w), 975 (w), 948, 933, 912, 880, 861, 803 (w, br), 762, 744, 734, 684, 614 (w), 585 (w), 552, 525 (br) cm^{-1}.

Ir (ν_{CN} region, CH_3CN solution): 2170 (w, sh), 2095 (s), 2025 (s), 1955 (w, sh) cm^{-1}.

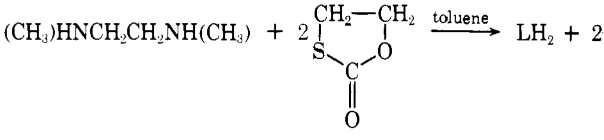
NMR: $CDCl_3$, δ 1.47 (s, 18 H), 2.0–2.3 (mult, 6 H), 2.5–3.0 (mult, 12 H).

MS: 26 V; most intense peak *m/e* 262 (100%), 524 (2), 294 (4), 244 (25), 216 (44), 201 (33), 188 (54), 172 (28), 145 (91), 102 (22), 99 (52). No parent ion observed.

Note: In the mass spectra of the compounds $FeL(CO)_2$ and $FeL(RNC)_2$ (R = CH_3, $t\text{-}C_4H_9NC$), the major fragment peaks are the same as those found in $(FeL)_2$.

Results and Discussion

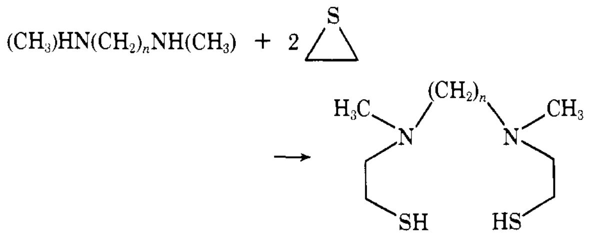
Synthesis of the Ligands and Their Iron(II) Complexes. As reported previously,[17] the ligand *N*,*N'*-dimethyl-*N*,*N'*-bis(2-mercaptoethyl)ethylenediamine, LH_2, can be synthesized by mercaptoethylation of *N*,*N'*-dimethylethylenediamine with ethylenemonothiocarbonate (eq 1). This route gives moderate



$$(CH_3)HNCH_2CH_2NH(CH_3) + 2\,\overset{CH_2-CH_2}{\underset{\underset{\displaystyle O}{\overset{\|}{C}}}{S\quad O}} \xrightarrow{\text{toluene}} LH_2 + 2CO_2 \qquad (1)$$

yields (60%) of impure compound. Ethylenemonothiocarbonate loses CO_2 to form ethylene sulfide in situ.[30] Although excess amine was employed to prevent further alkylation of product at sulfur (giving thioethers), NMR proton integration showed that this reaction still occurred. Infrared spectra of the product mixture revealed the presence of carbonyl impurities. In addition, a white solid always collected on the condenser, interfering with the reaction. This solid had an NMR spectrum identical with that of the starting substituted diamine, and could be synthesized by addition of CO_2 (as dry ice) to the diamine. The white solid is presumed to be a carbonate salt, $(RR'NH_2)_2CO_3$.

A superior synthesis of the ligands LH_2 and $L'H_2$ in high yields results from the stoichiometric addition of ethylene sulfide to the appropriate amine, eq 2. This reaction fails if the starting diamine is substituted with *tert*-butyl or benzyl instead of methyl groups; the ethylene sulfide polymerizes leaving the starting amine unreacted. Presumably, attack of amine nitrogen upon the carbon atom of ethylene sulfide is sterically



(2)

hindered by the large R groups, allowing ethylene sulfide to self-polymerize.

The iron compounds, $(FeL)_2$ and $(FeL')_2$, Figure 1, were synthesized in either of two possible routes: (1) reaction of iron pentacarbonyl with the appropriate ligand-disulfide, or (2) reaction of ferric acetylacetonate with an excess of ligand-dithiol. The reactions of metal carbonyl complexes with organic disulfides to form metal-thiolate compounds are well known.[31] Disulfides of LH_2 and $L'H_2$ were prepared by air oxidation of the free ligands. The standard method of disulfide preparation by iodine oxidation[32] gave an insoluble polymer not suitable for further reaction. Stoichiometric reaction with iron pentacarbonyl afforded pure products in low yield (eq 3).

$$Fe(CO)_5 + L \text{ or } L'_{\text{disulfide}} \longrightarrow (FeL)_2 \text{ or } (FeL')_2 \qquad (3)$$

The reduction of Fe(III) with excess thiol was found to be a much better method of synthesis of $(FeL)_2$ and $(FeL')_2$. The products of this reaction were isolated to determine its stoichiometry. Based on (1) the recovery of acetylacetone (NMR evidence; comparison with authentic material) and (2) the reduction in the relative number of sulfhydryl protons to non-sulfhydryl protons in the excess ligand recovered (from NMR integration), the reaction is suggested to proceed according to eq 4. As judged by the time it takes for precipitation

$$2Fe(acac)_3 + 3LH_2 \longrightarrow (FeL)_2 + 6acacH + L_{\text{disulfide}} \qquad (4)$$

of the product, the reaction proceeds at a higher rate when excess ligand is used instead of a stoichiometric amount. Excess LH_2 also improves the yield.

$(FeL)_2$ and $(FeL')_2$ are obtained as light brown microcrystalline solids which should be stored under anaerobic conditions. $(FeL)_2$ is quite soluble in dichloromethane and chloroform, but it slowly decomposes in these solvents as judged by changes in its electronic and ir spectra, and by an increase in its magnetic susceptibility.[33] It is sparingly soluble in benzene, toluene, and dimethylformamide, and essentially insoluble in all other common solvents in the absence of air. $(FeL')_2$ is much less soluble in all solvents under any conditions.

The mass spectra of $(FeL)_2$ and $(FeL')_2$ show parent peaks at *m/e* 524 and 552, respectively (see Experimental Procedure). The most intense peaks occur at *m/e* 262 and 276, however, which correspond to (FeL) and (FeL') monomers. These results substantiate their formulation as iron(II) complexes and rule out any possibility that the sulfur atoms are protonated. Protonated sulfur atoms (thiols) have been observed as ligands in iron[34] and ruthenium[35] compounds. If this occurred here, the oxidation state of the iron atoms would be lower than two. Further evidence in support of $(FeL)_2$ and $(FeL')_2$ as Fe(II) compounds comes from their Mössbauer spectra and magnetic properties (vide infra).

Transition metal complexes of similar N_2S_2 tetradentate ligands have been studied;[36-38] however, L and L' appear to be the first which contain both saturated nitrogen and thiolate groups. Other known ligands contain either thioether or thione sulfur and/or unsaturated imine nitrogen donor atoms. The compound $[Fe(edt)_2]_2^{2-}$, where edt = $^-SCH_2CH_2S^-$, is a five-coordinate iron(III) dimer in which the donor atoms are all saturated thiolate groups.[39,40] The coordination geometry in this complex is very similar to that in $(FeL)_2$ and $(FeL')_2$.[18,39]

Table I. Mössbauer Parameters for $(FeL)_2$, $(FeL')_2$, and Related Compounds

Compound[a]	T (°K)	δ (mm/s)[b]	ΔE_Q (mm/s)
$(FeL)_2$	4.2	0.84	3.57
	77	0.83	3.57
	87	0.78	3.61
	195	0.76	3.48
	Ambient	0.71	3.40
$(FeL')_2$	4.2	0.88	3.45
	77	0.87	3.42
	Ambient	0.76	3.23
$Fe(cys)_2{\cdot}2H_2O$[c]	Ambient	0.88	3.02
$[Fe(dtc)_2]_2$[d]	77	0.875	4.19

[a] L and L' are defined in the text; cys = cysteinate, $^-SCH_2CH(NH_3^+)(CO_2^-)$; dtc = diethyldithiocarbamate, $(C_2H_5)_2NCS_2^-$. [b] Isomer shifts are referred to iron metal. [c] H. G. Mathur, M. P. Gupta, and C. V. Kavedia, *Indian J. Chem.*, **4**, 337 (1966). [d] Reference 43.

Oxidation and Spin States of $(FeL)_2$ and $(FeL')_2$. Mössbauer effect measurements have been carried out on $(FeL)_2$ and $(FeL')_2$ from 4.2 K to room temperature. The results are summarized in Table I and typical unperturbed spectra are shown in Figure 2. The spectra consist of a single, quadrupole split, doublet as expected from the x-ray structural results (Figure 1). The additional weak peaks in the spectrum of $(FeL)_2$ come from an impurity, and these lines increase in intensity if the sample is exposed to air. The $(FeL')_2$ dimer is substantially less oxygen sensitive, judging from its Mössbauer spectra.

The observed isomer shift (δ) and quadrupole splitting (ΔE_Q) parameters are consistent with the presence of high-spin iron(II),[41] and are very similar to those of related high-spin ferrous complexes containing nitrogen[42] or sulfur[43,44] donor ligands. A closely related complex is $[Fe(S_2CNEt_2)_2]_2$, recently shown[45] to be a sulfur-bridged dimer with pentacoordinate iron atoms in distorted trigonal bipyramidal environment (cf. Figure 1). The isomer shift and quadrupole splitting of this complex, $Fe(cysteine)_2{\cdot}2H_2O$ (which may also be a thiolate-bridged dimer, vide infra), and the $(FeL)_2$ and $(FeL')_2$ dimers are all similar (Table I). It should be noted that the quadrupole splitting is larger for $(FeL)_2$ than for $(FeL')_2$ at any given temperature, a result consistent with the more distorted geometry of the former.[18]

The observed temperature dependence of the isomer shift in $(FeL)_2$ and $(FeL')_2$ is expected from the second-order Doppler effect.[46] The small temperature dependence of the quadrupole splittings indicates the presence of thermally accessible excited states over the temperature range. The relatively low symmetry of these complexes (departure from trigonal bipyramidal geometry as well as bonding anisotropy) lifts the degeneracy (in D_{3h} symmetry) of the d_{xz} and d_{yz} orbitals. If the splittings are not large in energy, then excited orbital states in $(FeL)_2$ and $(FeL')_2$ will be thermally populated. Although the temperature dependence of the quadrupole splitting has been used to deduce orbital splitting in tetrahedral iron(II) species,[47] the present changes in ΔE_Q with temperature are too small to extract meaningful results. Additional evidence for the thermally accessible excited states in $(FeL)_2$ and $(FeL')_2$ comes from magnetic studies discussed in the following paper.[14]

Mössbauer effect measurements were also made in the presence of an external magnetic field of 60 kOe at 4.2 K for both $(FeL)_2$ and $(FeL')_2$ (Figure 3). Comparison to calculated

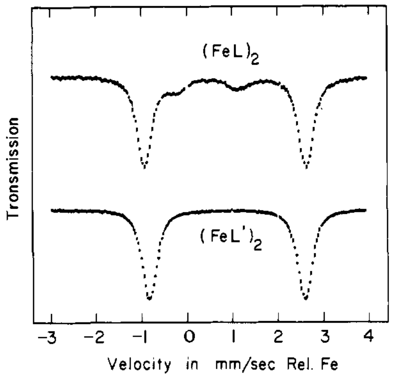


Figure 2. Mössbauer spectra of $(FeL)_2$ and $(FeL')_2$ at 4.2 K.

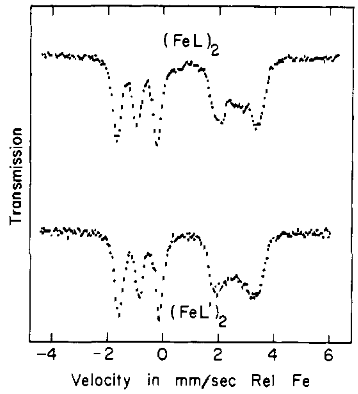


Figure 3. Magnetically perturbed Mössbauer spectra of $(FeL)_2$ and $(FeL')_2$ at 4.2 K.

Table II. Electronic Spectra of $(FeL)_2$ and $(FeL')_2$

Compound	Solid (Nujol mull)[a] (cm^{-1})	Dimethylformamide solution[c] (cm^{-1})
$(FeL)_2$	~10 000	~10 000
	18 500 (sh)[b]	18 500
	23 300 (sh)	22 700
	30 300	30 300
$(FeL')_2$	~10 000	
	18 500 (sh)[b]	
	22 700 (sh)	
	31 300	

[a] The relative intensity of the bands increases with decreasing wavelength. [b] This band (shoulder) is barely discernible. [c] Saturated solutions were prepared by letting solid samples stand in DMF under nitrogen atmosphere for several days.

spectra shows no enhancement of the splitting with the applied field indicating a diamagnetic ($S = 0$) ground state for both $(FeL)_2$ and $(FeL')_2$. This behavior suggests that the iron atoms are antiferromagnetically coupled in these compounds. Antiferromagnetic spin exchange was independently verified by the temperature dependence of the magnetic susceptibility over the temperature range $80 < T < 350$ K. In addition, the magnetic results revealed substantially greater coupling in $(FeL)_2$ than in $(FeL')_2$, the room temperature moments being 3.4 and 4.2 μ_B, respectively. It was not possible to fit the susceptibility vs. temperature curves with a simple Heisenberg exchange ($-2JS_1 \cdot S_2$),[48] however, and a more extensive experimental and theoretical analysis was therefore undertaken. The results are discussed separately.[14]

The lower energy triplet and higher energy "doublet" (Figure 3) in the magnetic Mössbauer spectra demonstrate that the principal component of the electric field gradient tensor (V_{zz}) is positive and that the asymmetry parameter is zero or small, suggesting nearly axial symmetry.[49] Positive V_{zz} corresponds to an excess of in-plane charge density. This result is consistent with the ground state orbitals found from analysis of the magnetic susceptibility data (see following paper).[14] Positive V_{zz} has been observed for high spin iron(II) compounds, both in trigonal bipyramidal and distorted tetragonal pyramidal coordination geometries.[43,49-51]

The possibility that the iron atoms in either $(FeL)_2$ or $(FeL')_2$ are in spin equilibrium[52] is quite unlikely, based on the magnetic and Mössbauer data. The magnetic properties[14] clearly show the iron atoms to have spin state $S = 2$, a result that rules out the possibility of a singlet–triplet spin equilibrium.[53] In the solid state, all known cases of singlet–quintet spin equilibria in iron(II) compounds exhibit two quadrupole doublets over the temperature range.[54] The two species in different spin states have distinctly different Mössbauer parameters, and the relative intensities of the two quadrupole doublets change with temperature as the relative population of spin states changes. The absence of two quadrupole doublets in the Mössbauer spectra of $(FeL)_2$ and $(FeL')_2$, therefore, demonstrates that a spin equilibrium does not occur.

Measurements of the electronic spectra of $(FeL)_2$ and $(FeL')_2$ are made difficult by the extremely low solubility of these compounds. Solid state spectra, obtained by using Nujol mulls of the compounds, were recorded in the region 300–2000 nm. Solution spectra of $(FeL)_2$ in dimethylformamide could also be measured. Extinction coefficients were not determined owing to the low solubility. The spectra are very similar for both compounds and the positions of the bands observed are given in Table II.

The visible region of the spectra is dominated by strong charge transfer bands. Aliphatic amine complexes of iron(II) show only weak absorptions in the visible region.[55,56] Thus, the strong absorptions observed are assigned to iron–sulfur charge transfer transitions. Both compounds show a broad d–d absorption (weak) at about 1000 nm in the region found for high-spin iron(II).[42,43] This band occurs at 9500 cm^{-1} for $[Fe(S_2CNEt_2)_2]_2$,[43] which is structurally related to $(FeL)_2$ and $(FeL')_2$, as discussed above. The ligand field splitting in the three compounds must therefore be very similar. The spectra of $(FeL)_2$ and $(FeL')_2$ did not show a band ~6000 cm^{-1} that is sometimes observed in the dithiocarbamate dimers.[43] If one is there, it is too weak to observe at room temperature under the conditions of our measurements.

Binding of Carbon Monoxide and Alkyl Isocyanides to $(FeL)_2$. The pentacoordinate $(FeL)_2$ and $(FeL')_2$ dimers contain two formally 16-electron iron atoms; thus they are both coordinatively unsaturated and have the potential to bind additional ligands. It was of interest to see what effect, if any, the structural differences in $(FeL)_2$ and $(FeL')_2$ have upon their reaction chemistry. Both compounds were therefore allowed to react with carbon monoxide. In the case of $(FeL)_2$, a reversible reaction with CO takes place, but no reaction occurs with $(FeL')_2$ under the conditions employed.

Many examples of reversible reaction of carbon monoxide with transition metal complexes have appeared in the literature.[12,57,58] The reaction of CO with $(FeL)_2$ involves a monomer–dimer equilibrium between $FeL(CO)_2$ and $(FeL)_2$ (eq 5).

$$(FeL)_2 + 4CO \rightleftharpoons 2FeL(CO)_2 \qquad (5)$$

When a suspension of $(FeL)_2$ in methanol or benzene is heated (60 °C) and bubbled vigorously with carbon monoxide, a deep red solution develops. An infrared spectrum shows two strong sharp CO absorption bands at 1970 and 2030 cm^{-1} (in methanol); however, workup under a nitrogen atmosphere in these solvents results in gradual loss of the red color and isolation of starting material, $(FeL)_2$. Alternatively, when $(FeL)_2$ is "dissolved" in dichloromethane at room temperature ($(FeL)_2$ reacts slowly with CH_2Cl_2, but this reaction does not appear to interfere), and the solution is immediately bubbled with CO and warmed, the deep red solution (same ir) develops within seconds. Addition of toluene, followed by preferential removal of CH_2Cl_2 by bubbling with nitrogen gas while heating, causes precipitation of crystals of $(FeL)_2$ (as identified by its infrared spectrum, solubility characteristics, and room temperature magnetic moment of 3.2 μ_B). This cycle of reversing the reactions alternatively between $(FeL)_2$ and the carbonyl adduct in CH_2Cl_2-toluene can be repeated three times with recovery of 87% of starting material.

If tetrahydrofuran (THF) is used as solvent under a carbon monoxide atmosphere, the red crystalline solid $FeL(CO)_2$ can be isolated in high yield. $FeL(CO)_2$ is diamagnetic and is stable in air in the solid state. It can be dried in vacuo without loss of carbon monoxide; however, quantitative loss of CO occurs above 80 °C in vacuo as judged by gravimetric measurements and loss of the carbonyl stretching bands in the infrared spectrum (the ir of the remaining solid is identical with that of $(FeL)_2$). The elemental analysis confirms the formulation as $FeL(CO)_2$, which is also substantiated by the mass spectrum. Stepwise loss of CO is evident in the mass spectrum and the most intense peak is the (FeL) monomer at *m/e* 262.

The presence of two strong carbonyl absorption bands in the infrared spectrum of $FeL(CO)_2$ suggests a cis stereochemistry for the CO ligands. In addition, the infrared spectra of both solid and solution samples always have an additional weak absorption band at about 1920 cm^{-1}. The proton NMR spectrum of $FeL(CO)_2$ is similar to that of the free ligand L except for the *N*-methyl resonances which are a poorly resolved broad multiplet. The infrared and NMR spectra suggest that more than one species is present, which could be due to the ligand wrapping, a small amount of the trans isomer, and/or FeL(CO). From the predominant intense ir doublet, however, the main species is assigned as six-coordinate $FeL(CO)_2$ with cis carbonyl groups.

In the synthesis of $(FeL)_2$ from $Fe(CO)_5$ and $L_{disulfide}$, eq 3, a red color developed during the course of the reaction. A spectrum of the reaction mixture in the visible region showed a band at 518 nm. $FeL(CO)_2$ also shows a band in the visible at 518 nm. Since $FeL(CO)_2$ decomposes in solution under nitrogen to $(FeL)_2$, the observations cited above suggest that $FeL(CO)_2$ is an intermediate in the synthesis of $(FeL)_2$ from iron pentacarbonyl. It should be noted that no red color was observed in the analogous synthesis of $(FeL')_2$.

The ease with which $FeL(CO)_2$ reverts back to $(FeL)_2$ provides a method of purification of this relatively insoluble dimer. Synthesis of the dicarbonyl adduct, followed by controlled decomposition, yields crystalline $(FeL)_2$.

The reaction of methyl or *tert*-butyl isocyanide with $(FeL)_2$ affords bis(isocyanide) complexes similar to $FeL(CO)_2$. Addition of an excess of freshly prepared CH_3NC to a suspension of $(FeL)_2$ in benzene yields a diamagnetic (NMR criterion), purple microcrystalline solid formulated as $FeL(CH_3NC)_2$. The similar reaction of *t*-BuNC in THF gives the purple solid $FeL(t\text{-}BuNC)_2$ (also diamagnetic). In both cases, recrystallization usually led to decomposition; thus physical characterization was carried out on the crude products. In the presence of air, both the solids and solutions of $FeL(CH_3NC)_2$ and $FeL(t\text{-}BuNC)_2$ turn to a brown color and become paramagnetic (Faraday measurements on the solid). At least in the case of $FeL(CH_3NC)_2$, qualitative experiments demonstrated that it can be synthesized directly by replacement of CO by CH_3NC in the complex $FeL(CO)_2$.

The chemical analyses for both isocyanide derivatives, particularly the carbon and hydrogen analyses, are somewhat low indicating possible loss of RNC from the compounds. However, proton NMR integration and gravimetric measurements (quantitative removal of RNC) confirm the formulation $FeL(RNC)_2$. The absence of infrared stretching vibrations in the 1600-1800-cm^{-1} region rule out the possibility of bridging isocyanide groups. The infrared spectra of both isocyanide derivatives show a broad, strong doublet in the 2000-cm^{-1} region, implying a cis configuration of RNC groups. In $FeL(CH_3NC)_2$ there is another weak but prominent band at 1970 cm^{-1} ($CHCl_3$ solution) indicating the presence of another or other isomers. $FeL(t\text{-}BuNC)_2$ does not show this band, but the breadth of the doublet observed does not rule out the possibility that additional isomers are present. As in the case of $FeL(CO)_2$, the NMR spectrum shows multiple resonances in the *N*-methyl region of L. The *tert*-butyl and methyl proton resonances in the NMR spectra occur as singlets and are found in the region expected for coordinated isocyanide groups.[59] Under the conditions used, mass spectra of $FeL(RNC)_2$ do not show parent ions, but give *m/e* 262 (FeL monomer) as the most intense peak. Free isocyanide (CH_3NC or *t*-BuNC) was also observed in the mass spectra, but it comes off at lower temperatures than required to observe the (FeL) monomer.

Quantitative removal of RNC from $FeL(RNC)_2$ was effected by heating under vacuum giving a material with an infrared spectrum identical with $(FeL)_2$. Attempts to remove RNC from $FeL(RNC)_2$ in solution to generate $(FeL)_2$, however, were unsuccessful.

It should be noted that reaction of either CH_3NC or *t*-BuNC with $(FeL')_2$ was *not* observed under similar conditions to the reactions with $(FeL)_2$.

Comparison with Iron(II) Cysteinate and Related Compounds. The properties of $FeL(CO)_2$ including its color, infrared spectrum, and ability to lose CO reversibly, resemble those of the known iron(II) cysteinate complex bis(cysteinato)dicarbonyliron(II),[8,10,12] which also loses carbon monoxide reversibly giving bis(cysteinato)iron(II).[8,12] By analogy to the known structure of $(FeL)_2$,[18] the iron(II) cysteinate complex may also be a thiolate bridged dimer. Cysteine is thought to bond through nitrogen and sulfur in the dicarbonyl adduct,[13] in which case the ligand donor atoms in $(FeL)_2$ and bis(cysteinato)iron(II) would be the same. Room temperature measurements[10] show that the magnetic moment of bis(cysteinato)iron(II) is 4.74 μ_B, which is lower than that expected for high spin iron(II). This suggests the possibility of spin coupling in a dimeric complex. The Mössbauer effect parameters are also comparable to those of $(FeL)_2$ (Table I).

$FeL(CO)_2$ is also similar to the dicarbonylbis(dialkyldithiocarbamato)iron(II) complexes, $Fe(CO)_2(S_2CNR_2)_2$.[60] These compounds have cis carbonyl groups and can be derived from bis(dialkyldithiocarbamato)iron(II),[43] which has been shown to be a pentacoordinate sulfur bridged dimer for the ethyl derivative.[45] As discussed above, the spectral, magnetic, and Mössbauer properties[43,44] of $[Fe(R_2NCS_2)_2]_2$ (R = Et, *n*-Pr, *n*-Bu) are strikingly similar to those of $(FeL)_2$ and $(FeL')_2$. Reversibility in the reaction of carbon monoxide with the (dithiocarbamato)iron(II) complexes has not yet been reported, however.

Recently, the reversible reaction of an iron-dithiolene complex, $[Fe(S_2C_2(CF_3)_2)_2]_2$, with carbon monoxide has been described yielding a monomeric pentacoordinate carbonyl complex, $Fe[S_2C_2(CF_3)_2]_2(CO)$. This is analogous to the $(FeL)_2$-$FeL(CO)_2$ equilibrium since it also involves a dimer-monomer interconversion;[58] however, the carbonyl complex formed has only one CO group.

Concluding Remarks

The x-ray structural studies on $(FeL)_2$ and $(FeL')_2$ demonstrated the influence of ligand steric constraints on the geometries of these complexes (Figure 1).[18] Mössbauer, magnetic, and electronic spectral properties of $(\mathrm{FeL})_2$ and $(\mathrm{FeL}')_2$ show the iron atoms to be in the +2 oxidation state with a high spin configuration. This oxidation and spin state gives rise to longer metal–ligand bond lengths compared to a low spin configuration or to iron in the +3 oxidation state.[61] The long metal–ligand bonds produce constrained N,N′- and N,S-chelate ring angles, especially in $(\mathrm{FeL})_2$. The extra methylene group in the N,N′-chelate ring of $(\mathrm{FeL}')_2$ relieves the steric constraint, resulting in the differences in the physical properties of the two compounds as described here and in the following paper.[14]

An important driving force in the conversion of $(\mathrm{FeL})_2$ to its carbonyl and isocyanide derivatives is the generation of low spin, six-coordinate 18-electron complexes from high spin, coordinatively unsaturated 16-electron metal centers. The high to low spin conversion occurring in eq 5 and the analogous isocyanide reaction produces compounds $\mathrm{FeL(CO)_2}$ and $\mathrm{FeL(RNC)_2}$ in which the metal–ligand bond distances should be substantially shorter.[61] The shortened Fe–N bonds require opening of the N–Fe–N chelate ring angle to near octahedral angles (90°) (see discussion, ref 18), thus relieving the steric constraints.

It is possible that steric constraints can account for differences in the reaction chemistry of $(\mathrm{FeL})_2$ and $(\mathrm{FeL}')_2$. The x-ray structure of $(\mathrm{FeL}')_2$ shows it to have a less constrained coordination geometry (Figure 1) and it does not appear to react with CO or RNC.[62] The relative ease of formation of the iron(II) cysteinate carbonyl adduct from $\mathrm{Fe(cys)_2}$ should be noted in this context, however, and it would be interesting to know the structure of the compound $\mathrm{Fe(cys)_2 \cdot 2H_2O}$.

Acknowledgments. This work was supported by Public Health Service Grant GM-16449. We thank Dr. George Lang and Professor C. S. Wu for Mössbauer effect studies and many helpful discussions.

References and Notes

(1) S. J. Lippard, *Acc. Chem. Res.*, **6**, 282 (1973).

(2) R. H. Holm, *Endeavour*, **34**, 38 (1975).

(3) W. Lovenberg, Ed., "Iron-Sulfur Proteins", Vol. I and II, Academic Press, New York, N.Y., 1973.

(4) W. H. Orme-Johnson, *Annu. Rev. Biochem.*, **42**, 159 (1973).

(5) J. C. M. Tsibris and R. W. Woody, *Coord. Chem. Rev.*, **5**, 417 (1970).

(6) R. H. Sands and W. R. Dunham, *Q. Rev. Biophys.*, **7**, 443 (1975).

(7) R. Malkin and J. C. Rabinowitz, *Annu. Rev. Biochem.*, **36**, 113 (1967).

(8) M. Schubert, *J. Am. Chem. Soc.*, **54**, 4077 (1932); *ibid.*, **55**, 4563 (1933).

(9) N. Tanaka, I. M. Kolthoff, and W. Stricks, *J. Am. Chem. Soc.*, **77**, 1996 (1955).

(10) J. H. Wang, A. Nakahara, and E. B. Fleischer, *J. Am. Chem. Soc.*, **80**, 1109 (1958).

(11) A. D. Gilmour and A. McAuley, *J. Chem. Soc. A*, 1006 (1970).

(12) A. Tomita, H. Hirai, and S. Makishima, *Inorg. Chem.*, **6**, 1746 (1967); **7**, 760 (1968).

(13) A. Tomita, H. Hirai, and S. Makishima, *Inorg. Nucl. Chem. Lett.*, 4, 715 (1968).

(14) A. P. Ginsberg, M. E. Lines, K. D. Karlin, S. J. Lippard, and F. J. DiSalvo, *J. Am. Chem. Soc.*, following paper in this issue.

(15) H. N. Rabinowitz, K. D. Karlin, and S. J. Lippard, submitted for publication.

(16) K. D. Karlin, H. N. Rabinowitz, D. L. Lewis, and S. J. Lippard, to be submitted for publication.

(17) W. J. Hu, D. Barton, and S. J. Lippard, *J. Am. Chem. Soc.*, **95**, 1170 (1973).

(18) W. J. Hu and S. J. Lippard, *J. Am. Chem. Soc.*, **96**, 2366 (1974).

(19) A. J. Gordon and R. A. Ford, "The Chemists Companion", Wiley, New York, N.Y., 1972, p 440.

(20) J. Casanova, Jr., R. E. Schuster, and N. D. Werner, *J. Chem. Soc.*, 4280 (1963).

(21) R. A. Bailey, *J. Chem. Educ.*, **49**, 297 (1972).

(22) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(23) The value of $\theta = +10°$ was used in the calibrations. Recent measurements on $\mathrm{Hg[Co(SCN)_4]}$ down to 4 K show that $\theta = -5°$.[24]

(24) H.-St. Räde, *J. Phys. Chem.*, **77**, 424 (1973).

(25) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1970, Chapter 25.

(26) B. H. Huynh, G. C. Papaefthymiou, C. S. Yen, J. C. Groves, and C. S. Wu, *J. Chem. Phys.*, **61**, 3750 (1974).

(27) G. Lang, R. Aasa, K. Garbett, and R. J. P. Williams, *J. Chem. Phys.*, **55**, 4539 (1971).

(28) K. D. Karlin, D. L. Lewis, H. N. Rabinowitz, and S. J. Lippard, *J. am. Chem. Soc.*, **96**, 6519 (1974).

(29) L. Baltusis, Columbia University, unpublished results.

(30) D. D. Reynolds, M. K. Massad, D. L. Fields, and D. J. Johnson, *J. Org. Chem.*, **26**, 5109 (1961).

(31) See, for example, R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1960).

(32) E. E. Reid, "Organic Chemistry of Bivalent Sulfur", Vol. I, Chemical Publishing Co., New York, N.Y., 1958, p 124.

(33) K. D. Karlin, Ph.D. dissertation, Columbia University, 1975, pp 188–190.

(34) J. P. Collman, T. N. Sorrell, and B. M. Hoffman, *J. Am. Chem. Soc.*, **97**, 913 (1975).

(35) C. G. Kuehn and H. Taube, *J. Am. Chem. Soc.*, **98**, 689 (1976).

(36) M. A. Akbar and S. E. Livingstone, *Coord. Chem. Rev.*, **13**, 101 (1974).

(37) D. St.-C. Black and A. J. Hartshorn, *Coord. Chem. Rev.*, **9**, 219 (1972–73).

(38) M. S. Elder, G. M. Prinz, P. Thornton, and D. H. Busch, *Inorg. Chem.*, 7, 2426 (1968).

(39) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 249 (1973).

(40) T. Herskovitz, B. V. Depamphilis, W. O. Gillum, and R. H. Holm, *Inorg. Chem.*, **14**, 1426 (1975).

(41) G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, **15**, 59 (1972).

(42) See, for example, D. P. Riley, P. H. Merrell, J. A. Stone, and D. H. Busch, *Inorg. Chem.*, **14**, 490 (1975).

(43) B. W. Fitzsimmons, S. E. Al-Mukhtar, L. F. Larkworthy, and R. R. Patel, *J. Chem. Soc., Dalton Trans.*, 1969 (1975).

(44) (a) L. F. Larkworthy, B. W. Fitzsimmons, and R. R. Patel, *J. Chem. Soc., Chem. Commun.*, 902 (1973); (b) J. L. K. F. de Vries, J. M. Trooster, and E. deBoer, *Inorg. Chem.*, **12**, 2730 (1973); (c) J. P. Fackler, Jr., and D. G. Holah, *Inorg. Nucl. Chem. Lett.*, **2**, 251 (1966).

(45) O. A. Ileparuma and R. D. Feltham, *Inorg. Chem.*, 14, 3042 (1975).

(46) (a) A. A. Maradudin, P. A. Flinn, and S. Ruby, *Phys. Rev.*, **126**, 9 (1962); (b) B. D. Josephson, *Phys. Rev. Lett.*, **4**, 341 (1960); (c) R. V. Pound and G. A. Rebka, jr., *ibid.*, 4, 274 (1960).

(47) (a) P. R. Edwards, C. E. Johnson, and R. J. P. Williams, *J. Chem. Phys.*, **37**, 2074 (1967); (b) M. Bond, R. L. Martin, and I. A. G. Roos, *Aust. J. Chem.*, **27**, 2307 (1974).

(48) Reference 33, pp 45–68.

(49) W. M. Reiff, *Coord. Chem. Rev.*, **10**, 37 (1973).

(50) W. M. Reiff, *Inorg. Chem.*, **13**, 239 (1974).

(51) R. B. Frankel, W. M. Reiff, I. Bernal, and M. L. Good, *Inorg. Chem.*, **13**, 493 (1974).

(52) R. L. Martin in "New Pathways in Inorganic Chemistry", E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, Cambridge, 1968, Chapter 9.

(53) L. H. Pignolet, G. S. Patterson, J. F. Weiher, and R. H. Holm, *Inorg. Chem.*, **13**, 1263 (1974).

(54) M. A. Hoselton, L. J. Wilson, and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 1722 (1975).

(55) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **11**, 980 (1972).

(56) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 1150 (1966).

(57) (a) W. R. McClellan and R. E. Benson, *J. Am. Chem. Soc.*, **88**, 5165 (1966); (b) R. Colton, G. R. Scollary, and I. B. Tomkins, *Aust. J. Chem.*, **21**, 15 (1968); (c) L. R. Melby, *Inorg. Chem.*, **9**, 2186 (1970); (d) R. Mason and G. Rucci, *Chem. Commun.*, 1132 (1971); (e) L. Vaska and T. Yamaji, *J. Am. Chem. Soc.*, **93**, 6673 (1971); (f) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *ibid.*, **95**, 4087 (1973); (g) D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, and N. J. Rose, *ibid.*, **95**, 5152 (1973); (h) V. L. Goedkin and S-M. Peng, *ibid.*, **96**, 7826 (1974); (i) S. J. Kim and T. Takizawa, *J. Chem. Soc., Chem. Commun.*, 356 (1974); (j) G. R. Eaton and S. S. Eaton, *J. Am. Chem. Soc.*, **97**, 235 (1975), and references therein; (k) J. W. McDonald, J. L. Corbin, and W. E. Newton, *ibid.*, **97**, 1970 (1975).

(58) J. S. Miller, *Inorg. Chem.*, 14, 2011 (1975).

(59) See, for example, M. Novotny and S. J. Lippard, *Inorg. Chem.*, **13**, 828 (1974).

(60) H. Büttner and R. D. Feltham, *Inorg. Chem.*, **11**, 971 (1972), and references therein.

(61) J. W. Lauher and J. A. Ibers, *Inorg. Chem.*, **14**, 348 (1975), and references therein.

(62) A referee suggests that "the failure of $(\mathrm{FeL}')_2$ to react may simply be due to thermodynamic lattice effects which strongly stabilize solid $(\mathrm{FeL}')_2$ over $[\mathrm{FeL'(CO)_2}]$ in either solvated or solid form."