accepts the electron is largely delocalized over the ligand, and the rapid rate is associated with resonance transfer directly from the reductant to the final acceptor orbital.[5]

Finally, it is noteworthy that the rate pattern for the reductions of $Ru(NH_3)_5py^{3+}$ and $Co(NH_3)_5py^{3+}$ by $Fe(CN)_6^{4-}$ extends to other reducing agents. The pertinent data are presented in Table V. It will be seen that the reactions of $Ru(NH_3)_5py^{3+}$ are ca. 5×10^5 faster than the corresponding reactions of $Co(NH_3)_5py^{3+}$, the ratio k_{Ru}/k_{Co} being fairly insensitive to the nature of the reductant. This is the expected result if Marcus' relation is applicable to all of these reactions. Since $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$, it follows that the ratio $k_{Ru}/k_{Co} = (k_{RuRu}/k_{CoCo})^{1/2}K_{RuCo}^{1/2}$ and therefore is independent of the nature of the reducing agent.

References and Notes

(1) (a) This work was supported by Grant GP-37057X and CHE7610449 from the National Science Foundation; (b) abstracted from the Ph.D. Dissertation of A.J.M., State University of New York, Stony Brook, N.Y., July 1974, and from the B.S. Thesis of R.E.A., State University of New York, Stony Brook, N.Y., May 1976; (c) holder of a fellowship from the Instituto Venezolano de Investigaciones Cientifcas, 1971–1974.
(2) N. Sutin in "Inorganic Biochemistry", Vol. 2, G. L. Eichhorn, Ed., Elsevier, Amsterdam, 1973, p 611.
(3) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **93**, 7347 (1971).
(4) F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **90**, 1162 (1968).
(5) R. G. Gaunder and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).
(6) L. H. Vogt, Jr., J. L. Katz, and S. E. Weberley, *Inorg. Chem.*, **4**, 1157 (1965).
(7) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).
(8) J. Victor and A. Haim, *Inorg. Chem.*, **14**, 3130 (1975).
(9) J. J. Jwo and A. Haim, *J. Am. Chem., Soc.*, **98**, 1172 (1976).
(10) I. M. Kolthoff and W. J. Tomsickek, *J. Phys. Chem*, **39**, 945 (1935).
(11) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1972), reported a value of 0.305 V at 25 °C in 0.10 M CF_3CO_2Na and 0.10 M CF_3CO_2H.
(12) The value 0.42 V reported in ref 5 appears to be in error: H. Taube, "Survey of Progress in Chemistry", **6**, 1 (1972).
(13) Blank experiments using only the iron or ruthenium solutions in 0.10 M KNO_3 showed no changes in transmittance even at high gain.
(14) A. Haim and N. Sutin, *Inorg. Chem.*, **15**, 476 (1976).
(15) The value for the $Ru(NH_3)_6^{3+/2+}$ couple is 0.051 V at 25 °C and 0.10 M $NaBF_4$.[11]
(16) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, Mass., 1974, p 183.
(17) J. C. Caton and J. E. Prue, *J. Chem. Soc.*, 671 (1956).
(18) R. G. Linck, *MPT Int. Rev. Sci., Inorg. Chem. Soc., Ser. One*, **9**, 303 (1971).
(19) The first-order rate constants at 25 °C and ionic strength 0.10 M for electron transfer in the ion pairs $Fe(CN)_6^{4-}$. $Co(NH_3)_5L^{3+}$, where L = nicotinamide, isonicotinamide, 4,4′-bipyridine, and bis(4-pyridyl)ethane are 5.0×10^{-2}, 3.5×10^{-2}, 2.4×10^{-2}, and 1.0×10^{-2} s^{-1}, respectively.
(20) H. Taube, private communication.
(21) In previous work[14] the factor used to correct coulombic terms for ionic strength effects was $\exp(-\kappa a)$. However, we pointed out that this factor overcorrects for ionic strength effects outside the Debye–Hückel limiting law, and therefore we used the average of the corrected value and the ionic strength O limit. This averaging procedure is arbitrary and has not been used by other workers in the field. Therefore, in the present paper we use the more generally accepted factor $1/(1 + \kappa a)$.
(22) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).
(23) A. Haim, *Acc. Chem. Res.*, **8**, 264 (1975).

Oxidative Addition of Nitrosonium Ion to Sulfur-Bridged Binuclear Iron(II) and Cobalt(II) Complexes

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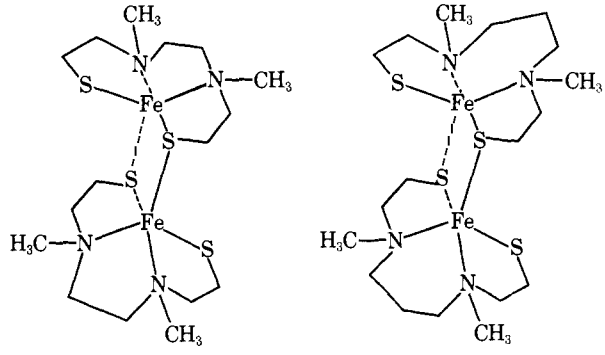
Abstract: The reactions of nitrosonium (NO^+) or nitronium (NO_2^+) salts with $(FeL)_2$, where L is the tetradentate N_2S_2 donor ligand derived from *N,N′*-dimethyl-*N,N′*-bis(2-mercaptoethyl)ethylenediamine (LH_2), afford $[(FeL)_2NO]^+$ in high yield. X-ray diffraction results show the product to consist of two distorted octahedra sharing a common face comprised of two bridging thiolate sulfur atoms and a symmetrically bridging nitrosyl ligand. An iron–iron single bond (2.468 (2) Å) enables each metal to have an 18-electron configuration. The analogous cobalt compound $(CoL)_2$, the synthesis of which is described, also reacts to form a binuclear adduct, $[(CoL)_2NO]^+$. An x-ray crystal structure analysis of the tetrafluoroborate salt of this cation shows it to have the same structure as the iron complex, but without a metal–metal bond (Co···Co = 2.770 (2) Å). The structural results, together with infrared (ν_{NO} ~1550 cm^{-1}) and Mössbauer studies (Fe complexes) of the adducts, are interpreted formally in terms of an oxidative addition of the nitrosonium ion to the bimetallic complexes, $(M^{II}L)_2 + NO^+ \rightarrow [(M^{III}L)_2(NO^-)]^+$, M = Fe or Co.

The synthesis,[1] structure,[2] and magnetic properties[3] of the iron(II) complexes $(FeL)_2$ and $(FeL')_2$ have been previously described. The five-membered ethylenediamine chelate ring in $(FeL)_2$ imposes a steric constraint[2] that is substantially relieved in $(FeL')_2$, which has a six-membered 1,3-propanediamine chelate ring. Since the complex $(FeL)_2$ contains high spin iron(II) atoms,[1,3] an alternative way of relieving the steric constraint in this molecule is to generate low spin iron, for example, by increasing the coordination number. A high to low spin conversion will shorten the Fe–N bond lengths with a concomitant increase in the N–Fe–N bond angle. The reactions of $(FeL)_2$ with carbon monoxide and alkyl isocyanides to form $FeL(CO)_2$ and $FeL(CNR)_2$ illustrate this point.[1]

It was also of interest to study the oxidation of the com-



$(FeL)_2$ $(FeL')_2$

pounds $(FeL)_2$ and $(FeL')_2$. A change from high spin iron (II) to iron(III) is known to cause a decrease in metal-ligand bond lengths.[4] Oxidation of $(FeL)_2$ to complexes containing iron(III) was therefore expected to be favorable. Since nitrosonium (NO^+) salts have been used to oxidize transition metal complexes,[5] their reactions with $(FeL)_2$ and $(FeL')_2$ were investigated. As briefly described in a previous communication,[6] stoichiometric addition of NO^+ yields a binuclear adduct containing a symmetrically bridging nitrosyl ligand, eq 1.

$$(ML)_2 + NO^+ \rightarrow [(ML)_2NO]^+ \quad (1)$$

Here we report additional details of this reaction together with the synthesis of the analogous cobalt compounds and the x-ray structure determination of the $[(CoL)_2NO]^+$ cation. The results clearly demonstrate (i) the influence of the electronic configuration of the metal on the extent of metal-metal bonding[7,8] in the two face-bridged, distorted octahedral $[(ML)_2NO]^+$ complexes, M = Fe, Co, and (ii) that reaction 1 may be considered as an oxidative addition[9] of the nitrosonium ion to the $(ML)_2$ complexes.

Experimental Procedure

Starting materials and methods are as reported previously.[1]

Synthesis of Compounds. $\{[Fe(C_8H_{18}N_2S_2)]_2NO\}^+$, $[(FeL)_2NO]^+$, Salts. (A) From $(FeL)_2$. Seventy milliliters of acetonitrile was added to 2.65 g (5 mmol) of $(FeL)_2$ and 0.875 g (5 mmol) of $NOPF_6$ in a 100-mL round-bottom (RB) flask. Disssolution (along with a bit of gas evolution) occurred immediately and the solution was allowed to stir overnight with mild heating (40-50 °C). After filtering the brown solution obtained into a 200-mL RB flask, approximately 100 mL of diethyl ether was added carefully to minimize mixing of the solvents. The flask was then placed in a freezer overnight. The precipitate obtained was filtered, washed with ether, and dried under vacuum. The yield of crude material was about 85%. Recrystallization twice more from acetonitrile-ether gave 2.40 g (37%) of brown flaky crystalline precipitate, 188-190 °C dec.

(B) From $FeL(CO)_2$. Fifty milliliters of acetonitrile was added to 636 mg (2 mmol) of $FeL(CO)_2$ and 175 mg (1 mmol) of $NOPF_6$ in a 100-mL flask. Stirring was continued for ~4 h after which the carbonyl bands at about 2000 cm^{-1} in the infrared spectrum of the reaction mixture had disappeared. The resulting brown solution was filtered into a 200-mL flask and about 100 mL of ethyl ether was added. This mixture was then placed in a freezer overnight. The precipitate obtained was filtered, washed with ether, and dried in vacuo. Yield 500 mg (72%) of $[(FeL)_2NO]PF_6$, identified by its infrared spectrum.

Tetrafluoroborate salts of $[(FeL)_2NO]^+$ can be synthesized in an analogous manner (method A) using $NOBF_4$ in the same solvent system. Use of dichloromethane as the solvent produced comparable yields. The $[(FeL)_2NO]^+$ cation can also be prepared using nitronium salts (NO_2PF_6 or NO_2BF_4) in the same stoichiometry as described in method A above. Acetonitrile or dichloromethane are again the solvents of choice. Crude yields are greater than 80% for these reactions. In all cases better yields and purer products are obtained using hexafluorophosphate salts. As has been noted,[5a] commercial tetrafluoroborate salts tend to be impure, and reactions using commercial NO_2BF_4 gave very poor yields of products.

X-ray quality crystals of $[(FeL)_2NO]PF_6$ were grown by dissolving the compound in a minimum amount of acetone and quickly adding a two-threefold excess (by volume) of ethanol. The mixture was then placed in a freezer overnight, yielding crystals having the formula $[(FeL)_2NO]PF_6$·acetone. The crystals decompose to powders in the air and were therefore mounted in sealed capillaries under nitrogen for crystallographic work.[6] All studies of $[(FeL)_2NO]^+$ salts were carried out under an inert atmosphere, and all compounds were stored in a drybox under nitrogen.

Anal. Analytical data were reported previously.[6] NMR, Proton NMR spectra of $[(FeL)_2NO]^+$ are difficult to obtain because of the relatively low solubility of these salts. The spectrum of $[(FeL)_2NO]PF_6$ in CD_3CN is similar to that of free ligand LH_2, having an apparent absorption singlet at δ 2.0, and multiplets at δ 2.1-2.4 and 2.5-2.7. The spectra were not integrated.

IR $[(FeL)_2NO]BF_4$ (Nujol, sodium chloride plates): 1553 (asymmetric), 1298, 1283, 1270 (sh), 1266, 1240, 1230, 1214, 1192 (w, sh), 1162, 1154, 1142, 1135, 1102 (sh), 1090, 1050 (s, br, mult), 1000, 970, 945 (br), 930 (sh), 860 (w), 834 (w), 767, 735, 686, 675 (w, sh), 627 cm^{-1}.

IR $[(FeL)_2NO]PF_6$ (Nujol, KBr): 1551 (symmetric), 1300, 1286, 1270 (sh), 1265, 1240, 1233, 1216, 1195 (w), 1162 (w, sh), 1155, 1140 (w), 1131 (w), 1052, 1026, 1021 (sh), 1003, 972, 950, 945 (sh), 877, 835 (s, br), 761, 740, 720 (w, sh), 692, 605, 555 (w, sh), 540, 460 (w), 380, 362 cm^{-1}.

IR $[(FeL)_2NO]PF_6$·acetone (Nujol, KBr): 1715 (asymmetric), 1552 (br, asymmetric), 1305 (sh), 1290, 1269, 1235 (ms), 1210 (sh), 1153, 1134, 1049, 1020, 997, 968, 937, 870 (sh), 820 (s, br), 750, 730, 690 (w), 620, 597 (w, sh), 568 (w, sh), 550, 537 (sh), 475 (w, sh), 465 cm^{-1}.

Electronic Spectrum. $[(FeL)_2NO]BF_4$ in acetonitrile has the following bands (ϵ_{max}, M^{-1} cm^{-1}, in parentheses): 321 nm (13 200), 465 (2870), and 615 (902, sh).

$[Co(C_8H_{18}N_2S_2)]_2$, $(CoL)_2$. Twenty milliliters of toluene was added to 7.71 g (0.03 mol) of cobaltous acetylacetonate and the mixture placed under a nitrogen atmosphere. To this pink, stirring suspension 9.50 g of LH_2 (0.045 mol) was added rapidly. The color turned green quickly and the mixture was stirred vigorously for an additional hour. The precipitate obtained was collected and washed, first with 25 mL of toluene, then with two 25-mL portions of methanol, and finally with 25 mL of diethyl ether. After drying under vacuum, the yield was 6.3 g (79%) of green microcrystalline material, 248 °C dec.

Anal. Analytical data were reported previously.[6]

IR (Nujol, NaCl): 1415 (w), 1345, 1308, 1298, 1271, 1233, 1205 (sh), 1198, 1158 (w), 1132, 1101 (w), 1077, 1049, 1030, 1016, 998, 944, 919 (w), 882, 810 (vw), 766, 742, 685, 676 cm^{-1}.

$[Co(C_9H_{20}N_2S_2)]_2$, $(CoL')_2$. The preparation of this compound was identical with that of $(CoL)_2$. The yield was 4.1 g (50%), 239 °C dec.

Anal. Calcd for $C_9H_{20}N_2S_2Co$: C, 38.70; H, 7.22; N, 10.03; S, 22.96. Found: C, 38.78; H, 6.84; N, 10.19; S, 23.17.

IR (Nujol, NaCl): 1420 (w), 1414 (w), 1330, 1307, 1291, 1272, 1262 (w), 1231 (w), 1221 (sh), 1199, 1151 (w), 1141 (w), 1132 (w), 1112, 1061, 1039 (mult), 1011 (vw), 995, 980, 963, 942 (mult), 917 (w), 892 (vw), 835 (w), 776, 737, 681 cm^{-1}.

$\{[Co(C_8H_{18}N_2S_2)]_2NO\}^+$, $[(CoL)_2NO]^+$, Salts. Under a nitrogen atmosphere 2.64 g of $(CoL)_2$ (5 mmol) and 0.875 g (5 mmol) of $NOPF_6$ were added to a 100-mL RB flask. Thirty-five milliliters of degassed methanol was added and the mixture was allowed to stir overnight. The brown solution was filtered in the air to yield a brown precipitate, which was dissolved in 25 mL of CH_2Cl_2 and filtered. To this solution 25 mL of petroleum ether was added yielding a brown precipitate. Two more recrystallizations from CH_2Cl_2/petroleum ether yielded 0.5 g (14%) of dark crystalline material. The synthesis of a tetrafluoroborate salt of $[(CoL)_2NO]^+$ was achieved in an analogous manner using $NOBF_4$.

Air-stable crystals of $[(CoL)_2NO](BF_4)$ were grown by carefully layering petroleum ether onto a methylene chloride solution of the compound. Slow diffusion of the two solvents produced x-ray quality crystals.

Anal. Analytical results for the hexafluorophosphate salt were previously reported.[6] Calcd for $C_{16}H_{36}N_5S_4OBF_4Co_2$: C, 29.68; H, 5.61; N, 10.82. Found: C, 29.24; H, 5.96; N, 10.40.

IR $[(CoL)_2NO]BF_4$ (Nujol, KCl): 1545 (asymmetric), 1299, 1281, 1265, 1240 (sh, w), 1230 (w), 1212, 1193 (w), 1151, 1140 (sh), 1132, 1102 (sh), 1088, 1055, 1045, 1030, 1015, 1001 (sh), 966, 949, 930 (vw), 855, 832 (sh), 780 (w), 700 (w), 688 (w), 615 cm^{-1}.

Collection and Reduction of X-ray Data. Dark brown needle-like crystals of $[(CoL)_2NO]BF_4$ were obtained as described above. Preliminary precession photographs taken with Cu K$\bar{\alpha}$ radiation showed the crystal to have $2/m$ Laue symmetry. Systematic absences of $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, established the space group to be $P2_1/n$.[10] The crystal used for data collection was a parallelepiped of approximate dimensions 0.05 mm between the (021) and $(0\bar{2}\bar{1})$ faces, 0.1 mm between (010) and $(0\bar{1}0)$, and 0.30 mm between (100) and $(\bar{1}00)$. The rotation axis was deliberately offset by ~10° from the mounting axis a^*. Details of the data collection and reduction are given in Table I.

Determination and Refinement of the Structure. The structure was solved by conventional heavy atom methods from Patterson and Fourier maps. Least-squares refinement of all 33 non-hydrogen atoms in the asymmetric unit employing isotropic temperature factors and

Table I. Experimental Details of the X-ray Diffraction Study of $[(CoL)_2NO]BF_4$

(A) Crystal Parameters at 23 °C[a]

a = 8.953 (6) Å	Space group $P2_1/n$
b = 26.260 (18) Å	Z = 4
c = 10.928 (8) Å	ρ(calcd) = 1.712 g/cm^3
β = 102.10 (3)°	ρ(obsd)[b] = 1.710 (5) g/cm^3
V = 2512 (3) Å^3	Mol wt = 647.4

(B) Measurement of Intensity Data

Instrument: Picker FACS-I-DOS diffractometer
Radiation: Mo Kα (λ_{α_1} 0.7093 Å), graphite monochromatized
Takeoff angle: 2.3°
Detector aperature: 6.3 mm × 6.3 mm
Crystal-detector distance: 33 cm
Scan technique: coupled θ(crystal)-2θ(counter)
Scan range: 1.50° (symmetric, pulse Kα_1-Kα_2 dispersion)
Scan rate: 1.0°/min
Maximum 2θ: 45°
Background measurements: stationary crystal, stationary counter; 20-s counts at each end of 2θ scan range
Standards: three reflections ($\bar{1}31$), ($\bar{3}2\bar{2}$), and ($1\bar{5}\bar{1}$) measured every 100 data showed only random, statistical fluctuations
No. of reflections collected: 4434 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] ϵ = 0.03[e]
Absorption correction: μ = 17.2 cm^{-1}; transmission factors varied between 0.811 and 0.927
Averaging: over equivalent forms with an agreement factor R_{av}[f] = 0.063
Scaling: Wilson's method[g]
Observed data: 3375 unique reflections of which 2371 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 25 reflections. [b] By suspension in $CCl_4/CHBr_3$ mixtures. [c] Programs for an IBM 360/91 computer used in this work: UMAT, the local version of the Brookhaven diffractometer setting and cell constant and orientation refinement program; 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).

unit weights resulted in values of 0.085 and 0.096 for the discrepancy factors R_1 and R_2, respectively.[11,12a] The isotropic thermal parameters were then converted to anisotropic form, anomalous dispersion corrections were applied to the scattering factors for the cobalt and sulfur atoms,[12b] and the weighting scheme was introduced. Structure factor calculations and difference Fourier maps revealed the positions of the 36 hydrogen atoms which were added to the refinement with isotropic temperature factors. Ten hydrogen atoms that did not refine well were assigned isotropic B values set at one greater than the final isotropic thermal parameter of the carbon atoms to which they are attached, and two of these hydrogen atoms had their positional parameters fixed as well. Refinement of 426 parameters converged at R_1 = 0.051 and R_2 = 0.048. In the final least-squares cycle, no parameter varied by more than 0.2 of its estimated standard deviation. Inspection of the function $\Sigma w\Delta^2$ for reflections ordered according to $|F_o|$ and (sin θ/λ) showed satisfactory consistency and the error in an observation of unit weight, $[\Sigma w\Delta^2/(NO - NV)]^{1/2}$, was 1.623. The weighting scheme was therefore considered to be adequate.[13] A final difference Fourier map showed residual electron density ($\leq$1.18 e/Å^3) in the vicinity of the tetrafluoroborate anion. This fact, together with the large temperature factors, suggests that this group may be partially disordered.

Results and Discussion

Synthesis and General Characterization of $(CoL)_2$, $(CoL')_2$, $[(FeL)_2NO]^+$, and $[(CoL)_2NO]^+$. The cobalt compounds $(CoL)_2$ and $(CoL')_2$ have infrared spectra that are nearly superimposable on those of their iron(II) analogues. Temperature dependent magnetic studies[14] show that, upon cooling, the susceptibility curves pass through maxima at ~190 K (broad) for $(CoL)_2$ and at 50 K for $(CoL')_2$. These magnetic results are consistent with the presence of antiferromagnetically coupled, high spin cobalt(II) centers. In view of the similarity in the infrared and magnetic properties, including the fact that the coupling is significantly greater for the $(CoL)_2$ complex, the cobalt compounds are taken as isostructural with their iron analogues[1-3] in the present discussion. The possible existence of clusters having a higher degree of oligomerization cannot be ruled out, however.[15]

Salts of the $[(FeL)_2NO]^+$ cation are obtained in good yields from a stoichiometric mixture of nitrosonium hexafluorophosphate or tetrafluoroborate and $(FeL)_2$ suspended in acetonitrile, in which the products are soluble (eq 1). The cation can also be synthesized using nitronium (NO_2^+) salts, which are known to produce nitrosyl derivatives.[16] The reaction, run stoichiometrically in acetonitrile according to eq 2, is accompanied by vigorous gas evolution.

$$(FeL)_2 + NO_2^+ \rightarrow [(FeL)_2NO]^+ + \tfrac{1}{2}O_2 \qquad (2)$$

Passage of the evolved gas through a solution of alkaline pyrogallol produced a brown color, confirming the presence of oxygen.[17] If the mixture of $(FeL)_2$ and nitrosonium or nitronium salts is chromatographed shortly after the start of the reaction, additional products are obtained. These give rise to infrared absorption bands at ~1700-1800 cm^{-1}. Among the products is the pentacoordinate monomer, FeL(NO). These compounds will be described elsewhere.[18]

The infrared spectrum of $[(FeL)_2NO]^+$ shows a peak of medium intensity at 1553 cm^{-1} assigned to the stretching vibration of the bridging nitrosyl ligand. The compound $[(FeL)_2NO](PF_6)$·acetone used in the crystallographic study[6] has an additional infrared band at 1715 cm^{-1}, confirming the presence of acetone in the lattice.[19] This band is not observed in the spectrum of the unsolvated compound. Heating a sample of the acetone adduct at 80 °C under vacuum results in quantitative loss of weight owing to acetone and in the disappearance of the acetone band in the infrared spectrum. These experiments were conducted to assure that refinement of the residual electron density as a disordered acetone molecule in the crystal structure analysis[6] had chemical validity.

The Mössbauer effect spectrum of $[(FeL)_2NO]BF_4$ (Figure S1)[20] exhibits a single quadrupole split doublet, consistent with the presence of chemically and electronically equivalent iron atoms. The isomer shift of 0.29 mm/s vs. iron metal at 77 K is in accord with values observed for low spin iron(III) complexes containing nitrogen[21] or sulfur[22] donor ligands but cannot be used as an unequivocal measure of the oxidation state since low spin iron(II) complexes also have isomer shift values in this range.[23]

Table II. Interatomic Distances (Å) in $[(CoL)_2NO]BF_4$ and Selected Values for $[(FeL)_2NO]PF_6$[a,b]

Coordination Sphere					
$[(CoL)_2NO]^+$				$[(FeL)_2NO]^+$	
Co1		Co2			
Co1···Co2	2.770 (2)			Fe-Fe′	2.468 (2)
Co1-S11	2.313 (3)	Co2-S21	2.315 (3)	Fe-S1	2.276 (2)
Co1-S21	2.282 (3)	Co2-S11	2.283 (3)	Fe-S1′	2.245 (2)
Co1-S12	2.239 (3)	Co2-S22	2.252 (3)	Fe-S2	2.298 (2)
Co1-N11	2.040 (6)	Co2-N21	2.039 (6)	Fe-N1	2.104 (5)
Co1-N12	2.058 (6)	Co2-N22	2.071 (6)	Fe-N2	2.086 (5)
Co1-N3	1.800 (6)	Co2-N3	1.817 (6)	Fe-N3	1.818 (5)
Internal Ligand Geometry					
Co1		Co2			
S11-C11	1.812 (9)	S21-C21	1.822 (10)		
S12-C16	1.828 (11)	S22-C26	1.807 (11)		
N11-C12	1.502 (10)	N21-C22	1.494 (10)		
N11-C13	1.495 (11)	N21-C23	1.476 (11)		
N11-C17	1.478 (11)	N21-C27	1.482 (11)		
N12-C14	1.464 (11)	N22-C24	1.495 (11)		
N12-C15	1.498 (11)	N22-C25	1.484 (11)		
N12-C18	1.472 (12)	N22-C28	1.495 (11)		
C11-C12	1.519 (13)	C21-C22	1.520 (13)		
C13-C14	1.466 (13)	C23-C24	1.498 (13)		
C15-C16	1.44 (2)	C25-C26	1.500 (14)		
N3-O 1.211 (7)					
Nonbonded Distances					
Co1		Co2			
S11-S21 2.863					
S11-N11	2.987	S21-N21	2.982		
S11-N12	3.325	S21-N22	3.363		
S11-N3	2.731	S21-N3	2.705		
S21-S12	3.376	S11-S22	3.380		
S21-N12	3.239	S11-N22	3.224		
S12-N11	3.276	S22-N21	3.297		
S12-N12	2.978	S22-N22	2.973		
S12-N3	2.904	S22-N3	2.948		
N11-N12	2.822	N21-N22	2.844		
N11-N3	2.835	N21-N3	2.839		
Anion Geometry					
B-F1	1.24 (2)	B-F3	1.27 (2)		
B-F2	1.19 (2)	B-F4	1.47 (3)		

[a] Atoms are labeled as shown in Figure 2. Standard deviations are given in parentheses beside each entry. Distances are not corrected for thermal motion. [b] The iron values are taken from ref 6.

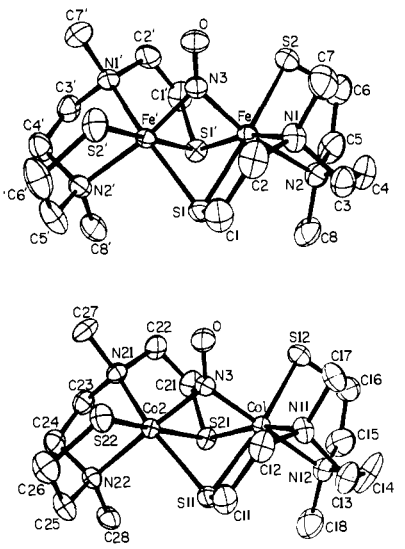


Figure 1. ORTEP drawings of the $[(FeL)_2NO]^+$ (top) and $[(CoL)_2NO]^+$ (bottom) cations showing the atom labeling scheme. The primed and unprimed atoms in the former are related by a crystallographically required twofold axis. In order to facilitate comparison of the structures, the coordinates for $[(CoL)_2NO]^+$ in Table S1 were transformed by the *n*-glide operation before the drawing was made. Thermal ellipsoids of 50% probability are shown in both cases.

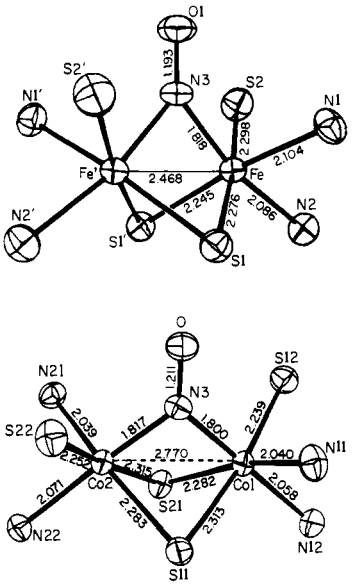


Figure 2. The core geometries of the $[(FeL)_2NO]^+$ (top) and $[(CoL)_2NO]^+$ (bottom) cations (see caption to Figure 1).

The synthesis of $[(CoL)_2NO]^+$ proceeds in a manner analogous to that of the iron complex, eq 1, with methanol as the solvent. The presence of a bridging nitrosyl ligand is suggested by an IR band at 1545 cm^{-1} and confirmed by the crystal structure analysis. Both the iron and cobalt nitrosyl bridged cations are diamagnetic as judged by NMR spectroscopic or magnetic susceptibility measurements.

Structures of the $[(FeL)_2NO]^+$ and $[(CoL)_2NO]^+$ Cations. Crystallographic results for $[(FeL)_2NO]PF_6$·acetone were reported previously.[6] Table S1[20] lists the final positional and thermal parameters for $[(CoL)_2NO]BF_4$. The root-mean-square amplitudes of thermal motion for anisotropically refined atoms, the final observed and calculated structure factor amplitudes, and all interatomic distances and angles involving hydrogen atoms for this compound are available as Tables S2-S4, respectively.[20] The structure of the $[(CoL)_2NO]^+$ cation is shown in Figure 1 along with the atom labeling scheme. The geometry of the core atoms in this cation appears in Figure 2. Tables II and III report interatomic distances and angles, respectively, for $[(CoL)_2NO]^+$ together with selected results for the iron analogue.[6]

The structures of the $[(FeL)_2NO]^+$ and $[(CoL)_2NO]^+$ cations are quite similar (Figures 1, 2), consisting of two distorted octahedra sharing a common face comprised of two bridging sulfur atoms and the nitrogen atom of the bridging nitrosyl ligand. The iron complex has a crystallographically required twofold axis passing through the nitrosyl ligand that is virtually present in the cobalt analogue (Tables II and III). The chief differences between the structures arise from the presence of a metal-metal bond in the iron cation that is lacking in the cobalt compound. Metal-metal bonding is discussed in the next section of this paper.

In both complexes the ligand L wraps in the cis-α configuration[24] with the two sulfur atoms trans to one another. The

Table III. Bond Angles (in deg) for $[(CoL)_2NO]BF_4$ and Selected Values for $[(FeL)_2NO]PF_6$[a]

Coordination Sphere					
$(CoL)_2NO^+$				$(FeL)_2NO^+$	
Co1		Co2			
S11-Co1-S12	171.40 (12)	S21-Co2-S22	170.88 (9)	S1-Fe-S2	175.3 (1)
S11-Co1-S21	77.05 (9)	S21-Co2-S11	77.00 (8)	S1-Fe-S1′	80.6 (1)
S11-Co1-N11	86.4 (2)	S21-Co2-N21	86.2 (2)	S1-Fe-N1	84.8 (1)
S11-Co1-N12	98.8 (2)	S21-Co2-N22	100.0 (2)	S1-Fe-N2	99.2 (1)
S11-Co1-N3	82.2 (2)	S21-Co2-N3	80.8 (2)	S1-Fe-N3	90.6 (1)
S12-Co1-S21	96.58 (10)	S22-Co2-S11	96.38 (9)	S2-Fe-S1′	95.9 (1)
S12-Co1-N11	99.8 (2)	S22-Co2-N21	100.3 (2)	S2-Fe-N1	98.7 (1)
S12-Co1-N12	87.6 (2)	S22-Co2-N22	86.8 (2)	S2-Fe-N2	84.3 (1)
S12-Co1-N3	91.3 (2)	S22-Co2-N3	92.2 (2)	S2-Fe-N3	86.2 (1)
S21-Co1-N11	163.4 (2)	S11-Co2-N21	163.2 (2)	S1′-Fe-N1	165.3 (1)
S21-Co1-N12	96.3 (2)	S11-Co2-N22	95.4 (2)	S1′-Fe-N2	95.8 (1)
S21-Co1-N3	82.1 (2)	S11-Co2-N3	82.7 (2)	S1′-Fe-N3	91.6 (1)
N11-Co1-N12	87.0 (3)	N21-Co2-N22	87.6 (3)	N1-Fe-N2	84.6 (2)
N11-Co1-N3	95.0 (3)	N21-Co2-N3	94.6 (3)	N1-Fe-N3	90.4 (2)
N12-Co1-N3	177.9 (3)	N22-Co2-N3	177.7 (4)	N2-Fe-N3	168.5 (2)
Internal Ligand Geometry					
Co1			Co2		
Co1-S11-Co2	74.11 (7)		Co2-S21-Co1	74.10 (8)	
Co1-S11-C11	99.1 (3)		Co2-S21-C21	99.3 (3)	
Co2-S11-C11	113.4 (4)		Co1-S21-C21	113.7 (4)	
Co1-S12-C16	98.9 (4)		Co2-S22-C26	100.5 (4)	
Co1-N11-C12	109.5 (5)		Co2-N21-C22	110.0 (5)	
Co1-N11-C13	104.7 (5)		Co2-N21-C23	104.0 (5)	
Co1-N11-C17	115.9 (6)		Co2-N21-C27	115.4 (6)	
C12-N11-C13	110.0 (7)		C22-N21-C23	110.5 (7)	
C12-N11-C17	107.5 (7)		C22-N21-C27	107.0 (7)	
C13-N11-C17	109.2 (8)		C23-N21-C27	110.1 (7)	
Co1-N12-C14	105.4 (5)		Co2-N22-C24	104.1 (5)	
Co1-N12-C15	109.6 (6)		Co2-N22-C25	109.7 (5)	
Co1-N12-C18	116.6 (6)		Co2-N22-C28	116.0 (5)	
C14-N12-C15	111.6 (8)		C24-N22-C25	109.7 (7)	
C14-N12-C18	109.0 (9)		C24-N22-C28	108.8 (7)	
C15-N12-C18	104.8 (9)		C25-N22-C28	108.4 (7)	
S11-C11-C12	112.5 (6)		S21-C21-C22	112.1 (7)	
C11-C12-N11	113.5 (7)		C21-C22-N21	114.1 (8)	
N11-C13-C14	110.9 (8)		N21-C23-C24	110.6 (8)	
C13-C14-N12	112.6 (9)		C23-C24-N22	109.6 (7)	
N12-C15-C16	113.9 (10)		N22-C25-C26	112.9 (8)	
C15-C16-S12	113.9 (8)		C25-C26-S22	111.0 (7)	
	Co1-N3-Co2	99.9 (3)			
	Co1-N3-O	130.8 (5)			
	Co2-N3-O	129.2 (5)			
Anion Geometry					
F1-B-F2	121 (1)		F2-B-F3	124 (2)	
F1-B-F3	113 (2)		F2-B-F4	101 (2)	
F1-B-F4	99 (2)		F3-B-F4	83 (1)	

[a] See footnotes *a* and *b*, Table II.

ethylene chains are all in the stable gauche conformation. The two methyl groups are on opposite sides of the N1-M-N2 planes. The fact that they are on the same side of this plane in $(FeL)_2$[2] suggests that reaction 1 is kinetically more complex than written and that, in particular, cleavage of metal-nitrogen bonds must occur somewhere along the reaction pathway. Independent evidence for metal-nitrogen bond breakage during this reaction has recently been obtained and will be presented elsewhere.[18b] The bond distances and angles within the five-membered chelate rings are unexceptional. The values listed in Tables II and III compare favorably with those reported for $(FeL)_2$[2] and $[(Zn_2LCl_2)]_2 \cdot 2H_2O$;[25] differences stem from the shorter metal-sulfur and metal-nitrogen bonds in the present, low-spin complexes.

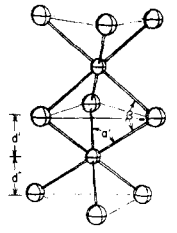
The metal-ligand bond lengths in spin-paired $[(FeL)_2NO]^+$ are all ~0.1-0.2 Å shorter than in high-spin $(FeL)_2$, as expected.[1,4] The reduction in bond distances is accompanied by an increase in the intrachelate ring angles. The largest effect occurs for the N1-Fe-N2 angle of the ethylenediamine chelate ring which opens up from 79.2° in $(FeL)_2$ to 84.6° in $[(FeL)_2NO]^+$. The opening of the intrachelate ring angles toward more octahedral values provides relief of the ligand constraints in $(FeL)_2$ and may help drive reaction 1. The N1-Co-N2 angle of 87.3° in $[(CoL)_2NO]^+$ suggests similar behavior for the cobalt analogues. Except for the bridging ligands, the M-N and M-S bond distances in the cobalt cation are all ~0.04 Å shorter than for the iron complex as expected from the smaller covalent radius of cobalt.[26] Differences in

metal-metal bonding reverse this trend for the bridging ligands (vide infra).

In both complexes the M-N distance to the symmetrically bridging nitrosyl ligand is ~1.81 Å, nearly 0.5 Å shorter than the M-S distances to the bridging sulfur atoms. The M-N3-M′ angles are correspondingly greater (Table II). Moreover, the short M-N3 bridge bonds require the two confacial pseudo-bioctahedra to be canted toward one another, the dihedral angles between the faces defined by N1, N2, and S2 being 33.0° for $[(FeL)_2NO]^+$ and 29.0° for $[(CoL)_2NO]^+$. Other structurally characterized transition metal complexes containing bridging nitrosyl ligands include $[(C_5H_5)Fe(NO)]_2$,[27] $[(C_5H_5)Cr(NO)_2]_2$,[28] $[(C_5H_5)Mn(CO)(NO)]_2$,[29] $(C_5H_5)_2Cr_2(NO)_3NH_2$,[30] $(C_5H_5)_3Mn_3(\mu_3\text{-}NO)(\mu_2\text{-}NO)_3$,[31] $(C_5H_5)_3Mn_2(NO)_3$,[32] $Ru_3(CO)_{10}(NO)_2$,[33] $Pt_4(acetate)_6(NO)_2$,[34] and $[Pt(NO)Cl_3]_2^{2-}$.[35] The N-O bond lengths in these compounds range from 1.19 to 1.27 Å. The NO bond lengths of the $[(FeL)_2NO]^+$ and $[(CoL)_2NO]^+$ cations, 1.193 (8) and 1.211 (7) Å, respectively, agree well with the literature values.

Metal-Metal Bonding. The iron-iron separation of 2.468 (2) Å in $[(FeL)_2NO]^+$ is quite short and suggests the presence of a metal-metal single bond.[7,8,26] Internuclear distances in ligand bridged complexes are not a sufficient criterion for metal-metal bonding, however.[7] The $[(FeL)_2NO]^+$ cation is diamagnetic as shown by NMR and by direct susceptibility measurements on the hexafluorophate salt. This result requires the presence of a metal-metal interaction regardless of how electrons are counted. Low-spin octahedral compounds containing strong π acceptor ligands such as nitrosyl generally obey the 18-electron rule. By *formally* considering each iron atom to be in the +3 oxidation state and the nitrosyl as NO^-, each d^5 metal center has 12 electrons contributed by six ligands, accounting for 17 electrons. The 18th electron comes from the neighboring iron atom and requires a metal-metal single bond. The compound $[(C_5H_5)Fe(NO)]_2$, containing symmetrically bridging nitrosyl ligands, has an iron-iron double bond.[27] The internuclear distance of 2.326 Å in this molecule is considerably shorter than the single bond value in $[(FeL)_2NO]^+$.

The replacement of iron by cobalt in the $[(CoL)_2NO]^+$ cation adds two more electrons to the system. Each cobalt atom can therefore achieve a stable closed shell (18-electron) configuration without metal-metal bond formation. The absence of metal-metal bonding in diamagnetic $[(CoL)_2NO]^+$ is nicely borne out by comparing its geometry with that of the iron analogue. The cobalt-cobalt distance of 2.770 (2) Å is more than 0.3 Å longer than the iron-iron distance. Cotton and Ucko compared several confacial bioctahedral compounds containing monodentate ligands and were able to correlate three structural parameters, d'/d'', $\beta - 70.53°$, and $90° - \alpha'$ (Figure 3), with the presence or absence of a metal-metal bond.[36] Although they have chelating ligands and nonequivalent metal-ligand bond lengths, it is quite informative to apply this analysis to $[(FeL)_2NO]^+$ and $[(CoL)_2NO]^+$. In an ideal confacial bioctahedron with no metal-metal interactions (attractive or repulsive), the value of $90 - \alpha'$ is zero and β is 70.53° (Figure 3). The average (of S1-M-S1′, S1-M-N3, and S1′-M-N3) values for $90 - \alpha'$ in $[(CoL)_2NO]^+$ and $[(FeL)_2NO]^+$ are 9.7° and 2.4°, respectively. The $\beta - 70.53°$ parameter at the bridging sulfur atoms is 3.6° in the cobalt cation and −3.9° in the iron cation. These values indicate a distortion in the cobalt complex owing to nonbonded repulsions along the cobalt-cobalt internuclear axis and reflect the metal-metal bonding in the iron analogue.[36] The M-N3-M′ angle, ideally 120° for an sp^2 hybridized nitrogen atom, is compressed to 85.5° in $[(FeL)_2NO]^+$, pointing to a more positive metal-metal interaction in this cation than in the cobalt analogue where the value is 99.9°. Finally, the d'/d'' ratios of 1.17 Å for



	Ideal confac bioct	$[(FeL)_2NO]^+$	$[(CoL)_2NO]^+$
d'/d''	1.00	0.79	1.17
$\beta - 70.53°$	0.00	At sulfur −3.9°	At sulfur 3.6°, 3.6° ave, 3.6°
$90° - \alpha'$	0.00	9.4°, −0.6°, −1.6° ave, 2.4°	13.0°, 13.0°, 7.8°, 9.2°, 7.9°, 7.3° ave, 9.7°

Figure 3. Sketch of an idealized confacial bioctahedron defining the d'/d'', $\beta - 70.53°$, and $90 - \alpha'$ parameters (see ref 36) and reporting values for $[(FeL)_2NO]PF_6$·acetone and $[(CoL)_2NO]BF_4$.

$[(CoL)_2NO]^+$ and 0.79 Å for $[(FeL)_2NO]^+$ clearly reveal the attractive metal-metal interaction in the latter and the metal-metal repulsion in the former.

The presence of an iron-iron bond in the $[(FeL)_2NO]^+$ cation has a number of interesting effects on the geometry of the ligand-bridged system. The compression of the angles (β) at the bridging atoms has already been cited and is similar to the "sharply acute" bridging angle criterion used to diagnose metal-metal bonding in edge-bridged complexes.[7] Another feature, not widely recognized, is the shortening of metal-ligand (especially the metal-sulfur) bonds to the bridging atoms in the metal-metal bonded compound. The Fe-S1 and Fe-S1′ bond lengths in $[(FeL)_2NO]^+$ are ~0.03-0.04 Å shorter than the corresponding values in the cobalt cation (Table II), reversing the normal trend discussed above. This diminution of metal-sulfur bond lengths for bridged thiolate systems appears to correlate with the presence of metal-metal bonding and, although not recognized at the time, is evident in other structural results for thiolate-bridged iron and cobalt complexes.[26,37]

Oxidative Addition. Equation 1 may be regarded as an oxidative addition reaction in which NO^+ formally adds to the bimetallic $M(II)_2$ unit in $(FeL)_2$ or $(CoL)_2$ yielding a binuclear $M(III)_2$ complex with a bridging NO^- ligand. As such, it is a unique example of an oxidative addition reaction where a bimetallic substrate is known to be involved. Oxidative addition reactions have been extensively investigated, particularly those of square d^8 complexes such as $Ir(CO)Cl(PPh_3)_2$, eq 3.[9,38]

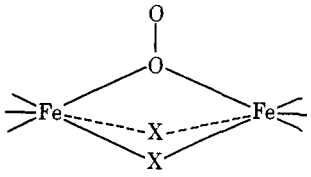
$$Ir^{I}(CO)Cl(PPh_3)_2 + XY \rightarrow Ir^{III}(CO)Cl(PPh_3)XY \quad (3)$$

$$XY = HCl, CH_3I, H_2, \text{etc.}$$

Recent electrochemical studies[39] of this and related complexes suggest that a dimeric iridium(II) compound might exist along the reaction pathway. This feature and the fact that in both cases a formally 16-electron metal atom (17 electron in the case of $(CoL)_2$) achieves an 18-electron configuration with reduction of the incoming ligand point to an analogy between eq 1 and 3. The difference is that the metal atoms involved in reaction 1 undergo a high- to low-spin conversion in which there is formally a one-electron oxidation per metal atom.

There is an interesting similarity between eq 1, considered as an oxidative addition reaction, and the activation of small molecules or ions by bimetallic centers such as those known or postulated to exist in metalloproteins. Thus the implied reduction of NO^+ to NO^- by $(FeL)_2$ or $(CoL)_2$ might be analogous to an early stage in the reduction of dinitrogen[40-42] or to the reversible binding of oxygen to hemerythrin which is thought to involve oxidative addition of the bimetallic iron center with concomitant formation of a peroxide-bridged ad-

duct.[43] With regard to the latter, it may be noted that the diiron center in *T. dyscritum* methemerythrin consists of two trigonal antiprisms sharing a common face,[44] a structure that is similar to those of the $[(FeL)_2NO]^+$ and $[(CoL)_2NO]^+$ cations. If oxyhemerythrin is structurally analogous to the $[(ML)_2NO]^+$ complexes studied here, it would contain the following geometric unit



Such a structure has recently been shown to be consistent with resonance Raman results for oxyhemerythrin.[45]

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Supplementary Material Available: Tables S1-S4 listing, respectively, the final atomic positional and thermal parameters, structure factor amplitudes, rms amplitudes of vibration, and interatomic distances and angles involving hydrogen atoms in $[(CoL)_2NO]BF_4$. Also available is Figure S1 depicting the 195 K Mössbauer spectrum of $[(FeL)_2NO]PF_6$·acetone (21 pages). Ordering information is given on any current masthead page.

References and Notes

(1) K. D. Karlin and S. J. Lippard, *J. Am. Chem. Soc.*, **98**, 6951 (1976).
(2) W. J. Hu and S. J. Lippard, *J. Am. Chem. Soc.*, **96**, 2366 (1974).
(3) A. P.Ginsberg, M. E. Lines, K. D. Karlin, S. J. Lippard, and F. J. DiSalvo, *J. Am. Chem. Soc.*, **98**, 6958 (1976).
(4) J. W. Lauher and J. A. Ibers, *Inorg. Chem.*, **14**, 348 (1975), and references cited therein.
(5) (a) M. T. Mocella, M. S. Okamoto, and E. K. Barefield, *Synth. React. Inorg. Metal-Org. Chem.*, **4**, 69 (1974); (b) K. G. Caulton, *Coord. Chem. Rev.*, **14**, 317 (1975).
(6) K. D. Karlin, D. L. Lewis, H. N. Rabinowitz, and S. J. Lippard, *J. Am. Chem. Soc.*, **96**, 6519 (1974).
(7) L. F. Dahl, E. R. DeGil, and R. D. Feltham, *J. Am. Chem. Soc.*, **91**, 1653 (1969).
(8) L. F. Dahl, J. D. Sinclair, and B. K. Teo in "Stereochemical and Bonding Aspects of the Organic Chemistry of Iron", R. B. King, Ed., Academic Press, New York, N.Y., in press. We thank Dr. B. K. Teo for a preprint.
(9) (a) J. P. Collman, *Acc. Chem. Res.*, **1**, 136 (1968); (b) J. Halpern, *ibid.*, **3**, 386 (1970).
(10) A nonstandard setting of $P2_1/c$; "International Tables for X-ray Crystallography", Vol. I, 2nd ed, Kynoch Press, Birmingham, England, 1965, p 99.
(11) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$. In the least-squares refinement, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized.
(12) (a) Scattering factors for the neutral, non-hydrogen atoms were taken from Vol. IV of ref 10, 1974, p 72 ff. Hydrogen atom scattering factors were those of R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965). (b) Anomalous scattering factors were those of D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(13) D. W. J. Cruickshank in "Computing Methods of Crystallography", J. S. Rollett, Ed., Pergamon Press, New York, N.Y., 1965, pp 112-115.
(14) A. P. Ginsberg, private communication. The magnetic properties of $(CoL)_2$ and $(CoL')_2$ are under further investigation.
(15) (a) I. G. Dance and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 762 (1975); (b) K. Garbett, G. W. Partridge, and R. J. P. Williams, *Bioinorg. Chem.*, **1**, 309 (1972).
(16) (a) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and L. L. Krasnolobodskaya, *Bull. Acad. Sci. USSR*, 807 (1970); (b) P. G. Douglas and R. D. Feltham, *J. Am. Chem. Soc.*, **94**, 5254 (1972); (c) A. Efraty, R. Arneri, and J. Sikora, *J. Organomet. Chem.*, **91**, 65 (1975).
(17) A. J. Gordon and R. A. Ford, "The Chemists Companion", Wiley, New York, N.Y., 1972, p 440. No such vigorous gas evolution is observed when the reaction is run in dichloromethane, and no O_2 was detected. The reaction appears to proceed in the same manner, however, as judged by monitoring it with infrared spectroscopy and by the fact that the final product is the same. The reasons for the differences observed in the two solvents are not clear.
(18) (a) K. D. Karlin, H. N. Rabinowitz, D. L. Lewis, and S. J. Lippard, in preparation; (b) L. Baltusis, H. N. Rabinowitz, K. D. Karlin, and S. J. Lippard, unpublished results.
(19) Sadtler Standard Spectra, Sadtler Research Laboratories, Inc., Philadelphia, Pa.
(20) Supplementary material.
(21) G. Renovitch and W. A. Baker, *J. Am. Chem. Soc.*, **90**, 3585 (1968).
(22) R. Rickards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Soc. A*, 1755 (1971).
(23) E. Fluck, "Chemical Applications of Mössbauer Spectroscopy", V. I. Goldanskii and R. H. Herber, Ed., Academic Press, New York, N.Y., 1968.
(24) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley-Interscience, New York, N.Y., 1971.
(25) W. J. Hu, D. Barton, and S. J. Lippard, *J. Am. Chem. Soc.*, **95**, 1170 (1973).
(26) D. F. Lewis, S. J. Lippard, and J. A. Zubieta, *J. Am. Chem. Soc.*, **94**, 1563 (1972), and references cited therein.
(27) J. L. Calderon, S. Fontana, E. Frauendorfer, V. W. Day, and S. D. A. Iske, *J. Organomet. Chem.*, **64**, C16 (1974).
(28) J. L. Calderon, S. Fontana, E. Frauendorfer, and V. W. Day, *J. Organomet. Chem.*, **64**, C10 (1974).
(29) R. M. Kirchner, T. J. Marks, J. S. Kristoff, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 6602 (1973).
(30) L. Y. Y. Chan and R. W. B. Einstein, *Acta Crystallogr., Sect. B*, **26**, 1899 (1970).
(31) R. C. Elder, *Inorg. Chem.*, **13**, 1037 (1974).
(32) J. L. Calderon, S. Fontana, E. Frauendorfer, V. W. Day, and B. R. Stults, *Inorg. Chim. Acta*, **17**, L31 (1976).
(33) J. Norton, J. P. Collman, G. Dolcetti, and W. T. Robinson, *Inorg. Chem.*, 11, 382 (1972).
(34) P. de Meester, A. C. Skapski, and J. P. Heffer, *J. Chem. Soc., Chem. Commun.*, 1039 (1972).
(35) J. M. Epstein, A. H. White, S. B. Wild, and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 436 (1974).
(36) F. A. Cotton and D. A. Ucko, *Inorg. Chim. Acta*, **6**, 161 (1972).
(37) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, **9**, 2775 (1970).
(38) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968).
(39) J. Večernik, J. Mašek, and A. A. Vlček, *J. Chem. Soc., Chem. Commun.*, 736 (1975).
(40) (a) J. H. Enemark and R. D. Feltham, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 3534 (1972); (b) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).
(41) J. Chatt, G. A. Heath, and R. L. Richard, *J. Chem. Soc., Chem. Commun.*, 1010 (1972).
(42) J. Chatt, *J. Organomet. Chem.*, **100**, 17 (1975).
(43) I. M. Klotz, G. L. Klippenstein, and W. A. Hendrickson, *Science*, **192**, 335 (1976), and references cited therein.
(44) R. E. Stenkamp, L. C. Sieker, and L. H. Jensen, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 349 (1976).
(45) D. M. Kurtz, Jr., D. F. Shriver, and I. M. Klotz, *J. Am. Chem. Soc.*, **98**, 5033 (1976).