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# Iron–Sulfur Complexes of NO. 2. Synthesis and Exchange Studies of $Fe(NO)X[S_2CN(CH_3)_2]_2$. Crystal and Molecular Structure of *cis*-$Fe(NO)(NO_2)(S_2CN(C_2H_5)_2)_2$[1]

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The synthesis of several new complexes including *trans*-$[FeNO(S_2CN(CH_3)_2)_2(CH_3CN)][BF_4]$, *trans*-$FeNO(S_2CN(CH_3)_2)_2NO_2$, *trans*-$FeNO(S_2CN(CH_3)_2)_2NCS$, *cis*-$FeNO(S_2CN(CH_3)_2)_2NO_2$, *cis*-$FeNO(S_2CN(CH_3)_2)_2Br$, *cis*-$FeNO(S_2CN(CH_3)_2)_2I$, *cis*-$[FeNO(S_2CN(CH_3)_2)_2(CH_3NC)][BF_4]$, and *cis*-$FeNO(S_2CN(CH_3)_2)_2Cl$ is reported. The complex *trans*-$[FeNO(S_2CN(CH_3)_2)_2(CH_3CN)][BF_4]$ resulted from the reaction of $NOBF_4$ with $Fe(S_2CN(CH_3)_2)_2$ in acetonitrile and served as a useful reaction intermediate from which the other complexes were prepared. These same isomers also resulted from oxidation of $FeNO(S_2CN(CH_3)_2)_2$ with $I_2$, $Br_2$, $Cl_2$, $(SCN)_2$, or $NO_2$ at room temperature, but the reaction between $NO_2$ and $FeNO(S_2CN(CH_3)_2)_2$ at −78 °C produced *trans*-$FeNO(S_2CN(CH_3)_2)_2NO_2$. The exchange of NO with the five-coordinate complex $FeNO(S_2CN(CH_3)_2)_2$ (fast) and the six-coordinate complex *cis*-$FeNO(S_2CN(CH_3)_2)_2I$ (slow) was investigated. The structure of *cis*-$FeNO(S_2CN(C_2H_5)_2)_2NO_2$ has been determined crystallographically. The compound crystallizes in space group $C_{2h}^5$-$P2_1/c$ with four molecules per unit cell of dimensions $a$ = 10.323 (4) Å, $b$ = 16.178 (6) Å, $c$ = 11.356 (4) Å, and $\beta$ = 101.5 (1)°. Full-matrix least-squares refinement using 2908 data having $F_o^2 > 3\sigma(F_o^2)$ gave $R_1$ = 0.059. The iron atom in the complex is six-coordinate with an Fe–N–O angle of 174.9 (5)° and an (O)N–Fe–N($O_2$) angle of 91.3 (2)°. The Fe–S bond trans to the NO group is normal (2.308 (2) Å) for low-spin iron(II) complexes, but the Fe–S bond trans to the $NO_2$ group is lengthened (2.321 (2) Å) due to the structural trans effect of the $NO_2$ group. The chemical reactivity and stereochemistry of these complexes are discussed in relation to their bonding.

## Introduction

Sulfur ligands are known to stabilize numerous nitrosyl complexes. However, there have been few systematic investigations of the chemical reactions of these sulfur-containing metal nitrosyl complexes.[2-4] The preparation of dithiocarbamate derivatives of the $\{FeNO\}^7$ group[5] $FeNO(S_2CNR_2)_2$ was first reported by Cambi and Cagnasso.[6] Both five-coordinate complexes $FeNO(S_2CN(CH_3)_2)_2$ and $FeNO(S_2CN(C_2H_5)_2)_2$ are paramagnetic and have square-pyramidal geometry with a nearly linear NO group in the axial position.[7-9] Spectroscopic investigations of these dithiocarbamate complexes by IR,[10] EPR,[11-13] vis–UV,[14] and XPS[15] place the unpaired electron in an antibonding orbital which is predominantly $d_{z^2}$(Fe) and $\sigma^*$(NO). Consequently, it was surprising that oxidation of $FeNO(S_2CNR_2)_2$ complexes appeared to consistently result in the formation of six-coordinated complexes of the $\{FeNO\}^6$ group $FeNO(S_2CNR_2)_2X$ which have cis geometry.[1] Cis geometry was unexpected for two reasons. First, examination of the literature shows that only trans isomers have been reported for most $\{MNO\}^6$ complexes. Second, both the geometry and electronic ground state of $FeNO(S_2CNR_2)_2$ favor formation of the trans isomers. The preparative studies described below were directed toward the isolation of the kinetic and thermodynamic products from these reactions. Both the kinetic (trans) and thermodynamic (cis) products were isolated for $FeNO(S_2CNR_2)_2NO_2$ and consequently an x-ray structural study of *cis*-$FeNO(S_2CN(C_2H_5)_2)_2NO_2$ was initiated. Concurrently, it was also found that the adjacent NO and $NO_2$ groups of *cis*-$FeNO(S_2CN(CH_3)_2)_2NO_2$ undergo a novel intramolecular exchange reaction,[4] so that its structural features assumed additional importance. The results of these structural and preparative studies are outlined below.

## Experimental Section

All reactions were carried out in an inert atmosphere using standard Schlenk-tube techniques. The solvents and reagents were carefully dried and stored under nitrogen. The infrared spectra were obtained using Perkin-Elmer 337 or 137 or Beckman IR-12 spectrophotometers. The $^1H$ NMR spectra were recorded on a Varian T-60 spectrometer using TMS as an internal standard. The elemental analyses (Table I) were obtained from Chemalytics Inc., Tempe, Ariz., and Huffman Laboratories, Wheatridge, Colo. The experiments involving $^{15}NO$ (95% enriched) were carried out in an all-glass vacuum line. Cylinders of NO and $NO_2$ were purchased from the Matheson Co. NO was purified by trap-to-trap distillation ($CO_2$/acetone baths) in a vacuum line. Traces of NO present in $NO_2$ were converted to $NO_2$ by reaction with excess oxygen. Pure $NO_2$ obtained by this procedure is a white solid at −78 °C. The solvents used were freshly distilled, purged with nitrogen at their boiling points, and allowed to cool under nitrogen. The solutions were further degassed on the vacuum line by freeze–thaw techniques.

The solution IR cells from Barnes Engineering were modified for use with air-sensitive samples by using neoprene gaskets. Solution IR spectra were obtained at controlled temperatures using a Barnes Engineering variable-temperature chamber. All reactions were carried out in the dark unless otherwise stated. Infrared spectra for kinetic studies were recorded on the Beckman IR-12 spectrophotometer. Solutions studied by IR spectroscopy were syringed directly into an IR cell with strict exclusion of air. The spectra were recorded in the nitrosyl region (1650–1900 $cm^{-1}$) vs. a reference cell containing the pure solvent. In some cases the exchange reactions were studied by quenching techniques in which aliquots of solutions were treated with an excess of a nonsolvent, and the resultant solids were separated and examined by IR spectroscopy.

**Preparation of Compounds.** The compounds described below were thoroughly characterized by elemental analyses (Table I) and IR, NMR, and EPR spectroscopy.

**Bis(diethyldithiocarbamato)nitrosyliron.** This compound was prepared as previously described.[16] However, satisfactory analyses could be obtained only from material recrystallized by slow evaporation from benzene.

**Bis(dimethyldithiocarbamato)nitrosyliron.** A solution of 5.56 g (20 mmol) of $FeSO_4\cdot7H_2O$ in 100 mL of distilled deoxygenated water was cooled to 0 °C in an ice bath. This solution was saturated with purified nitric oxide. A degassed solution of 7.2 g (50 mmol) of sodium dimethyldithiocarbamate in 75 mL of water was then added dropwise. The resultant dark green precipitate was filtered, dried, and recrystallized by slow evaporation from benzene: yield 6.1 g (93% based on the ligand); $\nu_{NO}$ 1724 ($CHCl_3$), 1691 $cm^{-1}$ (KBr).

**Bis(diphenyldithiocarbamato)nitrosyliron.** This complex was prepared as described above using 3.63 g (10 mmol) of $Fe(ClO_4)_2\cdot6H_2O$ dissolved in 50 mL of methanol and 5.34 g (20 mmol) of sodium diphenyldithiocarbamate dissolved in 30 mL of methanol. The green precipitate was removed by filtration, dried, and recrystallized from acetone: yield 3.3 g (57% based on the ligand); $\nu_{NO}$ 1707 $cm^{-1}$ (KBr).

**Bis(methylphenyldithiocarbamato)nitrosyliron.** The ammonium salt of methylphenyldithiocarbamic acid was prepared as described elsewhere.[17] A degassed solution containing 5.56 g of $FeSO_4\cdot7H_2O$

Table I. Elemental Analyses

| Compd | % C | | % H | | % N | | % O | |
|---|---|---|---|---|---|---|---|---|
| | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found |
| $FeNO(S_2CN(C_2H_5)_2)_2$ | 31.41 | 31.78 | 5.23 | 4.97 | 10.99 | 10.80 | | |
| $FeNO(S_2CN(CH_3)_2)_2$ | 22.08 | 22.34 | 3.68 | 3.88 | 12.88 | 12.78 | 4.91 | 5.61 |
| $FeNO(S_2CN(CH_3)(C_6H_5))_2$ | 42.66 | 42.49 | 3.58 | 3.53 | 9.33 | 9.26 | | |
| $FeNO(S_2CN(C_6H_5)_2)_2$ | 54.36 | 53.80 | 3.50 | 3.40 | 7.31 | 7.05 | | |
| *cis*-$FeNO(S_2CN(CH_3)_2)_2I$ | 15.89 | 16.12 | 2.65 | 2.71 | 9.27 | 9.18 | | |
| *cis*-$FeNO(S_2CN(CH_3)_2)_2Br$ | 17.73 | 17.66 | 2.96 | 2.99 | 10.34 | 10.12 | | |
| *cis*-$FeNO(S_2CN(CH_3)_2)_2NO_2$ | 19.35 | 19.66 | 3.25 | 3.28 | 15.05 | 14.89 | | |
| *trans*-$FeNO(S_2CN(CH_3)_2)_2CH_3CN^+BF_4^-$ | 21.15 | 21.16 | 3.33 | 3.25 | 12.33 | 11.90 | | |
| *cis*-$FeNO(S_2CN(CH_3)_2)_2CH_3NC^+BF_4^-$ | 21.15 | 21.19 | 3.33 | 3.45 | 12.33 | 12.07 | | |
| *trans*-$FeNO(S_2CN(CH_3)_2)_2SCN$ | 21.87 | 21.98 | 3.15 | 3.01 | 14.58 | 14.17 | | |
| *trans*-$FeNO(S_2CN(CH_3)_2)_2CH_3CN^+PF_6^-$ | 18.75 | 18.81 | 2.92 | 2.81 | 10.94 | 10.88 | | |
| *trans*-$FeNO(S_2CN(CH_3)_2)_2NO_2\cdot CHCl_3$ | 16.73 | 16.78 | 2.59 | 2.76 | 11.15 | 10.95 | | |

(20 mmol) in 100 mL of water was treated with NO for 10 min (0 °C), and 8.0 g (40 mmol) of ammonium methylphenyldithiocarbamate in 65 mL of deoxygenated water was added. After a green solid had formed, the NO was displaced with nitrogen. The dark green solid was collected, dried, and recrystallized from acetone/pentane at −78 °C: yield 4.3 g (48% based on the ligand); $\nu_{NO}$ 1714 $cm^{-1}$ (KBr).

*cis*-**Bis(dimethyldithiocarbamato)(iodo)nitrosyliron. Method I.** A solution of 0.14 g (1.1 mmol) of iodine in 8 mL of $CHCl_3$ was added dropwise to a solution of 0.326 g (1 mmol) of $FeNO(S_2CNMe_2)_2$ in 6 mL of $CHCl_3$ over a 15-min period. After stirring of the mixture for 1 h the solvent was removed by evaporation under vacuum, and the brown solid was collected, washed with ether, dried, and recrystallized from chloroform/pentane: yield 0.387 g (76% based on Fe); $\nu_{NO}$ 1815 $cm^{-1}$ (KBr); $^1H$ NMR $\tau$ 6.63, 6.70, 6.80, 6.87 (1:1:1:1).

**Method II.** A solution of 0.512 g (1 mmol) of $[FeNO(S_2CNMe_2)_2CH_3CN][PF_6]$ in 20.0 mL of acetone was treated with a solution of 0.134 g (1 mmol) of LiI in 10.0 mL of acetone. After filtration the solution was evaporated to dryness; yield 0.380 g (84% based on Fe). The resultant brown solid had properties identical with those of the complex obtained using method I.

*trans*-**Bis(dimethyldithiocarbamato)(acetonitrile)nitrosyliron Hexafluorophosphate. Method I.** A solution of $AgPF_6$ (0.252 g, 1 mmol) in 6.0 mL of $CH_3CN$ was added to a solution of 0.453 g (1 mmol) of *cis*-$FeNO(S_2CNMe_2)_2I$. After removal of AgI by filtration the dark solution was evaporated to dryness giving a black solid: $\nu_{NO}$ 1825 $cm^{-1}$; $^1H$ NMR $\tau$ 6.75, 7.97 (4:1).

**Method II.** The same compound was prepared from the reaction between 0.350 g (2 mmol) of $NOPF_6$ dissolved in 8.0 mL of $CH_3CN$ and 0.592 g (2 mmol) of $Fe(S_2CNMe_2)_2$. During the reaction gas was evolved and the solution turned black. Evaporation of the solution to dryness resulted in a black solid with properties identical with those described above.

*trans*-**Bis(dimethyldithiocarbamato)(acetonitrile)nitrosyliron Tetrafluoroborate.** A solution of 1.17 g of $NOBF_4$ (10 mmol) in 20.0 mL of $CH_3CN$ was added slowly to 2.96 g (10 mmol) of solid $Fe(S_2CNMe_2)_2$. During the reaction gas was evolved. The black solution which resulted was warmed and filtered and the filtrate was evaporated to dryness. The dark brown compound thus obtained was recrystallized from a minimum amount of acetonitrile/ether: yield 3.10 g (68% based on Fe); $\nu_{CH_3CN}$ 2240, $\nu_{NO}$ 1830 $cm^{-1}$ (KBr); $^1H$ NMR $\tau$ 6.73, 8.03 (4:1).

*trans*-**Bis(dimethyldithiocarbamato)(isothiocyanato)nitrosyliron. Method I.** To a solution of 0.326 g (1 mmol) of $FeNO(S_2CNMe_2)_2$ in 10.0 mL of $CHCl_3$ was added 10.0 mL of 0.1 N thiocyanogen[18] in $CHCl_3$ dropwise with stirring (15 min). The resultant dark brown solution was stirred for 1 h and evaporated to dryness. The dark brown solid was washed with ether, dried, and recrystallized from $CHCl_3$/ethanol (1:1); yield 0.289 g (75% based on Fe).

**Method II.** A solution of 0.256 g (0.5 mmol) of $[FeNO(S_2CNMe_2)_2CH_3CN][PF_6]$ in 10.0 mL of acetone was mixed with 0.049 g (0.5 mmol) of KSCN in 15.0 mL of acetone. The resultant mixture was filtered to remove $KPF_6$ and unreacted KSCN. Evaporation of the filtrate produced a brown solid: yield 0.16 g (82% based on Fe); $^1H$ NMR $\tau$ 6.62; $\nu_{NO}$ 1835, $\nu_{NCS}$ 2090 $cm^{-1}$.

*cis*-**Bis(dimethyldithiocarbamato)(bromo)nitrosyliron. Method I.** To a solution of 0.163 g (0.5 mmol) of $FeNO(S_2CNMe_2)_2$ in 15.0 mL of $CHCl_3$ was added a solution of 0.52 mmol of $Br_2$ in 15.0 mL of $CHCl_3$ dropwise with stirring over a period of 15 min. The solution was stirred for another 15 min and filtered and the filtrate was evaporated to dryness. The resultant brown oil was digested with 5.0 mL of ethanol and filtered, leaving a dark brown solid: $\nu_{NO}$ 1825 $cm^{-1}$; $^1H$ NMR $\tau$ 6.66, 6.73, 6.79, 6.87 (1:1:1:1).

**Method II.** A solution of 0.151 g (0.33 mmol) of $[FeNO(S_2CNMe_2)_2CH_3CN][BF_4]$ in 10.0 mL of acetone was treated with 0.082 g (0.67 mmol) of $LiBr\cdot 2H_2O$ in 10.0 mL of acetone. After stirring of the mixture for 1 h the solid was removed by filtration and the filtrate was evaporated to dryness. Recrystallization from benzene/ether gave a black product with properties identical with those of the product from method I.

*cis*-**Bis(dimethyldithiocarbamato)(nitro)nitrosyliron. Method I.** A solution of 1.1 mmol of $NO_2$ in 10.0 mL of nitromethane was added dropwise with stirring over a period of 15 min to a solution of 0.326 g (1 mmol) of $FeNO(S_2CNMe_2)_2$ in 5.0 mL of nitromethane. The mixture was stirred for another 15 min and the solvent was removed under vacuum. The resultant brown solid was recrystallized from dichloromethane/heptane and had properties identical with those of the compound described below.

**Method II.** A solution of 0.454 g (1 mmol) of $[FeNO(S_2CNMe_2)_2CH_3CN][BF_4]$ in 20.0 mL of acetone was treated with a solution of 0.176 g of $(C_2H_5)_4NNO_2$ in 8.0 mL of acetone. After stirring of the solution for 30 min the black solution which formed was filtered and the filtrate was evaporated to dryness. The solid was recrystallized from benzene/ether: $\nu_{NO}$ 1835, $\nu_{NO_2}$ 1382, 1305, $\delta_{NO_2}$ 812 $cm^{-1}$; $^1H$ NMR $\tau$ 6.67, 6.72, 6.78 (2:1:1).

**Method III.** This complex was also prepared from *cis*-$FeNO(S_2CNMe_2)_2I$. A solution of 0.151 g (0.33 mmol) of *cis*-$FeNO(S_2CNMe_2)_2I$ in 20.0 mL of acetonitrile was treated with a solution of 0.051 g (0.33 mmol) of $AgNO_2$ in 5.0 mL of $CH_3CN$. The solution was stirred for 15 min and the yellow precipitate which formed was removed by filtration. The filtrate was evaporated to dryness and the brown solid collected on a frit, washed with 5.0 mL of ethanol, and dried in vacuo; yield 0.076 g (62% based on Fe). The product from this reaction had properties identical with those of the materials prepared by methods I and II.

*cis*-**Bis(dimethyldithiocarbamato)(methyl isocyanide)nitrosyliron Tetrafluoroborate.** A solution of 0.151 g (0.33 mol) of *trans*-$[FeNO(S_2CNMe_2)_2CH_3CN][BF_4]$ in 10.0 mL of $CHCl_3$ was treated with 0.015 mL (0.33 mmol) of methyl isocyanide. The solution was stirred for 30 min and filtered. The filtrate was evaporated to dryness giving a light brown solid which was recrystallized from methanol: $\nu_{NO}$ 1870, $\nu_{NC}$ 2265 $cm^{-1}$; $^1H$ NMR $\tau$ 6.49 ($CH_3NC$) (1) and 6.73, 6.76, 6.79, 6.82 (1:1:1:1).

*trans*-**Bis(dimethyldithiocarbamato)(pyridine)nitrosyliron Tetrafluoroborate.** Pyridine (0.33 mmol) was added to a solution of 0.151 g (0.33 mmol) of *trans*-$[FeNO(S_2CNMe_2)_2CH_3CN][BF_4]$ in 15.0 mL of $CHCl_3$. After stirring of the solution for 1 h the green precipitate was removed by filtration, washed with ether, and dried. Recrystallization from chloroform/ether gave a green solid: $\nu_{NO}$ 1830 $cm^{-1}$; $^1H$ NMR $\tau$ 6.73.

**Attempted Preparation of Chloride and Azide Derivatives.** *trans*-$[FeNO(S_2CNMe_2)_2CH_3CN][BF_4]$ was treated with both $Cl^-$ and $N_3^-$ in various solvents. Although dark intermediates were observed in solution, the final product from each of these reactions was $FeNO(S_2CNMe_2)_2$. The reaction with $N_3^-$ produced considerable amounts of $N_2$. The fate of chlorine from the reaction with chloride ion was not established.

*trans*-**Bis(dimethyldithiocarbamato)(nitro)nitrosyliron.** A solution of 0.326 g of $FeNO(S_2CNMe_2)_2$ in 20.0 mL of $CHCl_3$ was treated

Table II. Experimental Data for X-Ray Diffraction Studies of *cis*-$Fe(NO)(NO_2)(S_2CN(C_2H_5)_2)_2$

| | | | |
|---|---|---|---|
| | | Crystal Parameters | |
| Crystal system | Monoclinic | $Z$ | 4 |
| Space group | $P2_1/c$ | Temp, °C | 23 (2) |
| $a$,[a] Å | 10.323 (4) | Mol wt | 428.399 |
| $b$, Å | 16.178 (6) | $\rho$(calcd), g cm$^{-3}$ | 1.530 |
| $c$, Å | 11.356 (4) | $\rho$(obsd), g cm$^{-3}$ | 1.519 (5)[b] |
| $\beta$, deg | 101.5 (1) | Absorption coeff, cm$^{-1}$ | 12.76 |
| $V$, Å$^3$ | 1858.5 (7) | Transmission factors (min–max)[c] | 0.682–0.730 |
| | | Data Collection | |
| Radiation | Mo K$\alpha$ | Scan speed, deg/min | 2.0 |
| Attenuators | Cu foil; used if $I > 10^4$ counts/s | Scan range, deg | From $[2\theta(K\alpha_1) - 0.6]$ to $[2\theta(K\alpha_2) + 0.7]$ |
| Detector aperture, mm | 4.0 × 4.0 | Background time, s | 20 |
| Takeoff angle, deg | 2.0 | $2\theta$(max), deg | 50 |
| Crystal–detector dist, mm | 240 | Unique reflections collected | 3606 |
| Scan type | $\theta$(crystal)–$2\theta$(counter) | | |

[a] Unit cell parameters are derived from a least-squares fit of 14 reflections ($25° < 2\theta < 40°$). [b] Flotation in $ZnBr_2$(aq). [c] No absorption correction was made.

with 1 mmol of $NO_2$ at −78 °C. The mixture was allowed to warm to 0 °C in an ice bath and was stirred for 1 h. Ether (50.0 mL) was added and the brown solid which formed was filtered and dried in vacuo: $\nu_{NO}$ 1840, $\nu_{NO_2}$ 1386, 1275, $\delta_{NO_2}$ 760 (KBr), $\nu_{NO}$ 1866 cm$^{-1}$ ($CHCl_3$ solution).

**Isomerization of *trans*-Bis(dimethyldithiocarbamato)(nitro)-nitrosyliron to *cis*-Bis(dimethyldithiocarbamato)(nitro)nitrosyliron.** A solution of 0.0386 g (0.1 mmol) of *trans*-$FeNO(S_2CNMe_2)_2NO_2$ in 10.0 mL of $CHCl_3$ was stirred for 0.5 h at 22 °C. The solvent was removed under vacuum producing a brown solid. The IR spectrum of this solid was identical with that of *cis*-$FeNO(S_2CNMe_2)_2NO_2$ (vide supra). In solution the trans complex ($\nu_{NO}$ 1866 cm$^{-1}$ in $CHCl_3$) completely isomerized to the cis complex ($\nu_{NO}$ 1857 cm$^{-1}$ in $CHCl_3$) in ca. 20 min.

**Exchange Reactions.** The exchange of $^{14}NO$ with several nitrosyl complexes isotopically labeled with $^{15}NO$ was studied using IR spectroscopy.

**$Fe^{15}NO(S_2CNMe_2)_2$ with $^{14}NO$.** A solution of 0.163 g (0.5 mmol) of $Fe^{15}NO(S_2CNMe_2)$ (95% $^{15}N$) in 20.0 mL of $CHCl_3$ was treated with 0.5 mmol of $^{14}NO$ at 77 K. The solution was allowed to thaw and an aliquot of solution was syringed into an IR cell. The solution IR spectrum between 1650 and 1760 cm$^{-1}$ was obtained in approximately 2 min.

***cis*-$Fe^{15}NO(S_2CNMe_2)_2I$ with $^{14}NO$.** A solution of 0.0090 g of *cis*-$Fe^{15}NO(S_2CNMe_2)_2I$ in 7.5 mL of $CHCl_3$ was treated with 0.02 mmol of $^{14}NO$. The reaction vessel was maintained at 5 °C, protected from light, and examined by IR spectroscopy. The intensity of the $^{14}NO$ band of *cis*-$Fe^{14}NO(S_2CNMe_2)_2I$ at 1848 cm$^{-1}$ increased with time at the expense of the $^{15}NO$ band of *cis*-$Fe^{15}NO(S_2CNMe_2)_2I$ at 1810 cm$^{-1}$ (Figure 4).

**Structure Determination of *cis*-$Fe(NO)(NO_2)(S_2CNEt_2)_2$.** Single crystals of *cis*-$Fe(NO)(NO_2)(S_2CNEt_2)_2$ prepared by the method of Büttner and Feltham[1] were obtained by dissolving the compound in ethyl acetate, adding an equal amount of hexane, and allowing the mixture to stand overnight at 0 °C. For data collection, one of the air-stable black crystals of approximate dimensions 0.4 × 0.3 × 0.3 mm was mounted on a glass fiber and oriented with its $c$ axis approximately collinear with the $\phi$ axis of the Picker FACS-I diffractometer. The mosaicity of the crystal ($\omega$ scans, takeoff angle 0.7°) gave peak widths of 0.15° or less. During data collection the intensities of three reflections in diverse regions of reciprocal space were monitored after every 75 reflections. The intensity of one of the standards dropped approximately 6%, but the maximum variation of the other two standards was <4%. The other experimental details are set out in Table II. The data were reduced to $F^2$ and $\sigma(F^2)$ by procedures similar to those previously described.[19,20]

The polarization correction used was $P = 0.5(\cos^2 2\theta_m + \cos^2 2\theta)$ where $\theta_m$ is the Bragg angle of the monochromator crystal and $\theta$ is the Bragg angle of the reflection being observed. Standard deviations were assigned to the intensities by the formula

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated peak count obtained in time $t_c$ and $B_1$ and $B_2$ are the background counts each obtained in time $t_b$, $I$ is the intensity, and $p$ was taken as 0.04. In the refinement the wavelength of Mo K$\alpha$ radiation was taken as 0.71070 Å.

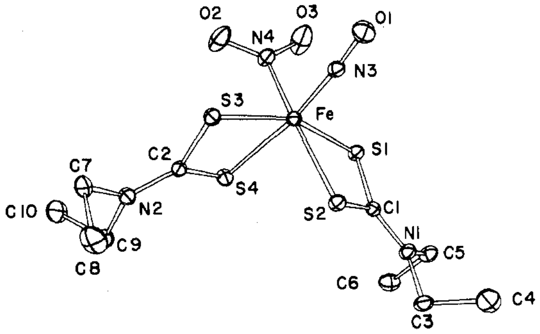

**Figure 1.** Perspective view of the *cis*-$Fe(NO)(NO_2)(S_2CN(C_2H_5)_2)_2$ molecule. The hydrogen atoms have been omitted for clarity.

**Solution and Refinement of the Structure.** Positions of the Fe and two S atoms were located from a Patterson map computed from the corrected intensities. A series of structure factor calculations, least squares refinements and electron density difference maps revealed all the nonhydrogen atoms of the formula unit.

Refinement of the structure based upon $F$ was begun[20] by minimizing $\sum w(|F_o| - |F_c|)^2$ with the weights, $w$, taken as $4F_o^2/\sigma^2(F_o)^2$. The atomic scattering factors for Fe, S, C, N, and O were obtained from Cromer and Waber.[21] The hydrogen scattering factors were from the calculations of Stewart, Davidson, and Simpson.[22] The effects of anomalous dispersion were included[23] in $F_c$. The values of $\Delta f'$ and $\Delta f''$ calculated by Cromer[24] were used for Fe and S.

One cycle of isotropic refinement with all nonhydrogen atoms gave $R_1 = \sum||F_o| - |F_c||/(\sum|F_o|) = 0.154$ and $R_2 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.200$ for 2908 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. Two more cycles of isotropic refinement gave $R_1 = 0.096$ and $R_2 = 0.146$. After two cycles of refinement with anisotropic thermal parameters for all atoms, the discrepancy indices were $R_1 = 0.063$ and $R_2 = 0.105$. A difference electron density map revealed reasonable positions for six H atoms. Positions were calculated for the remaining H atoms and all H atoms were included as fixed contributors in subsequent calculations.[21] Two final cycles of least-squares refinement (199 variables) gave $R_1 = 0.059$ and $R_2 = 0.101$. The largest peak in the final difference map (0.97 e/Å$^3$) was assigned to residual electron density of the Fe atom. All other peaks were less than 0.90 e/Å$^3$. The standard deviation of an observation of unit weight was 3.97. An analysis of the weighting scheme as a function of $(\sin\theta)/\lambda$ and $F_o$ showed that the low-angle reflections were slightly overweighted. The final atomic parameters appear in Table III.

## Results and Discussion

**Structure of *cis*-$Fe(NO)(NO_2)(S_2CN(C_2H_5)_2)_2$.** The iron atom is six-coordinate with the NO group and the $NO_2$ group occupying adjacent coordination sites (Figure 1). Although the N3–Fe–N4 angle is 91.3°, the coordination sphere of the iron atom is distorted from octahedral geometry because of the small bite angle of the dithiocarbamate ligand. This distortion is reflected in the inter- and intraligand bond angles which range from 74.9 (S3–Fe–S4) to 98.4° (N4–Fe–S3)

**Table III.** Final Atomic Parameters for $FeNO(S_2CN(C_2H_5)_2)_2NO_2$

| Atom$^a$ | $x$ | $y$ | $z$ | $10^3\beta_{11}$ | $10^3\beta_{22}$ | $10^3\beta_{33}$ | $10^3\beta_{12}$ | $10^3\beta_{13}$ | $10^3\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 0.2158 (1) | 0.4904 (1) | 0.2567 (1) | 7.7 (1) | 2.4 (1) | 5.8 (1) | 0.18 (1) | 1.6 (1) | 0.17 (1) |
| S1 | 0.1845 (2) | 0.4917 (1) | 0.4515 (1) | 10.7 (2) | 2.6 (1) | 6.5 (1) | −0.36 (1) | 2.9 (1) | −0.44 (1) |
| S2 | 0.1434 (2) | 0.3580 (1) | 0.2883 (1) | 10.6 (2) | 2.6 (1) | 6.4 (1) | −0.33 (1) | 2.6 (1) | −0.41 (1) |
| S4 | 0.4300 (2) | 0.4477 (1) | 0.3296 (1) | 8.5 (2) | 4.1 (1) | 6.2 (1) | 0.65 (1) | 0.11 (1) | 0.0 (1) |
| S3 | 0.2940 (2) | 0.4488 (1) | 0.0895 (1) | 8.7 (2) | 3.6 (1) | 5.7 (1) | 0.53 (8) | 1.6 (1) | 0.23 (7) |
| C1 | 0.1428 (5) | 0.3890 (4) | 0.4326 (5) | 7.8 (6) | 2.6 (2) | 6.2 (5) | 0.5 (3) | 1.9 (4) | 0.12 (30) |
| C2 | 0.4374 (6) | 0.4197 (4) | 0.1857 (5) | 8.3 (6) | 2.7 (2) | 6.9 (5) | −0.1 (3) | 2.7 (4) | 0.06 (30) |
| N1 | 0.1148 (5) | 0.1586 (3) | 0.0177 (4) | 11.4 (6) | 2.9 (2) | 7.0 (4) | −0.3 (3) | 3.7 (4) | −0.24 (26) |
| N2 | 0.5337 (5) | 0.3800 (3) | 0.1524 (5) | 8.1 (5) | 3.2 (2) | 9.0 (5) | 0.33 (3) | 2.3 (4) | 0.01 (27) |
| N3 | 0.0697 (5) | 0.5216 (3) | 0.1807 (4) | 9.5 (6) | 3.3 (2) | 6.1 (4) | −0.03 (30) | 1.7 (4) | 0.52 (25) |
| O1 | −0.0264 (5) | 0.5427 (4) | 0.1212 (5) | 10.7 (6) | 7.4 (3) | 10.8 (5) | 1.0 (4) | −0.9 (5) | 1.4 (3) |
| N4 | −0.2851 (6) | 0.1067 (4) | 0.2324 (5) | 12.0 (7) | 3.6 (3) | 7.6 (5) | 0.8 (3) | 3.6 (5) | 0.0 (30) |
| O2 | −0.3632 (7) | 0.1324 (4) | 0.2860 (6) | 29.0 (12) | 4.7 (3) | 17.4 (8) | 3.9 (5) | 13.5 (9) | 1.0 (4) |
| O3 | −0.2370 (8) | 0.1544 (4) | 0.1695 (8) | 34.8 (14) | 4.3 (3) | 28.8 (12) | 4.0 (5) | 22.2 (11) | 4.9 (5) |
| C3 | 0.0762 (7) | 0.2531 (4) | 0.4927 (6) | 13.3 (8) | 2.3 (2) | 9.6 (6) | −0.1 (4) | 3.2 (6) | 0.5 (3) |
| C4 | −0.0689 (9) | 0.2392 (5) | 0.4825 (9) | 15.0 (10) | 4.4 (4) | 16.7 (10) | −1.8 (5) | 1.6 (8) | −1.9 (5) |
| C5 | 0.1266 (7) | 0.1295 (4) | 0.1408 (5) | 13.0 (8) | 3.9 (3) | 5.7 (5) | 0.3 (4) | 2.7 (5) | 0.3 (3) |
| C6 | 0.2632 (8) | 0.1424 (5) | 0.2132 (7) | 14.5 (10) | 4.5 (4) | 10.1 (7) | −0.2 (5) | 0.0 (7) | −0.7 (4) |
| C7 | −0.4714 (7) | 0.3572 (5) | 0.0232 (6) | 12.2 (8) | 4.6 (4) | 8.9 (6) | 1.3 (4) | 4.7 (6) | −0.5 (4) |
| C8 | 0.4772 (9) | 0.2683 (6) | −0.0027 (8) | 17.5 (12) | 4.8 (4) | 15.5 (10) | −0.1 (5) | 3.4 (9) | −3.9 (5) |
| C9 | −0.3462 (6) | 0.3557 (4) | 0.2400 (6) | 8.1 (7) | 4.0 (3) | 10.0 (6) | 0.5 (4) | 1.3 (5) | 0.6 (4) |
| C10 | −0.2301 (7) | 0.4094 (6) | 0.2310 (8) | 9.2 (8) | 6.1 (4) | 14.8 (9) | −0.8 (5) | 1.5 (7) | 0.2 (5) |

| Atom$^b$ | $x$ | $y$ | $z$ | Atom$^b$ | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| H1 | 0.1050 | 0.3174 | 0.5126 | H11 | −0.5410 | 0.3953 | −0.0373 |
| H2 | 0.1369 | 0.2137 | 0.5611 | H12 | −0.5290 | 0.3201 | 0.0781 |
| H3 | −0.0800 | 0.2400 | 0.5600 | H13 | 0.4000 | 0.2600 | 0.0300 |
| H4 | −0.1286 | 0.2875 | 0.4318 | H14 | 0.5113 | 0.2265 | −0.0629 |
| H5 | −0.1011 | 0.1793 | 0.4427 | H15 | 0.5550 | 0.3113 | 0.0361 |
| H6 | 0.1024 | 0.0625 | 0.1387 | H16 | −0.3781 | 0.3409 | 0.3250 |
| H7 | 0.0542 | 0.1609 | 0.1841 | H17 | −0.4310 | 0.3440 | 0.1664 |
| H8 | 0.2800 | 0.1200 | 0.3000 | H18 | −0.2000 | 0.4200 | 0.1500 |
| H9 | 0.3365 | 0.1127 | 0.1669 | H19 | −0.2522 | 0.4719 | 0.2624 |
| H10 | 0.2866 | 0.2091 | 0.2174 | H20 | −0.1446 | 0.3856 | 0.2929 |

$^a$ $x, y, z$ are in fractional coordinates. Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The standard deviation of the last significant figure is given in parentheses. $^b$ An isotropic thermal parameter, $B$, of 7.0 Å$^2$ was assigned to each of the hydrogen atoms.

**Table IV.** Selected Interatomic Distances (Å) and Angles (deg) in $FeNO(S_2CN(C_2H_5)_2)_2NO_2$

Distances

| | | | |
|---|---|---|---|
| Fe–N3 | 1.659 (5) | S4–C2 | 1.712 (6) |
| Fe–N4 | 2.008 (6) | C1–N1 | 1.314 (7) |
| Fe–S1 | 2.299 (2) | C2–N2 | 1.301 (7) |
| Fe–S2 | 2.321 (2) | N1–C3 | 1.495 (8) |
| Fe–S3 | 2.306 (2) | N1–C5 | 1.457 (8) |
| Fe–S4 | 2.308 (2) | N2–C7 | 1.503 (8) |
| N3–O1 | 1.136 (6) | N2–C9 | 1.480 (8) |
| N4–O2 | 1.178 (7) | C3–C4 | 1.496 (11) |
| N4–O3 | 1.222 (8) | C5–C6 | 1.498 (10) |
| S1–C1 | 1.718 (6) | C7–C8 | 1.540 (12) |
| S2–C1 | 1.714 (6) | C9–C10 | 1.501 (10) |
| S3–C2 | 1.721 (6) | | |

Angles

| | | | |
|---|---|---|---|
| N3–Fe–N4 | 91.3 (2) | N1–C1–S1 | 124.2 (4) |
| N3–Fe–S1 | 102.2 (2) | S2–C1–S1 | 110.8 (3) |
| N3–Fe–S3 | 95.3 (2) | N2–C2–S4 | 126.2 (5) |
| N3–Fe–S4 | 169.8 (2) | N2–C2–S3 | 124.1 (5) |
| N3–Fe–S2 | 94.3 (2) | S4–C2–S3 | 109.7 (3) |
| N4–Fe–S1 | 92.8 (2) | C1–N1–C5 | 121.9 (5) |
| N4–Fe–S3 | 98.4 (2) | C1–N1–C3 | 120.7 (5) |
| N4–Fe–S4 | 87.4 (2) | C5–N1–C3 | 117.4 (5) |
| N4–Fe–S2 | 167.8 (2) | C2–N2–C9 | 121.4 (5) |
| S1–Fe–S3 | 159.0 (1) | C2–N2–C7 | 121.7 (5) |
| S1–Fe–S4 | 88.0 (1) | C9–N2–C7 | 116.9 (5) |
| S1–Fe–S2 | 75.4 (1) | O1–N3–Fe | 174.9 (5) |
| S3–Fe–S4 | 74.9 (1) | O2–N4–O3 | 118.6 (6) |
| S3–Fe–S2 | 92.0 (1) | O2–N4–Fe | 124.8 (5) |
| S4–Fe–S2 | 89.0 (1) | O3–N4–Fe | 116.5 (5) |
| C1–S1–Fe | 87.2 (2) | N1–C3–C4 | 112.5 (6) |
| C1–S2–Fe | 86.6 (2) | N1–C5–C6 | 111.8 (6) |
| C2–S3–Fe | 87.5 (2) | N2–C7–C8 | 111.1 (6) |
| C2–S4–Fe | 87.6 (2) | N2–C9–C10 | 111.9 (6) |
| N1–C1–S2 | 125.1 (5) | | |

(Table IV). In spite of the small bite angles of the dithiocarbamate ligands, the planes defined by S1, S2, S3, N4, by S1, S3, S4, N3, and by N3, Fe, N4 intersect at nearly 90° (89.3–93.2°, Table V) and indicate that a semblance of octahedral geometry is preserved in this complex. The two chelate rings Fe, S1, S2, C1 and Fe, S3, S4, C2 are planar within experimental error and also form planes which intersect at 90.9°. The four atoms of the $FeNO_2$ group are coplanar, but the $NO_2$ group is slightly twisted (23.4°) out of the plane defined by S1, S2, S3, N4.

To compare this structure with other $\{MNO\}^n$ complexes, it is convenient to describe this molecule as a distorted square pyramid with the NO group and S4 occupying the axial positions, and the atoms S1, S2, S3, and N4 defining the basal plane. The iron atom is displaced from this plane toward the nitrosyl group by 0.22 Å and the average N3–Fe–L angle with the adjacent ligands is 95.5° similar to those found for $Fe(NO)(CN)_5^{2-}$ by Manoharan and Hamilton[25] (0.2 Å and 96°, respectively). The Fe–N3 and N3–O1 distances (1.659 (5) and 1.136 (6) Å) in the present structure also compare favorably with the corresponding distances found for $Fe(NO)(CN)_5^{2-}$ (1.63 (2) and 1.13 (2) Å, respectively). The FeNO angles appear to differ only slightly (174.9 (5) vs. 178 (1) Å).

The nitrosyl group has normal temperature factors and is well resolved with no evidence for disorder. The Fe–N3 distance of 1.659 (5) Å, N3–O1 distance of 1.136 (2) Å, and Fe–N3–O1 angle of 174.9 (5)° are not greatly different from those observed for $FeNO(S_2CNMe_2)_2$: 1.720 (5) Å, 1.102 (7) Å, and 170.4 (6)°, respectively.[9] The Fe–S distances are also similar to those of low-spin $FeNO(S_2CNMe_2)_2$. In contrast the distances Fe–S1 = 2.299 (2) Å, Fe–S2 = 2.321 (2) Å,

**Table V.** Least-Squares Planes for *cis*-$Fe(NO)(NO_2)(S_2CNEt_2)_2$

Equation in the Form $Ax + By + Cz - D = 0$ by Hamilton's Method[a]

| Plane | A | B | C | D | Atoms defining the plane |
|---|---|---|---|---|---|
| 1 | 9.317 | −4.699 | 1.493 | 0.0879 | Fe, S1, S2, C1 |
| 2 | 3.721 | 14.987 | −2.032 | 7.632 | Fe, S3, S4, C2 |
| 3 | 8.321 | −6.086 | 3.26 | −0.0182 | S1, S2, S3, N4 |
| 4 | 6.014 | −4.128 | 7.268 | 1.138 | Fe, N4, O2, O3 |
| 5 | 2.619 | 5.636 | −1.020 | 7.745 | S1, S3, S4, N3 |

Deviations from the Planes, Å

| Plane | Fe | S1 | S2 | S3 | S4 | N3 | N4 | O2 | O3 | C1 | C2 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.001 | −0.005 | −0.004 | | | | | | | 0.061 | |
| 2 | −0.001 | | | 0.006 | 0.007 | | | | | | −0.092 |
| 3 | | 0.033 | −0.028 | 0.025 | | | −0.430 | | | | |
| 4 | 0.000 | | | | | | 0.017 | −0.009 | −0.012 | | |
| 5 | | −0.034 | | −0.049 | 0.045 | 0.410 | | | | | |

Dihedral Angles between the Planes

| Planes | Angles, deg | Planes | Angles, deg |
|---|---|---|---|
| 3–4 | 23.4 | 5–(N3, Fe, N4) | 92.4 |
| 3–5 | 89.3 | (Fe, S1, S2)–(Fe, S3, S4) | 90.9 |
| 3–(N3, Fe, N4) | 93.2 | (Fe, N3, N4)–(N4, O2, O3) | 69.9 |

[a] Reference 26.

**Table VI.** IR Data for $FeNO(S_2CNR_2)_2$ Complexes[a]

| Compd | $\nu_{NO}$(KBr) | $\nu_{NO}(CHCl_3)$ |
|---|---|---|
| $FeNO(S_2CNMe_2)_2$ | 1691 | 1724 |
| $FeNO(S_2CNEt_2)_2$ | 1690 | 1721 |
| $FeNO(S_2CN(Me)(Ph))_2$ | 1714 | 1726 |
| $FeNO(S_2CNPh_2)_2$ | 1707 | 1728 |

[a] All frequencies are measured in cm$^{-1}$ using the polystyrene band at 1601 cm$^{-1}$ as a standard.

Fe–S3 = 2.306 (2) Å, and Fe–S4 = 2.308 (2) Å are distinctly different from those of high-spin $Fe(S_2CNEt_2)_2$,[27] where the corresponding distances are Fe–S1 = 2.453 (2) Å, Fe–S2 = 2.402 (2) Å, Fe–S3 = 2.408 (2) Å, and Fe–S4 = 2.437(2) Å. The smaller Fe–S distances in the low-spin complexes can be directly attributed to the smaller covalent radii of iron atoms in low-spin states. The absence of substantial lengthening of the Fe–S4 bond trans to the NO group is consistent with the lack of strong structural trans effects in metal nitrosyls with linear MNO groups.[28] The Fe–S2 bond distance is ~0.015 Å (~7$\sigma$) longer than the other three Fe–S bonds and may reflect a structural trans effect of the $NO_2$ group. The Fe–$NO_2$ distance of 2.008 (6) Å is comparable to that reported for Co–$NO_2$ of 1.954 (7) Å in *trans*-dinitro(1,10-diamino-4,7-diazadecane)cobalt(III) bromide.[29] The N–O distances N4–O3 and N4–O2 of 1.222 (8) and 1.178 (6) Å are similar to the mean N–O distance of 1.223 (7) Å reported for the cobalt complex.

**$FeNO(S_2CNR_2)_2$ Complexes.** Several five-coordinate $FeNO(S_2CNR_2)_2$ complexes have been prepared and characterized. They were prepared either from the reaction of $FeNO^{2+}$ with $R_2NCS_2^-$ or from the reaction of $Fe(S_2CNR_2)_2$ with NO. These complexes are extremely air sensitive in solution and must be recrystallized carefully to obtain analytically pure samples. Each complex had a single broad NO absorption band near 1725 cm$^{-1}$ in solution (Table VI). Both $FeNO(S_2CNMe_2)_2$ and $FeNO(S_2CNEt_2)_2$ have square-pyramidal geometry in the solid state.[7–9] The similarity of their EPR spectra indicates that they are isoelectronic with the unpaired electron occupying an $a_1$ ($d_{z^2}$) molecular orbital.[11–13]

The reactions of $Fe(NO)(dtc)_2$ with oxidants discussed below suggested that they might add NO readily even though the previous reports of the formation of $Fe(NO)_2(S_2CNR_2)_2$ complexes were erroneous.[18] Wayland and Olson[30] have identified a closely related dinitrosyl complex $Fe(NO)_2TPP$ which was stable at 77 K under an NO atmosphere. Another dinitrosyl complex, $Fe(NO)_2(sacsac)_2$, has been reported by Broitman et al.,[31] but it has not been characterized further. Solutions of $FeNO(S_2CNMe_2)_2$ and excess NO were carefully examined by IR and EPR spectroscopy for the presence of $Fe(NO)_2(S_2CNMe_2)_2$, but no direct evidence for its formation was found. Even though a dinitrosyl intermediate was not observed, indirect evidence for its existence was obtained from a study of the reaction of $Fe(^{15}NO)(S_2CNMe_2)_2$ with $^{14}NO$. Complete exchange between $^{14}NO$ and $Fe(^{15}NO)(S_2CNMe_2)_2$ in $CHCl_3$ occurred in the time required to measure the IR spectrum of the solution (2 min). Previous studies of NO exchange with metal nitrosyl complexes[32–34] have found that the reactions are slow, as are those of the six-coordinate complexes $Fe(NO)X(S_2CNMe_2)_2$ discussed below. Thus, it is likely that the fast-exchange reaction observed between $^{14}NO$ and $Fe(^{15}NO)(S_2CNMe_2)_2$ proceeds through formation of $Fe(NO)_2(S_2CNMe_2)_2$, but the experiments described above do not conclusively show this.

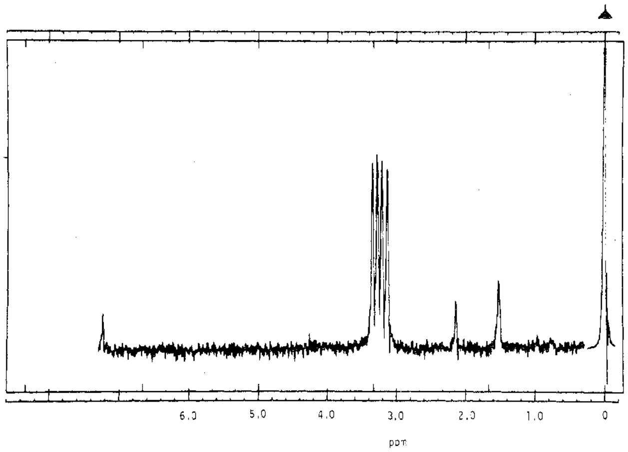

**Figure 2.** NMR spectrum of *cis*-$FeNO(S_2CNMe_2)_2Br$ in $CDCl_3$.

**$FeNO(S_2CNMe_2)_2X$ Complexes.** In solution at room temperature, $FeNO(S_2CNMe_2)_2$ is oxidized by $I_2$, $Br_2$, and $NO_2$ producing the six-coordinate complexes $FeNO(S_2CNMe_2)_2X$. The $^1H$ NMR spectra (Figure 2) of the halide complexes *cis*-$FeNO(S_2CNMe_2)_2X$ (X = Br, I) consist of four sharp evenly spaced peaks of equal intensity indicative of a cis complex without symmetry.

Three different synthetic routes were used to prepare *cis*-$FeNO(S_2CNMe_2)_2NO_2$ (reactions 1–3). This compound

$$FeNO(S_2CNMe_2)_2 + NO_2 \xrightarrow[25\,°C]{CHCl_3} cis\text{-}FeNO(S_2CNMe_2)_2NO_2 \quad (1)$$

$$trans\text{-}[FeNO(S_2CNMe_2)_2CH_3CN][BF_4] + NO_2^- \xrightarrow[25\,°C]{CHCl_3} cis\text{-}FeNO(S_2CNMe_2)_2NO_2 + BF_4^- \quad (2)$$

$$cis\text{-}FeNO(S_2CNMe_2)_2I + AgNO_2 \xrightarrow[25\,°C]{CH_3CN} cis\text{-}FeNO(S_2CNMe_2)_2NO_2 + AgI \quad (3)$$

has $\nu_{NO}$ 1835, $\nu_{NO_2}$ 1382, 1305, and $\delta_{NO_2}$ 812 $cm^{-1}$. However, when reaction 1 was carried out at −60 °C, the product of the reaction was *trans*-$FeNO(S_2CNMe_2)_2NO_2$. The IR spectrum of the trans isomer has $\nu_{NO}$ 1840, $\nu_{NO_2}$ 1386, 1275, and $\delta_{NO_2}$ 760 $cm^{-1}$. The only strong bands in the 1000–1100-$cm^{-1}$ region were due to the dithiocarbamate ligand, which indicates the absence of coordinated nitrito groups.[36,37] Thus in both cis and trans isomers the $NO_2$ ligand is attached to iron through the nitrogen atom. The trans complex is stable as a solid but rapidly isomerizes in solution at 25 °C forming the cis complex.

The $^1H$ NMR spectrum of *cis*-$FeNO(S_2CNMe_2)_2NO_2$ is both solvent and temperature dependent. In $CDCl_3$ at room temperature, *cis*-$FeNO(S_2CNMe_2)_2NO_2$ exhibited only three peaks at $\tau$ 6.67, 6.72, and 6.78 with an intensity ratio of 2:1:1, but at −40 °C the spectrum consisted of four peaks of equal intensity at $\tau$ 6.84, 6.77, 6.70, and 6.62 similar to those of the bromide and iodide complexes (vide supra.) Although the $^1H$ NMR spectrum of *cis*-$FeNO(S_2CNMe_2)_2NO_2$ was measured at only two temperatures, the data obtained show that the dithiocarbamate ligands of this chiral cis complex are participating in a dynamic process at room temperature. Numerous rearrangements of the dithiocarbamate ligands can be suggested, but several of the most obvious ones are not consistent with the experimental observations. Rotation of the $Me_2N$– group about the C–N bond would result in the coalescence of the NMR spectrum into two peaks of equal intensity corresponding to the averaged environment of the methyl groups on each of the two nonequivalent dithiocarbamate ligands, similar to the $^1H$ NMR spectrum observed for the closely related $Fe(S_2CNMe_2)_2(S_2C_2(CF_3)_2)$ complex.[38] Since there are four distinct pseudo-threefold axes in *cis*-$FeNO(S_2CNMe_2)_2NO_2$, there are eight different ways in which the environment of the methyl groups could be altered by twists about these axes.[39] However, a careful examination of the five trigonal twists which are possible shows that the resultant NMR spectra should consist of either four (1:1:1:1), two (1:1), or one methyl resonance. Since the $^1H$ NMR spectrum of the cis complex observed at room temperature consists of three methyl peaks with a 2:1:1 intensity ratio, it is not likely that any of the trigonal-twist mechanisms are responsible for the observed averaging of the methyl groups in the cis complex. Although it is conceivable that some combination of the processes mentioned above could possibly account for the observed NMR spectrum, a bond-rupture mechanism which produces a monodentate dithiocarbamate ligand seems more likely. The $NO_2$ group is known to have a strong trans labilizing effect in octahedral complexes.[40] It is not unreasonable that the Fe–S2 bond is so weakened that it ruptures in solution. This mechanism would account for the large solvent effect observed for the $^1H$ NMR spectrum of the cis complex and for the absence of temperature and solvent dependence in the NMR spectra of the cis iodide and bromide. However, further information is required before any of these mechanisms can be eliminated from consideration with certainty.

The highly reactive oxygen-sensitive $Fe(S_2CNMe_2)_2$ reacts readily with small molecules including NO, CO, and $NO^+$. The reaction of $Fe(S_2CNMe_2)_2$ with $NOBF_4$ in $CH_3CN$ produced the important intermediate *trans*-$[FeNO(S_2CNMe_2)_2(CH_3CN)][BF_4]$ (A) in good yield. The $^1H$ NMR spectrum (Figure 3) of the acetonitrile complex consists of two peaks at $\tau$ 6.73 ($(CH_3)_2N$–) and 8.03 ($CH_3CN$) in the ratio of 4:1 indicative of trans geometry. Its infrared spectrum (KBr) had prominent bands at 1830 ($\nu_{NO}$) and 2250 $cm^{-1}$ (coordinated $CH_3CN$). The fact that $\nu_{CN}$ is at a higher frequency than free acetonitrile was taken to indicate that the nitrile ligand is bound through the nitrogen atom.[35]

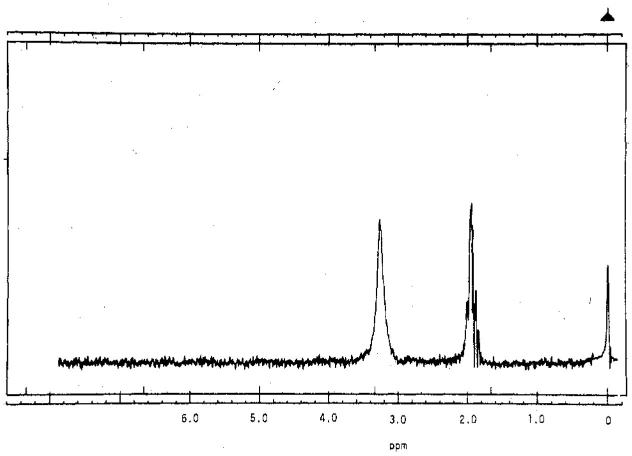

**Figure 3.** NMR spectrum of *trans*-$[FeNO(S_2CNMe_2)_2CH_3CN][BF_4]$ in $CD_3CN$.

Treatment of A with $I^-$ or $Br^-$ resulted in the displacement of coordinated acetonitrile and rearrangement of the dithiocarbamate ligands to give *cis*-$FeNO(S_2CNMe_2)_2X$. The $^1H$ NMR and the IR spectra of these complexes were identical with those of the complexes made by direct oxidation of $FeNO(S_2CNMe_2)_2$. Thus it is clear that the stereochemistries of $FeNO(S_2CNMe_2)_2Br$ and $FeNO(S_2CNMe_2)_2I$ are independent of their method of preparation.

To extend the scope of these investigations several other six-coordinate complexes were prepared and their stereochemistries determined. Treatment of A with $SCN^-$ produced *trans*-$FeNO(S_2CNMe_2)_2NCS$ ($\nu_{NO}$ 1835, $\nu_{SCN}$ 2090 $cm^{-1}$). Its $^1H$ NMR which consists of a single methyl peak at $\tau$ 6.73 establishes its geometry. The presence of bands at 835 and 440 $cm^{-1}$ indicates that the thiocyanate ligand is N bonded.[37,41,42] In view of the similarity between halogens and thiocyanates as ligands, the observation of trans geometry in the thiocyanate complex was surprising. To determine whether or not the trans complex is the thermodynamic product, the thiocyanate complex was also prepared by direct oxidation of $FeNO(S_2CNMe_2)_2$ with $(SCN)_2$. The product from this reaction had $^1H$ NMR and IR spectra identical with those of the trans complex made from A.

Treatment of A with $CH_3NC$ produced *cis*-$[FeNO(S_2CNMe_2)_2(CH_3NC)][BF_4]$. The IR spectrum of this complex had $\nu_{NO}$ at 1870 $cm^{-1}$ and $\nu_{NC}$ at 2070 $cm^{-1}$, and the NMR spectrum had peaks at $\tau$ 6.73 ($CH_3NC$), 6.67, 6.70, 6.72, and 6.75 ($(CH_3)_2N$–). This compound has the highest NO frequency in this series of FeNO–dtc complexes. A similar increase in $\nu_{CO}$ has been observed upon isocyanide ligation in iron carbonyls.[43]

Treatment of A with pyridine produced a green product with $\nu_{NO}$ at 1830 $cm^{-1}$ and two weak bands in the IR spectrum at 610 and 680 $cm^{-1}$ assignable to coordinated pyridine. The single peak at $\tau$ 6.70 in the $^1H$ NMR spectrum suggests that $[FeNO(S_2CNMe_2)_2py][BF_4]$ has trans geometry.

Attempts to isolate $FeNO(S_2CNMe_2)_2Cl$ were unsuccessful even though solutions of the complex were prepared by several

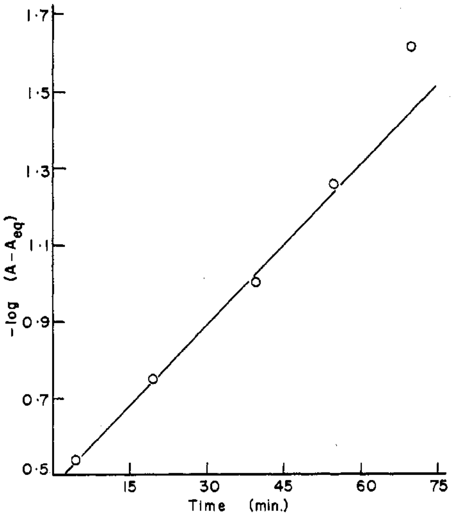

**Figure 4.** Plot of $-\log(A - A_{eq})$ vs. time for the exchange of $^{14}NO$ with *cis*-$Fe^{15}NO(S_2CNMe_2)_2I$.

independent methods: (a) direct oxidation of $FeNO(S_2CNMe_2)_2$ with $Cl_2$; (b) reaction of A with $Cl^-$; (c) reaction of $FeCl(S_2CNMe_2)_2$ with NO. In reaction (a) a mixture of $FeNO(S_2CNMe_2)_2Cl$ and $FeNO(S_2CNMe_2)_2$ was obtained which was impossible to separate. In reaction (b) the solution IR spectrum indicated the presence of $FeNO(S_2CNMe_2)_2Cl$, and the four peaks in the methyl region of the $^1H$ NMR spectrum indicated cis geometry for the complex. However, in solution, $FeNO(S_2CNMe_2)_2Cl$ rapidly decomposes to form $FeNO(S_2CNMe_2)_2$. Pathway (c) also produced an inseparable mixture of $FeNO(S_2CNMe_2)_2Cl$ and $FeNO(S_2CNMe_2)_2$. Although it is surprising that the chloride is more reactive than the bromide or iodide, a similar reaction has been observed for iron–porphyrin complexes.[44,45] It has been shown that the addition of methanol and nitric oxide to a solution of Fe(TPP)Cl results in reductive nitrosylation to form Fe(TPP)NO. In this reaction, methanol was assumed to be required for reaction with coordinated NO in the reduction step. However, $FeNO(S_2CNMe_2)_2Cl$ decomposes to give high yields (65–70%) of $FeNO(S_2CNMe_2)_2$ even in nonhydroxylic solvents such as $CHCl_3$ and benzene. Consequently, the key step in the reduction of $FeNO(S_2CNMe_2)_2Cl$ does not require the attack of a hydroxyl group on coordinated NO. However, since the fate of chlorine in this reaction was not discovered, the instability of $FeNO(S_2CNMe_2)_2Cl$ and the course of its decomposition reaction are not understood.

**Exchange of *cis*-$Fe^{15}NO(S_2CNMe_2)_2I$ with $^{14}NO$.** Because an associative mechanism was proposed for the exchange of NO with $FeNO(S_2CNMe_2)_2$, it was also important to study the possible exchange reactions of the six-coordinate complexes. The exchange reaction between $^{14}NO$ and *cis*-$Fe^{15}NO(S_2CNMe_2)_2I$ was found to be complete in 1.5 h in the dark. A plot of $-\log(A - A_{eq})$ vs. $t$ gave a straight line (Figure 4). A first-order rate constant of $1.22 \times 10^{-4}\ s^{-1}$ was obtained. When the reaction was carried out in laboratory light, the reaction was complete in 0.5 h with a first-order rate constant of $1.65 \times 10^{-4}\ s^{-1}$. The net reaction is

$$Fe^{15}NO(S_2CNMe_2)_2I + {}^{14}NO \rightleftharpoons Fe^{14}NO(S_2CNMe_2)_2I + {}^{15}NO \quad (4)$$

One possible pathway which accounts for reaction 4 is illustrated in Scheme I. Reactions 6 and 7 have been studied separately (vide supra), are fast, and are not light dependent. Thus the rate-determining step in Scheme I is reaction 5. The enhancement of reaction 4 by light is probably due to the photolysis of the Fe–I bond. Further evidence for the homolytic dissociation of Fe–X bonds in $FeNO(S_2CNR_2)_2X$ comes from the decomposition of solutions of these complexes

**Scheme I**

$$cis\text{-}Fe^{15}NO(S_2CNMe_2)_2I \rightleftharpoons Fe^{15}NO(S_2CNMe_2)_2 + I\cdot \quad \text{(slow)} \quad (5)$$

$$Fe^{15}NO(S_2CNMe_2)_2 + {}^{14}NO \rightleftharpoons Fe^{14}NO(S_2CNMe_2)_2 + {}^{15}NO \quad \text{(fast)} \quad (6)$$

$$Fe^{14}NO(S_2CNMe_2)_2 + I\cdot \rightleftharpoons cis\text{-}Fe^{14}NO(S_2CNMe_2)_2I \quad \text{(fast)} \quad (7)$$

in the presence of light to form $FeNO(S_2CNMe_2)_2$.

**Exchange between $Fe^{14}NO(S_2CNMe_2)_2$ and *cis*-$Fe^{15}NO(S_2CNMe_2)_2I$.** A solution of $Fe^{14}NO(S_2CNMe_2)_2$ in $CHCl_3$ was treated with a solution of *cis*-$Fe^{15}NO(S_2CNMe_2)_2I$ in $CHCl_3$. Even though the solution spectrum between 1650 and 1900 $cm^{-1}$ was obtained within 2 min, the four NO bands with equal intensities observed in solution at 1848, 1810, 1724, and 1698 $cm^{-1}$ indicated that an equilibrium mixture had already been established (reaction 8). This reaction is fast

$$Fe^{14}NO(S_2CNMe_2)_2 + cis\text{-}Fe^{15}NO(S_2CNMe_2)_2I \rightleftharpoons Fe^{15}NO(S_2CNMe_2)_2 + cis\text{-}Fe^{14}NO(S_2CNMe_2)_2I \quad (8)$$

compared to the exchange of $^{14}NO$ with *cis*-$Fe^{15}NO(S_2CNMe_2)_2I$ which requires 0.5 h for completion under comparable conditions.

**Exchange between $Fe^{15}NO(S_2CNMe_2)_2$ and *trans*-$[Fe^{14}NO(S_2NMe_2)_2CH_3CN][BF_4]$.** A solution of $Fe^{15}NO(S_2CNMe_2)_2$ in $CHCl_3$ was treated with a chloroform solution of *trans*-$[Fe^{14}NO(S_2CNMe_2)_2CH_3CN][BF_4]$ and the solution spectrum was obtained within 2 min. The four NO bands of equal intensity observed at 1852, 1822, 1724, and 1698 $cm^{-1}$ indicate the presence of equal amounts of *trans*-$[Fe^{14}NO(S_2CNMe_2)_2CH_3CN][BF_4]$, *trans*-$[Fe^{15}NO(S_2CNMe_2)_2CH_3CN][BF_4]$, $Fe^{14}NO(S_2CNMe_2)_2$, and $Fe^{15}NO(S_2CNMe_2)_2$, respectively (reaction 9). Since reactions 8 and 9 take place in the dark, they are not photoinduced free-radical reactions and may be outer-sphere electron-transfer reactions related to those of $\{RuNO\}^6$ complexes reported by Callahan et al.[46] (reaction 10).

$$trans\text{-}[Fe^{14}NO(S_2CNMe_2)_2CH_3CN][BF_4] + Fe^{15}NO(S_2CNMe_2)_2 \rightleftharpoons Fe^{14}NO(S_2CNMe_2)_2 + trans\text{-}[Fe^{15}NO(S_2CNMe_2)_2CH_3CN][BF_4] \quad (9)$$

$$Ru(bpy)_2{}^{14}NOCl^{+} + Ru(bpy)_2{}^{15}NOCl^{2+} \rightleftharpoons Ru(bpy)_2{}^{14}NOCl^{2+} + Ru(bpy)_2{}^{15}NOCl^{+} \quad (10)$$

Reaction 10 is fast ($k > 10^2\ M^{-1}\ s^{-1}$) and the electron transfer presumably takes place to and from a coordinated NO group. Even though reaction 10 has not been demonstrated previously for iron nitrosyls, facile electron-transfer reactions between $Fe^{2+}$ and $Fe^{3+}$ in tris(phenanthroline) complexes are known[47] (reaction 11).

$$Fe(phen)_3{}^{3+} + Fe(phen)_3{}^{2+} \rightleftharpoons Fe(phen)_3{}^{2+} + Fe(phen)_3{}^{3+} \quad (11)$$

## Conclusions

EPR and Mössbauer studies indicate that the unpaired electron in $FeNO(S_2CNMe_2)_2$ occupies an orbital which is mainly comprised of $d_{z^2}$(Fe) and $\sigma^*$(NO). Enemark and Feltham[5] have suggested a qualitative molecular orbital scheme for this complex. Some of the features of this MO diagram are (a) the FeNO group is essentially linear because the $3b_1$ and $3b_2$ orbitals are not occupied and (b) the highest occupied orbital is $5a_1$. The $5a_1$ orbital is somewhat antibonding with respect to both Fe–N and N–O. Oxidation of $FeNO(S_2CNEt_2)_2$ to *cis*-$Fe(NO)(NO_2)(S_2CNEt_2)_2$ results in an increase in $\nu_{NO}$ and in shortening of the Fe–N bond but in no important change in the Fe–N–O angle. These structural and spectroscopic changes are consistent with the removal of an unpaired electron from an antibonding orbital ($5a_1$).

Moreover, since the unpaired electron in $FeNO(S_2CNMe_2)_2$ presumably occupies a vacant coordination site of the square pyramid, direct oxidation by coordinating ligands would be expected to favor formation of trans six-coordinate complexes. The present studies have shown that although *cis*-$FeNO(S_2CNMe_2)_2NO_2$ is thermodynamically more stable than *trans*-$FeNO(S_2CNMe_2)_2NO_2$, the trans isomer is the one formed initially and consequently is the kinetic product of the oxidation of $FeNO(S_2CNMe_2)_2$ by $NO_2$. The fact that the trans isomer is the kinetically favored product is in agreement with the ground-state properties of $FeNO(S_2CNMe_2)_2$ and the MO diagram in Figure 12 of ref 5. These facts also suggest that the molecular and electronic structure of $FeNO(S_2CNMe_2)_2$ controls the stereochemistry of the kinetic products from each of these reactions although only the formation of the nitro complex has been studied in any detail.

On the other hand, the thermodynamically stable forms of the six-coordinate $\{FeNO\}^6$ complexes are determined by the sixth ligand attached to the iron atom. Trans geometry is favored by ligands such as $CH_3CN$ and N-bonded $NCS^-$ which are relatively weak $\sigma$ donors and relatively poor $\pi$ acceptors, while strong $\sigma$ donors and strong $\pi$ acceptors such as $NO_2$ and $CH_3NC$ favor cis geometry. However, the cis geometry of the $I^-$, $Br^-$, and $Cl^-$ complexes cannot be so easily explained in terms of their $\sigma$- and $\pi$-donor abilities. The halides are not particularly good $\sigma$ donors but are modestly good $\pi$ donors, properties which should favor trans geometry. Fenske and DeKock[48] have proposed that $\pi$-donating ligands such as halides can donate electron density into empty $\pi^*$ orbitals of cis ligands by direct overlap between the large $\pi$ orbitals of the halide and the $\pi^*$ orbitals more effectively than by indirect overlap via the metal into the $\pi^*$ orbitals of trans ligands. This suggestion nicely accounts both for the cis geometry of the halides and for their relative stability: $I > Br > Cl$.

The six-coordinate $\{FeNO\}^6$ complexes also have a remarkable tendency, especially in the presence of light, to be reduced in good yields to $FeNO(S_2CNMe_2)_2$ in a variety of organic solvents. In solution, these six-coordinate complexes have the following order of decreasing stability: $CH_3CN > CH_3NC > I > SCN > Br > NO_2 > Cl >> N_3$. This order roughly parallels two properties of these ligands: (a) the ease with which the ligand radicals X· can be formed (i.e., $CH_3CN^+$, I·, etc.) and (b) the reactivity of the X· radicals themselves. The facts that these complexes are photoreduced, are reduced by radical scavenging solvents, and have the order of stability listed above suggest that they decompose by a homolytic cleavage of the Fe–X bond (reaction 12). The

$$FeNO(S_2CNMe_2)_2X \rightleftharpoons FeNO(S_2CNMe_2)_2 + X\cdot \qquad (12)$$

position of equilibrium for reaction 12 should be dependent on the nature of X·. The more reactive X· is, the more easily it will be scavenged, thus shifting (12) toward $FeNO(S_2CNMe_2)_2$. On the other hand, ligands which do not readily form free radicals should be relatively stable to reduction as is found experimentally.

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**Registry No.** $FeNO(S_2CN(C_2H_5)_2)_2$, 14239-50-0; $FeNO(S_2CN(CH_3)_2)_2$, 14263-11-7; $FeNO(S_2CN(CH_3)(C_6H_5))_2$, 62637-78-9; $FeNO(S_2CN(C_6H_5)_2)_2$, 23792-49-6; *cis*-$FeNO(S_2CN(CH_3)_2)_2I$, 62637-83-6; *cis*-$FeNO(S_2CN(CH_3)_2)_2Br$, 62637-84-7; *cis*-$FeNO(S_2CN(CH_3)_2)_2NO_2$, 60876-36-0; *trans*-$FeNO(S_2CN(CH_3)_2)_2CH_3CN^+BF_4^-$, 62637-82-5; *cis*-$FeNO(S_2CN(CH_3)_2)_2CH_3NC^+BF_4^-$, 62637-74-5; *trans*-$FeNO(S_2CN(CH_3)_2)_2SCN$, 62637-75-6; *trans*-$FeNO(S_2CN(CH_3)_2)_2CH_3CN^+PF_6^-$, 62637-77-8; *trans*-$FeNO(S_2CN(CH_3)_2)_2NO_2$, 60895-59-2; $Fe(S_2CNMe_2)_2$, 15339-38-5; *trans*-$FeNO(S_2CNMe_2)_2C_5H_5N^+BF_4^-$, 62637-72-3; $Fe^{15}NO(S_2CNMe_2)_2$, 62637-70-1; *cis*-$Fe^{15}NO(S_2CNMe_2)_2I$, 62637-69-8; *cis*-$Fe(NO)(NO_2)(S_2CN(C_2H_5)_2)_2$, 36413-49-7.

**Supplementary Material Available:** A listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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