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Iron–Sulfur Complexes of Nitric Oxide and Carbon Monoxide

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Several new iron nitrosyl and carbonyl complexes stabilized with dithiocarbamate ligands have been prepared and characterized. These new complexes include *cis*-$Fe[S_2CN(C_2H_5)_2]_2(Br)(NO)$, *cis*-$Fe[S_2CN(C_2H_5)]_2(I)(NO)$, *cis*-$Fe[S_2CN(C_2H_5)_2]_2(CO)_2$, and the dimeric sulfur-bridged species $[Fe(S_2CN[C_2H_5]_2)(CO)_2SCH_3]_2$. In addition, the compound previously identified as a dinitrosyliron complex has now been shown to be a compound containing one nitrosyl group and one nitro group, *cis*-$Fe[S_2CN(C_2H_5)_2]_2(NO_2)(NO)$. The compounds were characterized by means of ir and nmr spectroscopy.

Introduction

Sulfur ligands are useful for preparing stable iron complexes of nitric oxide and carbon monoxide.[1–4] Moreover, polymeric iron sulfur complexes are an integral part of several enzymes[5–7] some of which are important in binding and modifying the reactivity of small molecules. Notable among these non-heme iron proteins are those associated with the enzyme nitrogenase.[8–10] While some iron–sulfur complexes of nitric oxide and carbon monoxide are known, there has been little systematic investigation of the preparation and properties of these compounds. The present investigations describe the synthesis of some new monomeric and dimeric iron–sulfur complexes of NO and CO.

Experimental Section

All of the solvents used were reagent grade and were dried, distilled, and stored under nitrogen before use. Several of the starting materials for these investigations including $[Fe(CO)_3SCH_3]_2$ (A), $Fe[S_2CN(C_2H_5)_2]_3$ (B), and $Fe(NO)[S_2CN(C_2H_5)_2]_2$ (C) were prepared using methods described in the literature.[11–13] The infrared spectra were obtained using a Perkin-Elmer Model 337 spectrometer. The nmr spectra were recorded on the Varian Model T-60 spectrometer. The molecular weight determinations were carried out in chloroform solutions using a Mechrolab Model 301a vapor pressure osmometer. The apparatus was calibrated before each set of measurements with benzil which had been recrystallized three times (mp 94.5–95.0°). The elemental analyses were obtained from Huffman Laboratories, Wheatridge, Colo., and from Chemalytics, Inc., Tempe, Ariz.

Di-μ-methanethiolato-bis(diethyldithiocarbamato)tetracarbonyldiiron(II).—It was found that A reacts with solutions of sodium diethyldithiocarbamate in alcohols under nonoxidizing conditions to liberate significant quantities of CO. However, the products from this reaction could not be isolated. A solution of 1.39 g (5.0 mmol) of A in 80 ml of degassed absolute methanol was prepared in a 250-ml round-bottom flask fitted with a gas inlet and 3.42 g (20.0 mmol) of anhydrous sodium diethyldithiocarbamate was added under a flow of nitrogen. After stirring for 90 min, the nitrogen inlet was replaced by a drying tube. The solution was stirred at intervals over a 2-day period. During this time, red-brown crystals had formed, which were finally removed by filtration, washed with several portions of methanol, and dried under vacuum. After recrystallization from $CHCl_3$–CH_3OH large, well-formed crystals were obtained. The complex decomposes rapidly in chloroform solution exposed to air but is stable as a crystalline solid. *Anal.* Calcd for $C_{16}H_{26}Fe_2N_2O_4S_6$: C, 31.7; H, 4.2; O, 10.4; N, 4.5; S, 31.1; Fe, 18.1; mol wt 618.5. Found: C, 31.2; H, 4.5; O, 10.8; N, 4.6; S, 30.8; Fe, 18.3; mol wt 611 (osmometrically in $CHCl_3$). The compound is diamagnetic.

It was subsequently found that this same compound could be prepared using iodine as the oxidant. Compound A (0.70 g, 2.5 mmol) and 1.20 g (5.3 mmol) of sodium diethyldithiocarbamate trihydrate were dissolved in 30 ml of anhydrous degassed methanol. After stirring the mixture for 3 hr under nitrogen, 0.32 g (2.5 mmol) of iodine was added under nitrogen, and the reaction mixture was stirred for 30 min. After standing for 4 days, the resultant red-brown crystals were removed by filtration, washed with several portions of methanol, and dried under vacuum. The yield was 0.417 g or 27% based on A. The infrared and nmr spectra were identical with those of the compound prepared by the method described above.

Bis(dimethyldithiocarbamato)dicarbonyliron(II).—A solution of 1.39 g (5.0 mmol) of A was dissolved in 80 ml of methanol at 50° under nitrogen. Next, 1.43 g (10.0 mmol) of anhydrous sodium dimethyldithiocarbamate was added and the solution was stirred for 2 hr at 50°. After cooling the solution, the reaction mixture was allowed to stand under nitrogen for 12 hr without stirring. Then an open drying tube replaced the nitrogen inlet as before, and the solution was stirred intermittently for 48 hr. At the end of this time, the orange-brown crystals which had formed were removed by filtration washed several times with methanol, and dried under vacuum. The yield was 1.28 g or 36% based on A. The compound was recrystallized from $CHCl_3$–CH_3OH. *Anal.* Calcd for $C_8H_{12}FeN_2O_2S_4$: C, 27.3; H, 3.4; O, 9.1; N, 8.0; S, 36.4; Fe, 15.9; mol wt 352.3. Found: C, 27.1; H, 3.5; O, 11.3; N, 7.3; S, 35.1; Fe, 16.2; mol wt 348. The compound is diamagnetic.

The same compound can be more readily prepared in higher yields and purity in the following way. To a solution of 1.79 g (10.0 mmol) of sodium dimethyldithiocarbamate trihydrate in 60 ml of carefully degassed acetone was added 1.80 g (6.5 mmol) of $FeSO_4 \cdot 7H_2O$. Carbon monoxide, which had been purified by passing it over BTS catalyst, NaOH pellets, and P_4O_{10}, was bubbled into the solution for 3.5 hr. The solvent was removed under vacuum, and the brown solid was then extracted with 15 ml of warm degassed $CHCl_3$ (30–35°). After filtering the chloroform solution under nitrogen, the solid was extracted with a further 2-ml portion of $CHCl_3$ and filtered, and the extracts were combined. A total of 85 ml of degassed methanol was then added slowly under nitrogen and the solution was stirred for 5 min. The brown needles which formed were collected by filtration, washed twice with methanol, and dried under vacuum over P_4O_{10} overnight; yield 1.44 g or 79% based on $FeSO_4 \cdot 7H_2O$. *Anal.* Calcd: C, 27.3; H, 3.4; N, 8.0; O, 9.1; S, 36.4; Fe, 15.9. Found: C, 27.2; H, 3.6; N, 7.7; O, 9.2; S, 36.2; Fe, 15.7.

Bis(diethyldithiocarbamato)dicarbonyliron(II).—To a solution of 6.79 g (30 mmol) of sodium diethyldithiocarbamate trihydrate saturated with carbon monoxide was added 4.50 g (16.2 mmol) of

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powdered $FeSO_4 \cdot 7H_2O$. The solution was stirred and CO was added over a period of 4 hr. The dark brown solution was filtered under nitrogen, and the solid residue was washed twice with acetone. The filtrates were combined and dried with anhydrous Na_2SO_4. The solution was filtered and the solvent was removed under vacuum. The product was purified by Soxhlet extraction under nitrogen with pentane; yield 5.72 g or 93% based on $FeSO_4 \cdot 7H_2O$. *Anal.* Calcd for $C_{12}H_{20}FeN_2O_2S_4$: C, 35.3; H, 4.9; N, 6.9; O, 7.8. Found: C, 35.3; H, 5.2; N, 6.9; O, 7.8.

Bis(diethyldithiocarbamato)(nitro)nitrosyliron.—The preparation of bis(diethyldithiocarbamato)dinitrosyliron has been previously reported from the reaction of compound C with nitric oxide. However, it was suspected from the properties of this material that it was in fact the nitro–nitrosyl derivative of iron. Following the literature prescription for the preparation of the dinitrosyl iron complex, 0.5 g (1.3 mmol) of C was suspended in 8 ml of ethanol which had been degassed and cooled to 0° in an ice bath, and NO (*unpurified*) was added directly from the gas cylinder. The NO addition was continued for 2 hr resulting in a brown precipitate. After removal of excess NO by passing nitrogen through the solution for 15 min, the solid was removed by filtration, washed several times with a little ethanol and ether, and then dried under vacuum; yield 0.384 g or 69% based on C. When the same reaction was attempted using NO which had been purified by passing it slowly through several traps at −77° to remove the NO_2 which is present in all NO cylinders, no observable reaction took place. In order to prove that NO_2 was the reactant from the NO cylinder, a solution of 1.1 mmol of NO_2 dissolved in 10 ml of nitromethane was added slowly to 0.382 g (1.0 mmol) of C suspended in 5 ml of nitromethane and the mixture was stirred for 20 min. The solvent was removed under vacuum, and the brown oil was digested with 4 ml of ethanol. This treatment resulted in the formation of a brown crystalline solid which was removed by filtration, washed four times with 1-ml portions of ethanol and then with ether, and dried over P_4O_{10} under vacuum; yield 0.22 g or 51% based on C. This material had properties identical with those prepared by use of impure NO. The analyses reported are for the compound prepared (1) from the reaction with impure NO and (2) from the reaction with NO_2. *Anal.* Calcd for $C_{10}H_{20}FeN_4O_3S_4$: C, 28.0; H, 4.7; N, 13.1; O, 11.2; S, 29.9; mol wt 428.4. Found (1): C, 28.5; H, 4.6; N, 13.0; O, 11.7; S, 29.9; mol wt 427 (osmometrically in $CHCl_3$). Found (2): C, 27.9; H, 4.5; O, 11.3; S, 29.2.

Bis(diethyldithiocarbamato)nitrosyliron.—This compound, prepared according to the literature methods, was found to be somewhat impure, and the following modification was found to give large amounts of very pure material. A solution of 5.56 g (20.0 mmol) of $FeSO_4 \cdot 7H_2O$ in 100 ml of carefully degassed water was cooled in an ice bath and saturated with NO purified as described above. Next, a solution of 9.01 g (40.0 mmol) of sodium diethyldithiocarbamate trihydrate in 25 ml of degassed water was added over a 10-min period, and the mixture stirred for another 20 min. The remaining NO was removed from the system by passing nitrogen through the solution until no further brown fumes were observed at the exit tube (about 10 min). The green powder was collected by filtration, washed several times with water and finally three times with methanol, and dried under vacuum; yield 6.65 g or 87% based on $FeSO_4 \cdot 7H_2O$. Recrystallization from $CHCl_3$–CH_3OH gave well-formed black-green crystals, which were further purified by Soxhlet extraction with pentane to remove any residual tris(diethyldithiocarbamato)iron(III) which was always present in these samples. *Anal.* Calcd for $C_{10}H_{20}FeN_3OS_4$: C, 31.4; H, 5.3; N, 11.0; S, 33.5. Found: C, 31.5; H, 5.1; N, 10.7; S, 33.2.

Bis(diethyldithiocarbamato)(iodo)nitrosyliron.—It was found that C would also react with other mild oxidizing agents to form derivatives analogous to those formed from the reaction with NO_2. Carefully purified C (0.382 g or 1.0 mmol) suspended in 4 ml of ethanol was treated with a solution of 0.14 g (1.1 mmol) of iodine in 3 ml of ethanol, which was added dropwise over a 15-min period. After stirring for another 60 min, the brown precipitate which had formed was removed by filtration, washed four times with 1-ml portions of ethanol, and dried under vacuum; yield 0.435 g or 85% based on C. An analytical sample was prepared by recrystallization from benzene–ether followed by drying over P_4O_{10} at 56° overnight. *Anal.* Calcd for $C_{10}H_{20}FeIN_3OS_4$: C, 23.6; H, 4.0; I, 24.9; N, 8.3; S, 25.2; mol wt 509.3. Found: C, 24.1; H, 4.0; I, 25.0; N, 7.9; S, 25.2; mol wt 495 (osmometrically in $CHCl_3$).

Bis(diethyldithiocarbamato)(bromo)nitrosyliron.—A total of 1.91 g (5.0 mmol) of C was suspended in 50 ml of CCl_4, and a solution of 5.03 mmol of bromine in 30 ml of CCl_4 was added dropwise over a period of 30 min. The brown crystals which had formed were removed by filtration, washed twice with CCl_4, and dried under vacuum; yield 2.29 g of impure black-brown crystals. An analytical sample was prepared by recrystallization from benzene–ether. *Anal.* Calcd for $C_{10}H_{20}BrFeN_3OS_4$: C, 26.0; H, 4.4; Br, 17.3; N, 9.1; O, 3.5; mol wt 462.3. Found: C, 26.1; H, 4.3; Br, 17.8; N, 9.1; O, 3.2; mol wt 451 (osmometrically in $CHCl_3$).

Attempted Preparation of Bis(diethyldithiocarbamato)(chloro)nitrosyliron.—A solution of C was treated with Cl_2 in chloroform, and $FeCl[S_2CN(C_2H_5)_2]_2$ was treated with NO. The materials from each of these reactions resulted in dark oils which could not be further purified. An ir spectrum of each of these materials showed the presence of NO absorption bands at 1840 and 1680 cm^{-1}. This evidence indicates that the title compound is formed but could not be separated from major impurities present in the product mixture.

Attempted Preparation of Dimeric Nitrosyl Compounds.—A solution of 1.71 g (10.0 mmol) of sodium diethyldithiocarbamate (dried and recrystallized) in 80 ml of methanol was added to 1.20 g (4.3 mmol) of A under nitrogen flow. The reaction mixture was stirred and refluxed for 140 min until gas evolution had ceased. After cooling the solution to room temperature, NO purified as described above was passed through the solution for a period of about 2 hr. The NO was removed by use of nitrogen, and the resultant black crystals were removed by filtration, washed with methanol, and dried under vacuum; yield 0.50 g. The compound was identified by elemental analyses, by molecular weight determination, and by its infrared spectrum as $Fe(NO)[S_2CN(C_2H_5)_2]_2$.

Results and Discussion

Iron Nitrosyl Complexes.—Although the nitrosyl derivatives of iron–sulfur complexes are among the earliest nitrosyls to be prepared, many of these compounds have still not been fully characterized. The composition and structure of the paramagnetic five-coordinate mononitrosyl complexes, $FeNOS_4$, have now been well established by several single-crystal X-ray studies.[14–17] These compounds all have a square-pyramidal structure with the four sulfur atoms occupying the basal plane, and the NO group in the axial position. While there is some controversy about the linearity of the Fe–N–O group, there is little doubt that the nitrosyl nitrogen is bonded to the iron.

Manchot[18] first reported that a related dinitrosyliron dithiocarbamate, $Fe[S_2CN(C_2H_5)_2]_2(NO)_2$, could also be prepared from the reaction of NO with $Fe[S_2CN(C_2H_5)_2]_2NO$. This compound was studied more recently by Carlin,[19] but it was found to be difficult to purify. The presence of a band in the ir spectrum at 814 cm^{-1} and the apparent presence of three oxygen atoms per iron (by difference) in Carlin's preparation suggested that this compound was in fact a nitro derivative of a mononitrosyliron complex. We found that when NO_2 is rigorously excluded from the NO supply, no reaction was observed to take place between NO and $Fe[S_2CN(C_2H_5)_2]_2NO$. The use of NO contaminated with NO_2 (~3%) or direct oxidation of $Fe[S_2CN(C_2H_5)_2]_2NO$ with pure NO_2 results in the formation of the compound previously described by Man-

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TABLE I

SOME INFRARED FREQUENCIES OF THE $FeNO^{3+}$ SPECIES (cm^{-1})

Compound	ν_{NO}	Other freq	Medium	Ref
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	1947	2174, 2162 (CN)	Single crystal	*a*
$[(n\text{-}C_3H_7)_4N]_2[Fe(CN)_5NO]$	1890	2170, 2145 (CN)	KBr	*b*
trans-$[FeBrNO(das)_2]^{2+}$	1850	. . .	KBr	*c*
trans-$[FeClNO(das)_2]^{2+}$	1840	. . .	KBr	*d*
cis-$[FeNO_2[S_2CN(C_2H_5)_2]_2NO]$	1820	1470, 1410, 814 (NO_2)	Nujol	*e*
cis-$[FeCl[S_2CN(C_2H_5)_2]_2NO]$	1840	. . .	Nujol	*e*
cis-$[FeBr[S_2CN(C_2H_5)_2]_2NO]$	1810	. . .	Nujol	*e*
cis-$[FeI[S_2CN(C_2H_5)_2]_2NO]$	1800	. . .	Nujol	*e*
$[Fe(C_2H_5OH)_5NO]^{3+}$	1775	. . .	Ethanol	*f*

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TABLE II

NMR CHEMICAL SHIFTS OF SOME DITHIOCARBAMATE COMPLEXES

Compound	δ, ppm	Solvent
anti-$[Fe(CO)_3SCH_3]_2$	1.54 (1),[a] 1.16 (1)	Benzene (int TMS)
syn-$[Fe(CO)_3SCH_3]_2$	1.48	Benzene (int TMS)
$[Co[S_2CN(CH_3)_2]_3]$	3.30	$CDCl_3$ (int TMS)
cis-$[Fe[S_2CN(CH_3)_2]_2(CO)_2]$	3.28 (1), 3.20 (1)	$CDCl_3$ (int TMS)
cis-$[Fe[S_2CN(C_2H_5)_2]_2(CO)_2]$	3.70 (2) quintet with approx intensity ratios of 1:4:6:4:1 due to $-CH_2-$ groups; 1.25, 1.18 (3) two overlapping triplets due to $-CH_3$ groups	$CDCl_3$ (int $CHCl_3$)
cis-$[FeNO_2[S_2CN(C_2H_5)_2]_2NO]$	3.50 (2) quintet with approx intensity ratios of 1:4:6:4:1 due to $-CH_2-$ groups; 1.15, 1.10 (3) two overlapping triplets due to $-CH_3$ groups	$CDCl_3$ (int $CHCl_3$)
cis-$[FeI[S_2CN(C_2H_5)_2]_2NO]$	3.63 (2) asymmetric eight-line pattern due to $-CH_2-$ groups; 1.24 (3) complex eight-line pattern due to $-CH_3$ groups	$CDCl_3$ (int TMS)
cis-$[FeBr[S_2CN(C_2H_5)_2]_2NO]$	3.70 (2) asymmetric eight-line pattern; 1.34, 1.26 (3) complex eight-line pattern due to $-CH_3$ groups	$CDCl_3$ (int TMS)
$[Fe[S_2CN(C_2H_5)_2](CO)_2(SCH_3)]_2$	3.65 asymmetric quintet; 1.68, 1.25 singlets due $-SCH_3$ groups; 1.40, 1.10 two overlapping triplets due to $-CH_3$ groups	$CDCl_3$ (int $CHCl_3$)

[a] The relative intensities are indicated in parentheses.

chot and Carlin. The identity of this compound was established by means of its ir spectrum, elemental analysis and melting point. Direct chemical analysis for oxygen in this complex established the presence of three oxygen atoms per atom of iron in the complex formed *via* the reaction

$$Fe[S_2CN(C_2H_5)_2]_2NO + NO_2 \longrightarrow Fe[S_2CN(C_2H_5)_2]_2(NO_2)(NO) \quad (1)$$

A careful examination of the infrared spectrum of this compound shows the presence of four absorption bands, which are not present in C. Three of these bands, found at 814, 1419, and 1470 cm^{-1}, are not present in the other derivatives of diethyldithiocarbamic acid here reported (Table I). These bands are characteristic of an NO_2 group which is coordinated to the metal *via* the nitrogen atom.[20] The compound is monomeric in chloroform, and consequently the presence of any other more complicated ligands can be ruled out.

In order further to establish the nature of this compound, C was treated with other oxidizing agents including chlorine, bromine, and iodine. The products from the reaction of C with these halogens had properties which are closely related to those of the nitro compound. Oxidation of $Fe[S_2CN(C_2H_5)_2]NO$ proceeds readily

$$2Fe[S_2CN(C_2H_5)_2]_2NO + X_2 \longrightarrow 2Fe[S_2CN(C_2H_5)_2]_2XNO \quad (2)$$

Of these compounds, only the chloride could not be isolated in a pure form. The bromide and iodide are diamagnetic and monomeric in chloroform. Except for the NO_2 frequencies listed above, the infrared spectra of the bromide, iodide, and nitro complexes are nearly identical.

The nmr spectra of these compounds were obtained in order to define the steric arrangement of the ligands in the coordination sphere (Table II). The nmr spectrum of $FeNO_2[S_2CN(C_2H_5)_2]_2NO$ consists of two sets of resonance absorptions: one due to the $-CH_2-$ groups and one to the $-CH_3$ groups in the expected intensity ratio of $^2/_3$. The multiplet in the $-CH_2-$ region consists of an apparent quintet with intensity ratios of approximately 1:4:6:4:1. This multiplet is what would be expected for two overlapping quartets arising from the coupling of two inequivalent $-CH_2-$ groups with the methyl protons. The $-CH_3-$ region near δ 1.1 is more complex but can be ascribed to two overlapping triplets. In order to simplify the spectrum of this compound, the $-CH_2-$ and $-CH_3$ groups were decoupled using the T-60 spin-decoupler. The resultant spectrum consisted of two peaks of approximately equal height in the $-CH_2-$ region with a separation of 6 Hz. The $-CH_3$ region was also reduced to two peaks of approximately equal intensity with a separation of 4 Hz. These results are almost identical with those obtained for *cis*-$[Fe[S_2CN(C_2H_5)_2](CO)_2]$ (*vide infra*). Thus the NO and NO_2 groups must be cis to one another, since

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(20) D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin Press, New York, N. Y., 1968.

there is only one type of ethyl group possible for the trans isomer.

The nmr spectra of the iodide and bromide compounds are somewhat more complex. The $-CH_2-$ region is very complicated, consisting of at least eight peaks of varying intensity. However, irradiation of the $-CH_3$ groups simplified the nmr spectrum near δ 4 to four singlets of equal intensity. This is the maximum number of lines expected for a cis complex of the type FeL_4XY. The $-CH_3$ region consists of at least seven bands, two of which are well separated from the others. Irradiation of the $-CH_2-$ protons produced a simplified $-CH_3$ spectrum consisting of a singlet with a relative intensity of 1 and three poorly resolved lines with a relative intensity of 3. The $-CH_2-$ coupling is 3.5 Hz for each of the $-CH_3$ groups. The bromide complex has an nmr spectrum almost indistinguishable from the iodide and consequently also has a cis configuration. Thus the nmr results show conclusively that all of these new nitrosyl complexes have a cis configuration.

These new diamagnetic six-coordinate complexes, FeL_4XNO, are closely related to $[FeNO(CN)_5]^{2-}$ and the diamagnetic complexes of *o*-phenylenebis(dimethylarsine), $[FeXNO(das)_2]^{2+}$. The infrared spectra of these complexes of the $FeNO^{3+}$ group are summarized in Table I.

Iron Carbonyl Complexes.—There have been two previous reports of dicarbonyl derivatives of iron(II) dithiocarbamates.[21,22] Bis(dimethyldithiocarbamato)-dicarbonyl iron(II) was initially prepared from the reaction between $Fe(CO)_4Br_2$ and sodium dimethyldithiocarbamate. While no assignment was made of the stereochemistry of their complex, two strong CO bands were observed in the infrared spectrum, indicating a cis arrangement of the carbonyl ligands. More recently, it has been reported[22] that Bernal has determined the structure of the bis(piperidyldithiocarbamato)dicarbonyliron(II) and shown the two carbonyl groups to have the expected cis configuration in that complex.

The bis(dithiocarbamato)iron(II) complexes were found to be very reactive toward CO, forming the *cis*-dicarbonyl derivative under very mild conditions in yields of 80–90%. These compounds are reasonably stable to air as solids but rapidly decompose in solution. The nmr spectrum of $Fe[S_2CN(CH_3)_2]_2(CO)_2$ consists of two closely spaced absorption bands of equal intensity at δ 3.28 and 3.20. This is the expected pattern for a cis complex, since there are two inequivalent groups of methyl protons. The infrared spectrum (Table III) of this complex has two absorption bands in the infrared spectrum typical of *cis*-dicarbonyl compounds.[20] The nmr spectrum of $Fe[S_2CN(C_2H_5)_2]_2(CO)_2$ is somewhat more complicated due to the nonequivalence of both the $-CH_2-$ and $-CH_3$ groups. The $-CH_2-$ region near δ 3.5 consists of a quintet with approximate relative intensities of 1:4:6:4:1 as would be expected for two overlapping quartets of the chemically nonequivalent $-CH_2-$ groups coupled to the methyl protons with a coupling constant equal to the chemical shift between the two $-CH_2-$ groups. The methyl protons were spin decoupled from the $-CH_2-$ protons, and the resultant spectrum consisted of two peaks of equal intensity in the $-CH_2-$ region with a separation of 4 Hz which is almost equal to the separation of the quintet observed in the normal nmr spectrum (3.5 Hz). Similar results were obtained for the methyl protons. The normal nmr spectrum consists of two overlapping triplets with a coupling constant of 4.5 Hz and a chemical shift between the two methyl groups of 2 Hz. This interpretation was confirmed by spin-decoupling experiments which gave a spectrum consisting of two methyl peaks with a separation of 2 Hz. The infrared spectrum of the ethyl derivative exhibited two strong absorption bands in the infrared spectrum typical of a *cis*-dicarbonyl compound. These spectra show unequivocally that the dicarbonyl compounds have cis stereochemistry. The interpretation of the nmr spectrum of $Fe[S_2CN(C_2H_5)_2]_2(CO)_2$ was important in determining the stereochemistry of the nitrosyl complexes (*vide supra*).

TABLE III

SOME INFRARED FREQUENCIES OF THE IRON(II) DITHIOCARBAMATE CARBONYL COMPLEXES (CM^{-1})

Compound	νCO	Ref
anti-$[Fe(CO)_3SCH_3]_2$	2085, 2050, 2000	*a*
syn-$[Fe(CO)_3SCH_3]_2$	2075, 2040, 2000, 1995	*a*
$[Fe[S_2CN(C_2H_5)_2](CO)_2SCH_3]_2$	2020, 1950 (Nujol)	*b*
cis-$[Fe[CN(C_2H_5)_2]_2(CO)_2]$	2010, 1945 (Nujol)	*b*
cis-$[Fe[CN(CH_3)_2]_2(CO)_2]$	2020, 1955 (Nujol)	*b*
	2090, 2040 (in CH_2Cl_2)	*c*

[a] R. B. King, *J. Amer. Chem. Soc.*, **84**, 2460 (1962). [b] This work. [c] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964).

Dimeric Iron–Sulfur Complexes.—A number of sulfur-bridged iron compounds are known[23–26] in which the iron atoms are bridged by mercaptide groups. There appear to be few general routes for the synthesis of such compounds. Since the Fe_2S_2 four-membered ring appeared to be rather stable, a possible route for the synthesis of additional dimeric species would be *via* ligand displacement reactions or oxidative addition reactions of the preformed dimeric system. The dimeric compound, $[Fe(CO)_3SCH_3]_2$, proved to be a convenient starting material for the attempted preparation of other sulfur-bridged dimeric iron complexes. Oxidative addition reactions using $[(CH_3)_2NCS_2]_2$ resulted only in the formation of $Fe[(CH_3)_2NCS_2]_3$. The same observation was noted recently by McCleverty, but he was able to isolate interesting tetramers when this type of reaction was carried out using dithietene as the oxidizing agent.[27]

The reactions of $[Fe(CO)_3SCH_3]_2$ with bidentate ligands *o*-phenylenebis(dimethylarsine), sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate, and sodium maleonitrile dithiolate slowly liberated approximately 25% of the expected CO, but in no case could any intermediates be isolated.[28] However, the addition of a mild oxidant such as iodine oxidizes these intermediates which are present in solution. When the attacking ligand is diethyldithiocarbamate,

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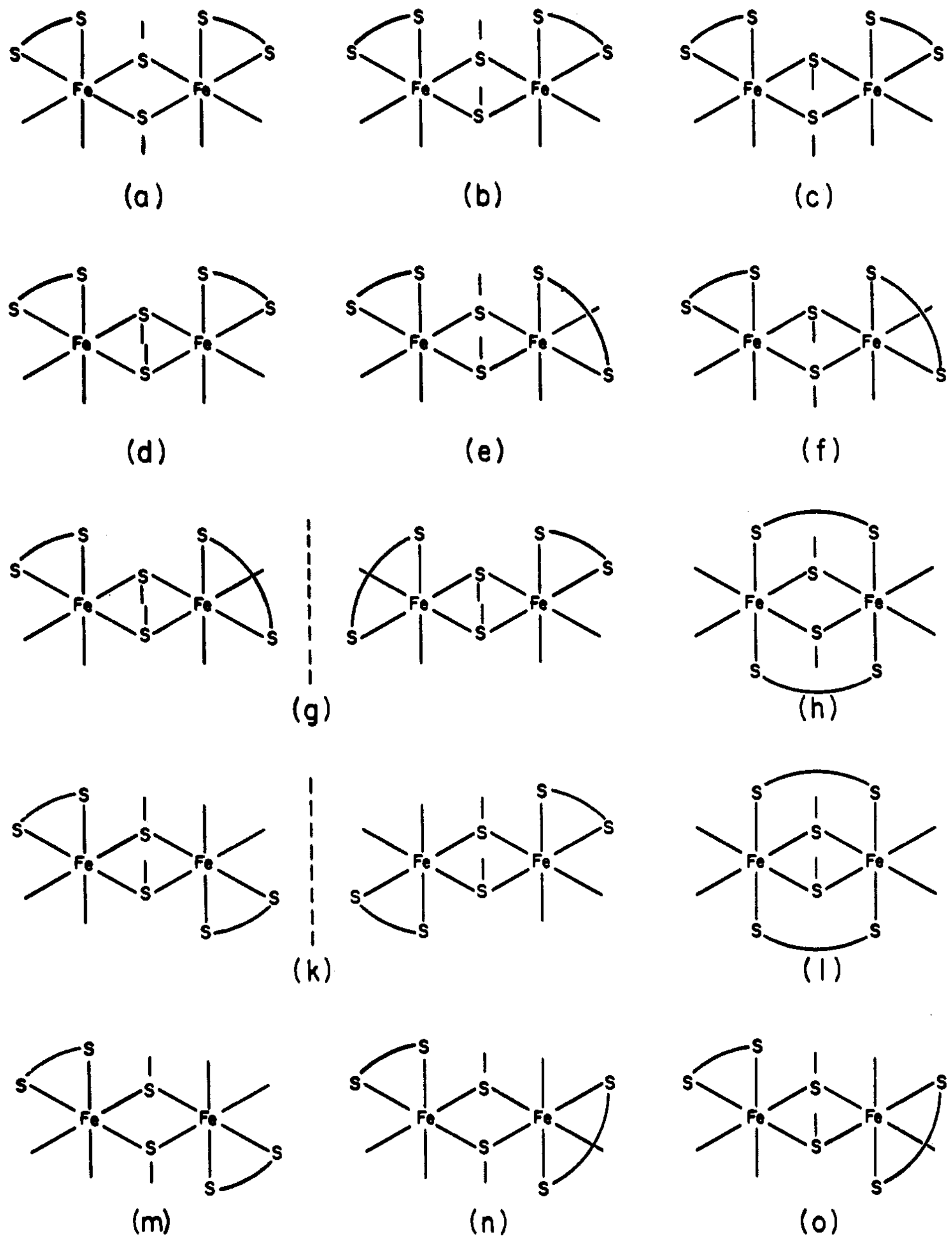

Figure 1.—Some of the possible isomers for $[Fe[S_2CN(C_2H_5)_2]_2(CO)_2SCH_3]_2$.

oxidation with either air or iodine produces the substituted and oxidized product $[Fe[S_2CN(C_2H_5)_2](CO)_2SCH_3]_2$. The diamagnetism, elemental analyses and molecular weight data allow this product to be assigned a dimeric structure. Although a large number of isomers are possible, the material isolated from this reaction appeared to consist entirely of a single isomer. This conclusion was based on the simplicity of the nmr and ir spectra and on the failure to separate this material by chromatography. The ir spectrum indicates that the CO groups are cis, and the nmr spectrum indicates that the $-SCH_3$ groups are still in the bridging positions (*vide infra*). Even eliminating all of the complexes with trans CO groups and those without $-SCH_3$ bridges, there are 15 possible isomers, including two optically active pairs. These isomers are shown diagramatically in Figure 1.

The infrared and nmr spectra of this compound are very similar to that of the monomeric *cis*-$[Fe[S_2CN(C_2H_5)_2]_2(CO)_2]$ except for the presence of bands due to the $-SCH_3$ group. The ir spectrum of this dimer has two CO bands at 1950 and 2020 cm^{-1} typical of *cis*-dicarbonyl compounds. The nmr spectrum of the dimer gave peaks in three distinct regions of the spectrum which were easily assignable to the $-CH_2-$ group (δ 3.65), the $-SCH_3$ group (δ 1.68), and the diethyldithiocarbamate $-CH_3$ groups (δ 1.1). The normal nmr spectrum consisted of a slightly asymmetric quintet in the $-CH_2-$ region centered at δ 3.65, which was very similar in appearance to the $-CH_2-$ region of *cis*-$[Fe[S_2CN(C_2H_5)_2]_2(CO)_2$. Irradiation at the $-CH_3$ frequencies produced a spectrum consisting of only two peaks in the $-CH_2-$ region with a separation identical with that observed for the original quintet of 8 Hz. The singlet at δ 1.68 can readily be assigned to the $-SCH_3$ group. However, the relative intensity of this peak is approximately half that expected from the ratio of $-SCH_3$ to $-S_2CN(C_2H_5)_2$ in the complex. The peaks centered at δ 1.1 were very complex in the normal nmr spectrum. However, irradiation of the $-CH_2-$ protons produced a somewhat simplified spectrum. In the $-CH_3$ region, the decoupled spectrum consisted of at least four singlets at δ 1.68, 1.40, 1.25, and 1.10. Comparison with the normal nmr spectrum showed that the two peaks at δ 1.40 and 1.10 were each the center of a triplet, while the peaks at δ 1.68 and 1.25 were unaffected by decoupling the $-CH_2-$ protons. These decoupling experiments allowed the two peaks at δ 1.40 and 1.10 to be unambiguously assigned to the $-S_2CN(C_2H_5)_2$ groups, and the peak at δ 1.25, to the remaining $-SCH_3$ group. The chemical shifts of the two $-SCH_3$ groups of this dimer at δ 1.68 and 1.25 also compare favorably to those found for *anti*-$[Fe(CO)_3SCH_3]_2$ at δ 1.54 and 1.16. Several of the isomers in Figure 1 can be eliminated from consideration by these results. Isomers e, f, h, l, and m can be eliminated since their $-SCH_3$ groups are equivalent. However, the nmr spectrum gives insufficient information to distinguish among the remaining 10 isomers.

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The Carbonyl Insertion Reaction of Iron Pentacarbonyl with Nonaromatic Nitro Compounds

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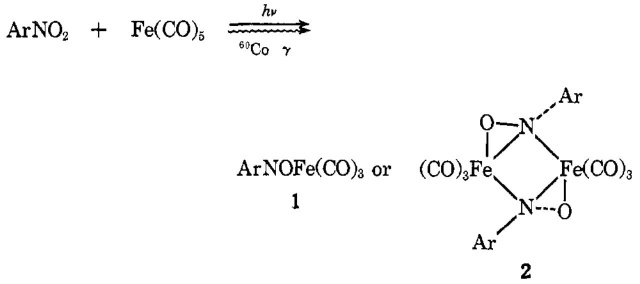
Aliphatic, cycloalkyl, and α,β-unsaturated nitro compounds were allowed to react with iron pentacarbonyl in dry diglyme. Carbonyl insertion products were obtained from nitroalkanes and nitrocycloalkanes, the product distribution being dependent on the size of the group attached to the nitro function. Treatment of 1-nitropropane and 2-methyl-2-nitropropane with diiron enneacarbonyl in benzene gave organoiron carbonyl complexes of the types $(RN)_2Fe_3(CO)_9$, $(RN)_2Fe_2(CO)_6$, $(RNH)_2Fe_2(CO)_6$, and $(RN)_2Fe_2(CO)_7$, identified by elemental and infrared and mass spectral analyses. The complexes were converted to formamide and/or ureas by heating in diglyme. A multistep reaction sequence involving these iron carbonyl complexes is proposed for the reductive carbonylation reaction. α,β-Unsaturated nitro compounds failed to react with iron pentacarbonyl in diglyme.

The reduction of aromatic nitro compounds by carbon monoxide and hydrogen in the presence of catalytic quantities of transition metal carbonyls has been investigated in considerable detail.[1,2] Amines, coupling, and carbonyl insertion products have been isolated from these reactions, the nature of the product(s) depending on the nitro compound, the type of catalyst, and the reaction conditions.

Few reports have appeared in the literature concerning the photochemical or thermal reactions of nitro compounds with metal carbonyls functioning as reagents. Irradiation of a mixture of iron pentacarbonyl and an aromatic nitro compound gives novel monomeric (1) or dimeric (2) nitrosobenzene complexes.[3] The crystal structure of one of the dimeric complexes, bis(tricarbonyl-2-methyl-3-chloronitrosobenzeneiron), has been determined by Barrow and Mills.[4] As part of a study of the utility of iron pentacarbonyl as a reagent for organic synthesis,[5] we have recently shown that the metal carbonyl is a useful reagent for thermally converting aromatic nitro compounds to azoxy or azo compounds, or amines, subject to reagent concentration and the nature of substitution on the benzene ring.[6] This paper describes the first results of the reactions of a number of aliphatic, cycloalkyl, and α,β-unsaturated nitro compounds with iron pentacarbonyl. The purpose of this investigation was to determine the products formed in these reactions and the pathways leading to their formation. A thorough understanding of the reaction mechanism may ultimately lead to a rationale for the catalytic reduction process, an important but not well-understood reaction.



Results and Discussion

Primary, secondary, tertiary, and α,β-unsaturated nitro compounds were allowed to react with iron pentacarbonyl in dry diglyme at 120–132° for 15–17 hr. The results are recorded in Table I. Saturated nitro compounds gave the carbonyl insertion products, formamides (3) and ureas (4), in modest yields. It is

$$RNO_2 + Fe(CO)_5 \xrightarrow[120-132^\circ]{\text{diglyme}} \underset{3}{RNHCHO} + \underset{4}{(RNH)_2CO}$$

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