Transition Metal–Dithiolene Complexes. III.[1] Nitrosyl Complexes of Iron and Cobalt

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Abstract: A series of five-coordinate mononitrosy-1,2-dithiolene complexes of iron and cobalt is described. The complexes, of empirical formula $[M(NO)(-S_4)]^z$, where $z = +1, 0, -1, -2$, or -3, are related by one-electron-transfer reactions which have been studied voltammetrically. Spectral and magnetic results, and a tentative description of the electronic structures of the complexes, are presented.

We have described previously[4,5] the synthesis and properties of *cis*-dinitrosylbisdicyano-1,2-dithiolene complexes of molybdenum and tungsten, $[M(NO)_2\text{-}S_4C_4(CN)_4]^{-2}$. We were able to show that in these six-coordinate complexes containing low-valent metal ions, the dicyano-1,2-dithiolene ligand functioned as a π acceptor of power apparently comparable to NO, and, as part of an extended study of the donor–acceptor behavior of these unsaturated sulfur ligands, we decided to investigate the possibility of forming five-coordinate species containing NO which would be similar to the known bisdithiocarbamates, $M(NO)(S_2CNR_2)_2$, where M = Fe or Co.[6] A preliminary report of our work has been presented.[7]

We have now established the existence of a series of five-coordinate mononitrosyl complexes formulated as $[M(NO)(-S_4)]^z$, where M = Fe and z may be $+1, 0, -1, -2$, or -3, and where M = Co and z may be $-1, -2$, or -3. The ligands include disubstituted *cis*-ethylene-1,2-dithiolates, $S_2C_2R_2$, tetrachlorobenzene-1,2-dithiolate, and toluene-3,4-dithiolate. The existence of the various complexes has been established by voltammetry, and many of them have been isolated by chemical methods. In this paper, we describe the synthetic work and some of the physical and chemical properties which characterize these novel nitrosyl complexes.

Experimental Section

Disodium *cis*-1,2-dicyanoethylene-1,2-dithiolate, $Na_2S_2C_2(CN)_2$, was synthesized by a published procedure,[8] as was the dithiophosphoric ester of stilbenedithiol,[9] and bisperfluoromethyldithietene.[10] Toluene-3,4-dithiol was purchased from Eastman Kodak, and nitric oxide was generated from sodium nitrite and sulfuric acid in a nitrogen stream, purification being effected by the normal methods;[11] in this section, use of NO generated in this way is referred to as "NO/N_2." Pure NO gas, in cylinders, was obtained from Cambrian Chemicals Ltd.

Conductivity measurements were determined using a Phillips conductivity meter in acetone solutions. Magnetic moments were measured at room temperature using the Gouy method, and nmr spectra were obtained using a Varian A-60 instrument. Esr spectra were obtained in solution at room temperture using a Varian V4500 X-band spectrometer with 100-kc field modulation. Electronic spectra were recorded on Unicam SP700 and Carey 14 spectrophotometers and infrared spectra were obtained using a Unicam SP100 instrument.

Polarographic measurements were made using a Heathkit Model EUW-401 polarographic instrument with a dropping mercury electrode, and voltammetric measurements were obtained with the same instrument using a platinum electrode rotating at 620 rpm. The results were checked against those obtained using a Sargent XV instrument and were found to agree within 10 mv. All measurements were standardized against a calomel cell. Dried and redistilled dichloromethane was employed as solvent and the supporting electrolyte was $[(C_2H_5)_4N]ClO_4$ or $[(n\text{-}C_3H_7)_4N]ClO_4$. All melting points are uncorrected.

$[(C_2H_5)_4N][Fe(NO)S_4C_4(CN)_4]$. $Na_2S_2C_2(CN)_2$ (3.72 g) in 50 ml of water was added to 2.70 g of $FeCl_3 \cdot 6H_2O$ in 50 ml of water. The resultant black precipitate of "$Na[FeS_4C_4(CN)_4]$" was washed thoroughly with water and extracted with 80 ml of acetone. From this solution salts of the anion, $[FeS_4C_4(CN)_4]_2^{-2}$,[12] with heavy organic countercations, could be easily obtained by addition of the appropriate tetraalkylammonium or tetraarylphosphonium salts. The dark red solution containing the sodium salt was filtered and degassed with N_2, and a steady stream of NO/N_2 was passed in until the color of the solution had become deep red-brown (about 30 min). Excess NO was purged from the solution with a stream of pure N_2, and 1.66 g of $[(C_2H_5)_4N]Cl$ in 25 ml of water was added. The solvent was then gradually removed using a water pump until crystallization was nearly complete. The compound was collected by filtration, twice recrystallized from acetone–water, washed with 2-propanol and ether, and air-dried. The yield of black crystals was 2.29 g (46% based on $FeCl_3 \cdot 6H_2O$), mp 200–202°. The complex is soluble in acetone, DMF, or dichloromethane, giving red-brown solutions.

The $(C_6H_5)_4P^+$ salt was prepared similarly and recrystallization was effected from acetone–water. The dark red crystals, mp 211–213°, retained acetone, as was evident from their infrared spectra, but this could be removed if recrystallization was effected from dichloromethane–2-propanol.

$[(C_2H_5)_4N]_2[Fe(NO)S_4C_4(CN)_4]$. **Method 1.** $[(C_2H_5)_4N]\text{-}[Fe(NO)S_4C_4(CN)_4]$ (0.50 g) in 30 ml of acetone was heated on a steam bath with 1.0 g of $Na_2SO_3 \cdot 7H_2O$ in 20 ml of water. After

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[1] Part II: A. Davison, J. A. McCleverty, E. T. Shawl, and E. J. Wharton, *J. Am. Chem. Soc.*, **89**, 830 (1967).

[2] To whom all correspondence regarding this paper should be addressed.

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[9] G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **4**, 1615 (1965).

[10] C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960).

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[12] It is assumed that most of the iron and cobalt "monoanions," $[M\text{-}S_4]^-$, are dimeric in the solid state and in some solutions, particularly in nonpolar or weak donor solvents. Evidence for this has been presented both in the solid[13,14] and in solution.[15,16]

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15 min, the solution had become pale green and was filtered. $[(C_2H_5)_4N]Cl$ (0.17 g) in 100 ml of water was added and, on standing, brown plate-like crystals precipitated. These were collected by filtration, recrystallized from acetone–water containing a small amount of $Na_2SO_3 \cdot 7H_2O$, washed with water, *t*-butyl alcohol, and ether, and air-dried. The yield was 0.39 g (62% based on $[(C_2H_5)_4N][Fe(NO)S_4C_4(CN)_4]$), mp 109–115°. The complex is soluble in acetone or dichloromethane, forming green-brown solutions, and is slowly reoxidized to the monoanion if these solutions are exposed to air for long periods.

Method 2. $[(C_2H_5)_4N]_2[FeS_4C_4(CN)_4]_2$[12] (1.0 g) in 25 ml of hot acetone was treated with 3.0 g of $NaNO_2$ in 30 ml of acetone. On refluxing on a steam bath for 15 min, the solution turned from dark red to green-brown, and 0.50 g of $Na_2SO_3 \cdot 7H_2O$ in 10 ml of water was added to complete the reduction of any $[Fe(NO)S_4C_4(CN)_4]^-$ which may have been present. After filtration and addition of 0.36 g of $[(C_2H_5)_4N]Cl$ in 50 ml of water, an oil separated. This oil solidified on standing and the solid was collected by filtration and recrystallized overnight from acetone–water (3:1 v/v). The brown crystals which were formed were twice recrystallized in the same way, always in the presence of sulfite ion. The yield was 0.52 g (39% based on $[(C_2H_5)_4N]_2[FeS_4C_4(CN)_4]_2$).

The $(C_6H_5)_4P^+$ and $C_5H_5NCH_3^+$ salts were prepared similarly.

$[(C_6H_5)_4P]_2[Co(NO)S_4C_4(CN)_4]$. **Method 1.** $[(C_6H_5)_4P]_2[CoS_4C_4(CN)_4]$ (1.25 g) in 10 ml of degassed DMF was treated with a slow stream of NO/N_2 for 30 min, during which time the solution turned from dark red to dark orange-red. Excess NO was purged from the solution in a stream of N_2, and water (*ca.* 30 ml) was added dropwise until the solution became cloudy. The solid which separated on standing was twice recrystallized from acetone–water, washed with ethanol, and air-dried. The yield of red-brown crystals was 1.01 g (79% based on $[(C_6H_5)_4P]_2[CoS_4C_4(CN)_4]$), mp 225–228°. The complex is soluble in acetone, chloroform, dichloromethane, or DMF giving orange-red solutions.

Method 2. $[(C_6H_5)_4P]_2[CoS_4C_4(CN)_4]_2$[12] (2.00 g) was suspended in 100 ml of hot acetone and treated with 3.0 g of $NaNO_2$ in 20 ml of water. The mixture was boiled on a steam bath for *ca.* 1 hr, during which time the solid gradually dissolved forming a dark orange-red solution. After filtration and addition of 2.50 g of $[(C_6H_5)_4P]Br$ in 30 ml of ethanol, water was added until the solution became cloudy. On standing, black crystals were formed, the yield of the complex being 1.66 g (54% based on $[(C_6H_5)_4P]_2[CoS_4C_4(CN)_4]_2$).

Method 3. $Na_2Co(NO_2)_6$ (1.00 g) and $Na_2S_2C_2(CN)_2$ (1.38 g) were suspended in 25 ml of ethanol and warmed on a steam bath for 20 min. The solution gradually became dark yellow-brown and was filtered. To the filtrate was added 3.0 g of $[(C_6H_5)_4P]Br$ in 40 ml of aqueous ethanol (1:1 v/v), and the brown precipitate which formed was collected by filtration and recrystallized four times from acetone–water. The yield was 0.36 g (14% based on $Na_3Co(NO_2)_6$).

$[C_5H_5NCH_3][Co(NO)S_4C_4(CN)_4]$. $[C_5H_5NCH_3]_2[CoS_4C_4(CN)_4]_2$[12] (*ca.* 1.5 g) was dissolved in 40 ml of hot acetone, cooled, degassed with N_2, and treated with a slow stream of NO/N_2 for 1 hr. The solution became dark green and 50 ml of water (degassed with N_2) was added dropwise while passage of NO/N_2 was maintained. The solution became dark brown and a black solid precipitated. Excess NO *above* the solution was removed in a stream of N_2 and the black solid was collected by filtration. It was washed with ethanol and ether and air-dried, yielding small black crystals of the mononitrosyl. The complex is soluble in acetone or DMF giving unstable green solutions. These solutions gradually lost their green color if NO was not maintained above and in the solution, and the solid itself smelled strongly of oxides of nitrogen within a few hours of isolation. Extensive decomposition of the complex had taken place within a week. Analytical and spectral measurements were made on the complex within 6 hr of preparation and isolation.

Other Cobalt Mononitrosyl Monoanions. These were prepared in solution in the same way as the complex described above. However, it was found advantageous to use pure NO gas instead of the NO/N_2 mixture. All attempts to isolate these monoanionic nitrosyls were unsuccessful.

$[N_2H_5][FeS_4C_4(C_6H_5)_4] \cdot N_2H_4$. $[FeS_4C_4(C_6H_5)_4]_2{}^0$ (3.00 g)[12,17] was heated for 1 hr in 50 ml of ethanol containing 10 ml of hydrazine hydrate (99–100%), during which time the solution became deep red. After filtration and standing overnight at 0°, black crystals had separated. These were collected by filtration, washed with ethanol, and recrystallized from a mixture of 75 ml of hot ethanol and 10 ml of hydrazine hydrate. After standing at 0° for several hours, the resulting black crystals were collected, washed with 45 ml of ethanol–hydrazine mixture (8:1 v/v) and ether, and air-dried. The yield of the large shiny black crystals was 1.03 g (31% based on $[FeS_4C_4(C_6H_5)_4]_2{}^0$), mp 292–300°. The crystals were stored *in vacuo* for 4 hr prior to analysis. The complex was soluble in hot ethanol containing hydrazine, affording red solutions, and was sparingly soluble in acetonitrile giving *unstable* green solutions. It is essential to exclude air rigorously from all solutions containing the complex since it is readily reoxidized to $[FeS_4C_4(C_6H_5)_4]_2{}^0$.

$[(C_2H_5)_4N]_2[FeS_4C_4(C_6H_5)_4]_2$.[12,18] To 1.0 g of $[N_2H_5][FeS_4C_4(C_6H_5)_4] \cdot N_2H_4$ in hot ethanol–hydrazine was added 1.16 g of $[(C_2H_5)_4N]Br$ in 45 ml of hot ethanol containing 5 ml of hydrazine hydrate. The mixture was heated for 5 min on a steam bath and then allowed to stand at 0° for 3 hr. The shiny black irregular crystals were collected, washed with ethanol and ether, and air-dried, affording 2.67 g of the complex, mp 200–203°. Like the hydrazinium complex, the compound is sparingly soluble in acetonitrile giving very unstable green solutions. Elemental analysis indicated that some hydrazine was retained in the complex despite repeated recrystallizations and washings.

$[(C_2H_5)_4N]_2[CoS_4C_4(C_6H_5)_4]_2$.[12,18] This complex was prepared in exactly the same way as its iron analog and also appeared to retain traces of hydrazine.

$[(C_2H_5)_4N][Fe(NO)S_4C_4(C_6H_5)_4]$. $[(C_2H_5)_4N]_2[FeS_4C_4(C_6H_5)_4]_2$ (2.00 g) was suspended in 30 ml of acetone, and the solution was thoroughly purged with N_2. NO/N_2 was then passed in while the mixture was stirred magnetically. The solution gradually turned orange-red and brown crystals were deposited. When no further color change was apparent, the excess NO was flushed from the solution by a stream of N_2 and the acetone was totally removed *in vacuo*. The residue was recrystallized three times from DMF–water, the crystals being washed with ethanol and ether and air-dried. The yield of pale brown crystals was 1.59 g (76% based on $[(C_2H_5)_4N]_2[FeS_4C_4(C_6H_5)_4]_2$), mp 116–117°. Deep orange-red solutions of the complex are formed in dichloromethane, acetone, and DMF.

The $C_5H_5NCH_3^+$ and $(CH_3)_4N^+$ salts were obtained in the same way. However, only the tetraethylammonium salt was stable as a solid, whereas the other salt decomposed gradually over several weeks.

$[Fe(NO)S_4C_4(C_6H_5)_4]^0$. **Method 1.** $[FeS_4C_4(C_6H_5)_4]_2{}^0$ (5.00 g) was suspended in thoroughly degassed chloroform and a slow stream of NO/N_2 was passed in for 3 hr. After this time had elapsed, excess NO was purged from the mixture and undissolved $[FeS_4C_4(C_6H_5)_4]_2{}^0$ was removed by filtration. Ethanol (30 ml) was added to the filtrate and, on partial removal of the solvent using a water pump, black crystals were obtained. The yield of black crystals was 2.11 g (40% based on $[FeS_4C_4(C_6H_5)_4]_2{}^0$), mp 135–140° dec. The complex dissolved in dichloromethane, chloroform, and acetone giving yellow-brown solutions.

Method 2. $[(C_2H_5)_4N][Fe(NO)S_4C_4(C_6H_5)_4]$ (0.70 g) dissolved in 10 ml of DMF was treated with 0.13 g of I_2 in 25 ml of acetone. The dark brown solution was filtered, 25 ml of ethanol added, and sufficient solvent removed using a water pump to encourage crystallization. The product obtained after standing for 1 hr was recrystallized twice from chloroform–ethanol yielding 0.42 g of black crystals (74% based on $[(C_2H_5)_4N][Fe(NO)S_4C_4(C_6H_5)_4]$).

The proton magnetic resonance spectrum of this complex in acetone consisted of a single line at τ 2.06, attributable to the phenyl protons.

$[(C_2H_5)_4N][Fe(NO)S_4C_4(CF_3)_4]$. **Method 1.** $[(C_2H_5)_4N]_2[FeS_4C_4(CF_3)_4]_2$[12] (0.75 g) in 50 ml of acetone was treated with a stream of NO/N_2 for 30 min during which time the color of the solution changed from green to yellow-brown. After filtration and removal of the acetone using a water pump, the residue was dissolved in 30 ml of ether and filtered, and 30 ml of petroleum ether (bp 40–60°) was added. Slow evaporation of the solvent afforded a black solid which was collected by filtration. Recrystallization of the complex was effected by the same procedure giving 0.55 g of black crystals (70% based on $[(C_2H_5)_4N]_2[FeS_4C_4(CF_3)_4]_2$), mp 150° dec.

Method 2. $[FeS_4C_4(CF_3)_4]_2{}^0$[19] (0.65 g) was dissolved in 150 ml of acetone thereby generating the green anion, $[FeS_4C_4(CF_3)_4]_2{}^{-2}$.[12]

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(17) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *J. Am. Chem. Soc.*, **88**, 4604 (1966).

(18) $[(C_6H_5)_4As]^+$ salts of these anions have been reported elsewhere.[17]

(19) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 3, 814 (1964); this complex was described in this paper as $[FeS_6C_6(CF_3)_6]^0$ but has since been reformulated as the dimeric complex.[16,17]

NO/N_2 was passed in for 2 hr by which time the solution had become yellow-brown. $[(C_2H_5)_4N]Br$ (1.0 g) in 50 ml of ethanol–acetone was added to the solution which was then evaporated to dryness. The residue was washed with warm water to remove excess $[(C_2H_5)_4N]Br$ and then dissolved in ether and recrystallized as in method 1. The complex is soluble in chloroform, dichloromethane, DMF, and acetone forming yellow-brown solutions.

The $(C_6H_5)_4P^+$ and $(C_6H_5)_4As^+$ salts were prepared in the same way.

$[(C_6H_5)_4As]_2[Fe(NO)S_4C_4(CF_3)_4]$. $Na_2SO_3 \cdot 7H_2O$ (2.0 g) in 30 ml of water was added to a degassed solution of 0.7 g of $[(C_6H_5)_4As][Fe(NO)S_4C_4(CF_3)_4]$ in 40 ml of acetone. The mixture was refluxed under nitrogen for 30 min, during which time the color of the solution changed from deep yellow-brown to pale yellow-green. Part of the product crystallized during the refluxing and was subsequently collected by filtration under nitrogen. The filtrate was treated with a solution of 1.0 g of $[(C_6H_5)_4As]Cl$ in 75 ml of ethanol–water (1:2 v/v), and the solution was reduced using a water pump until further crystallization ensued. The dark green-brown crystals were collected by filtration and recrystallized from a mixture of acetone and water containing a small amount of sulfite ion. The yield of the complex was 0.8 g (80% based on $[(C_6H_5)_4As][Fe(NO)S_4C_4(CF_3)_4]$), mp 168° dec. The complex is soluble in dichloromethane, acetone, and DMF giving deep yellow-green solutions which are sensitive to aerial oxidation.

$[(n\text{-}C_4H_9)_4N][Fe(NO)(S_2C_6H_3CH_3)_2]$. Method 1. $[(n\text{-}C_4H_9)_4N]_2[Fe(S_2C_6H_3CH_3)_2]_2$[12] (1.0 g) was gradually dissolved in 250 ml of refluxing acetone. After filtration, NO/N_2 was passed in for 30 min during which time the solution changed from deep purple to deep red in color. The acetone solution was then partially evaporated to about 20 ml using a water pump, and 25 ml of ether was added, the solution being reevaporated until crystallization began. The deep red crystals were collected by filtration and recrystallized twice from the same solvent mixture (1:1 v/v) in the same way. The yield of the complex was 0.73 g (69% based on $[(n\text{-}C_4H_9)_4N]_2[Fe(S_2C_6H_3CH_3)_2]_2$), mp 152° dec. The complex is soluble in acetone, chloroform, dichloromethane, and DMF giving deep red solutions.

Method 2. Treatment of $[(n\text{-}C_4H_9)_4N]_2[Fe(S_2C_6H_3CH_3)_2]_2$ in acetone with an aqueous acetone solution of $NaNO_2$ afforded red solutions of the mononitrosyl which was isolated as a red powder on gradual removal of the solvent *in vacuo*. Recrystallization was effected as in method 1.

The $(C_2H_5)_4N^+$ and $(C_6H_5)_4P^+$ salts were obtained similarly.

$[(C_6H_5)_4P]_2[Fe(NO)(S_2C_6H_3CH_3)_2]$. $[(C_6H_5)_4P][Fe(NO)(S_2C_6H_3CH_3)_2]$ (6.0 g) was dissolved in 100 ml of degassed THF to which was added 0.3 g of $NaBH_4$ in small portions (two drops of water were added to facilitate reduction). During the reduction, an atmosphere of N_2 was maintained above the solution which changed in color from deep red to yellow-green. After the reduction appeared to be complete, the solution was filtered quickly under N_2 into a degassed mixture of 150 ml of water and 75 ml of ethanol containing 7.5 g of $[(C_6H_5)_4P]Br$. A brown microcrystalline solid precipitated and was collected by filtration. More of the compound was obtained on partial removal of the filtrate, and both samples were dried *in vacuo*. The combined yield was 6.09 g (64% based on $[(C_6H_5)_4P][Fe(NO)(S_2C_6H_3CH_3)_2]$), mp 185° dec. The complex was only slightly soluble in chloroform and dichloromethane, but very soluble in DMSO, giving yellow-green solutions; solutions containing the dianion are very unstable toward air.

$[(n\text{-}C_4H_9)_4N]_2[Fe(S_2C_6Cl_4)_2]_2$.[12,29] Hexachlorobenzene (30 g), $Na_2S \cdot 9H_2O$ (48 g), iron powder (3 g), and DMF (700 ml) were stirred and refluxed continually for 15 hr, during which time the solution first became deep green and finally orange-brown. The mixture was filtered hot, and the filtrate was diluted with *ca.* 1100 ml of water containing 30 g of NaOH. After standing for 1 hr, a fine blue-black solid had precipitated and this was collected by filtration, washed with 100 ml of water, and air-dried. The yield of the solid, which may have been $[Fe(S_2C_6Cl_4)_2]_n^0$, was *ca.* 20 g.

A 20-g portion of the blue-black compound was dissolved in *ca.* 1100 ml of acetone–DMF (10:1 v/v) and warmed until the solution was deep orange-brown in color. After filtration and concentration to *ca.* 300 ml, the solution was treated with 15 g of $[(n\text{-}C_4H_9)_4N]I$ in 100 ml of ethanol. This mixture was then further concentrated to *ca.* 250 ml and treated with 100 ml of ether. On standing, black crystals were formed which were collected by filtration, washed with ether, and air-dried. The yield of black crystals was 9.5 g (21% based on Fe powder), mp 262°.

$[(n\text{-}C_4H_9)_4N][Fe(NO)(S_2C_6Cl_4)_2]$. NO/N_2 was passed into a solution containing 0.8 g of $[(n\text{-}C_4H_9)_4N]_2[Fe(S_2C_6Cl_4)_2]_2$[12] in 250 ml of acetone. After 15 min the color of the solution had changed from deep red-purple to red, and the solution was filtered and evaporated *in vacuo* to about 25 ml, ethanol (50 ml) containing 0.3 g of $[(n\text{-}C_4H_9)_4N]I$ was then added, and the volume was again reduced to about 20 ml *in vacuo* until crystallization began. Black crystals (0.4 g) were obtained (52% based on $[(n\text{-}C_4H_9)_4N]_2[Fe(S_2C_6Cl_4)_2]_2$), mp 262°. The complex is soluble in chloroform, dichloromethane, and acetone, giving red solutions.

$[(n\text{-}C_4H_9)_4N]_2[Fe(NO)(S_2C_6Cl_4)_2]$. $[(n\text{-}C_4H_9)_4N][Fe(NO)(S_2C_6Cl_4)_2]$ (0.85 g) dissolved in 15 ml of THF containing 5 ml of water was treated with 0.3 g of $NaBH_4$ in an atmosphere of N_2. After 10 min the color of the solution had changed from red to grass-green and a degassed solution of 1.2 g of $[(n\text{-}C_4H_9)_4N]I$ in 20 ml of ethanol–water (2:1 v/v) was added. The green microcrystalline precipitate was collected by filtration and washed thoroughly with water, ethanol, and ether. The complex was recrystallized from a mixture of 15 ml of THF, 15 ml of ethanol, and 5 ml of water containing *ca.* 1.0 g of $NaBH_4$ and *ca.* 0.2 g of $[(n\text{-}C_4H_9)_4N]I$. The solvent mixture was reduced slowly *in vacuo*, and 0.7 g of small green crystals was obtained (64% based on $[(n\text{-}C_4H_9)_4N][Fe(NO)(S_2C_6Cl_4)_2]$), mp 198°. The complex is soluble in THF, acetone, and dichloromethane giving deep yellow-green solutions which were slightly unstable to air. In the solid state, the complex reoxidized very slowly to the monoanion.

Infrared Spectra. The following spectral data (cm^{-1}) apply.

$[(C_2H_5)_4N][Fe(NO)S_4C_4(CN)_4]$ (CH_2Cl_2 solution): 3015 w, 3000 w, 2221 sh, 2210 s, 1716 m, 1487 m, 1478 sh, 1462 m, 1396 m, 1371 w, 1187 vw, 1173 w, 1157 m, 1114 w, 1036 w, 1002 m.

$[(C_6H_5)_4P][Fe(NO)S_4C_4(CN)_4]$ ($CHCl_3$ solution): 3054 sh, 3024 m, 3008 sh, 2305 vw, 2265 vw, 2207 s, 1592 w, 1489 m, 1462 w, 1448 s, 1442 s, 1368 w, 1343 w, 1318 w, 1246 w, 1197 w, 1158 m, 1113 s, 1038 w, 1003 m, 930 w, 887 vw, 860 w.

$[(C_2H_5)_4N]_2[Fe(NO)S_4C_4(CN)_4]$ (CH_2Cl_2 solution): 3065 w, 3012 w, 3000 w, 2953 vw, 2294 w, 2257 w, 2209 sh, 2197 s, 1484 s, 1462 sh, 1395 w, 1282 br, 1185 sh, 1173 m, 1148 s, 1113 m, 1054 w, 1036 w, 1001 m, 862 w.

$[(C_6H_5)_4P]_2[Co(NO)S_4C_4(CN)_4]$ ($CHCl_3$ solution): 3065 vw, 3010 br, 2290 vw, 2258 vw, 2211 sh, 2197 vs, 1488 s, 1445 s, 1441 s, 1341 w, 1318 w, 1148 s, 1112 vs, 1002 m, 862 w.

$[C_5H_5NCH_3][Co(NO)S_4C_4(CN)_4]$ (KBr disk): 3130 vw, 3088 w, 2306 vw, 2270 vw, 2220 sh, 2208 vs, 1587 w, 1490 s, 1450 w, 1419 w, 1387 w, 1310 w, 1289 m, 1222 vw, 1194 m, 1161 m, 1153 m, 1136 vw, 1112 w, 1055 br, 1004 m, 953 vw, 942 vw, 858 w, 803 vw, 762 s, 674 s.

$[N_2H_5][FeS_4C_4(C_6H_5)_4] \cdot N_2H_4$ (KBr disk): 1595 w, 1574 w, 1560 vw, 1532 m, 1491 m, 1477 m, 1444 m, 1400 m, 1283 vw, 1248 vw, 1180 vw, 1157 vw, 1107 s, 1083 sh, 1030 m, 1002 vw, 972 vw, 957 vw, 913 w, 860 w, 810 w, 769 m, 745 s, 700 s.

$[(C_2H_5)_4N]_2[FeS_4C_4(C_6H_5)_4]_2$ (KBr disk): 3060 w, 3010 w, 2985 w, 1640 vw, 1620 vw, 1595 s, 1574 w, 1533 w, 1480 s, 1457 w, 1443 m, 1393 s, 1250 vw, 1172 s, 1097 s, 1077 m, 1030 m, 1002 m, 908 w, 860 w, 785 vw, 763 s, 740 s, 698 s.

$[(C_2H_5)_4N][Fe(NO)S_4C_4(C_6H_5)_4]$ (CH_2Cl_2 solution): 3040 br, 1777 vs, 1595 m, 1575 w, 1485 w, 1460 s, 1438 m, 1397 w, 1370 vw, 1165 s, 1078 w, 1030 m, 1004 w, 917 vw, 858 s.

$[Fe(NO)S_4C_4(C_6H_5)_4]$ (CH_2Cl_2 solution): 3100 vw, 3035 vw, 1802 vs, 1575 w, 1493 w, 1448 w, 1390 vs, 1175 m, 1165 s, 1080 w, 1030 m, 1001 w, 970 vw, 917 vw, 895 m.

$[(C_2H_5)_4N][Fe(NO)S_4C_4(CF_3)_4]$ (KBr disk): 1580 m, 1544 w, 1517 w, 1483 s, 1476 sh, 1461 w, 1455 w, 1441 w, 1395 s, 1386 vw, 1371 w, 1236 vs, 1178 vs, 1139 vs, 1059 s, 1013 s, 1003 s, 895 w, 880 w, 845 w, 783 m, 729 w, 720 m, 692 m.

$[(C_6H_5)_4As]_2[Fe(NO)S_4C_4(CF_3)_4]$ (KBr disk): 1579 vw, 1536 s, 1485 m, 1439 s, 1402 vw, 1340 vw, 1312 vw, 1250 vs, 1190 w, 1122 vs, 1148 vs, 1082 s, 1023 w, 987 s, 896 s, 858 vw, 833 m, 746 vs, 715 s, 689 s. (CH_2Cl_2 solution): 1530 s, 1486 s, 1446 s, 1370 vw, 1339 vw, 1313 vw, 1255 vs, 1187 vw, 1154 s, 1117 s, 1083 s, 1025 vw, 997 s, 903 w, 833 w.

$[(n\text{-}C_4H_9)_4N][Fe(NO)(S_2C_6H_3CH_3)_2]$ (KBr disk): 3030 w, 2960 s, 2945 sh, 2880 s, 2410 vw, 1583 w, 1523 w, 1481 s, 1444 s, 1380 m, 1370 sh, 1362 sh, 1350 w, 1296 w, 1280 s, 1240 m, 1203 s, 1178 w, 1151 w, 1137 w, 1107 w, 1080 s, 1030 vw, 1000 vw, 936 vw, 880 s, 800 s, 740 w, 712 vw, 690 ms, 658 w. (CH_2Cl_2 solution): 3027 m, 2065 s, 2938 sh, 2875 w, 1795 vs, 1604 w, 1582 w, 1533 w, 1482 s, 1463 s, 1447 m, 1381 m, 1285 s, 1250 vw, 1150 vw, 1085 s, 1000 vw, 887 vw, 870 vw.

$[(C_6H_5)_4P]_2[Fe(NO)(S_2C_6H_3CH_3)_2]$ (KBr disk): 3052 w, 2918 w, 1587 m, 1574 sh, 1530 w, 1484 m, 1438 s, 1376 vw, 1338 w, 1319 w, 1276 s, 1262 w, 1244 w, 1204 w, 1192 w, 1176 m, 1132 w, 1108 vs, 1084 m, 1039 vw, 1029 w, 996 s, 863 m, 848 w, 807 m, 795 m, 755 s,

Table I. Analytical[a] and Conductometric Data for the Iron and Cobalt Nitrosyl 1,2-Dithiolene[a]

Complex	Calcd, %				Found, %				
	C	H	N	S	C	H	N	S	Λ[f]
$[Et_4N][Fe(NO)S_4C_4(CN)_4]$	38.7	4.1	16.9	25.8	38.9	4.2	16.9	25.8	176
$[Ph_4P][Fe(NO)S_4C_4(CN)_4]$[b]	54.5	2.8	9.9	18.2	54.6	3.0	9.7	16.5	150
$[Et_4N]_2[Fe(NO)S_4C_4(CN)_4]$	46.0	6.4	15.6	20.4	46.3	6.5	15.7	20.6	340
$[Ph_4P]_2[Co(NO)S_4C_4(CN)_4]$	64.2	3.9	6.7	12.2	64.3	4.2	6.6	12.0	349
$[pyMe][Co(NO)S_4C_4(CN)_4]$[c]	36.6	1.7	18.1	27.7	36.5	1.8	17.9	27.9	..[g]
$[Ph_4P][Fe(py)S_4C_4(CN)_4]$	58.9	2.3	9.3	...	59.0	3.5	10.2	...	143
$[N_2H_5][FeS_4C_4Ph_4]\cdot N_2H_4$	55.6	4.8	9.3	21.2	55.8	5.1	9.8	17.1	..[g]
$[Et_4N][FeS_4C_4Ph_4]_2$	64.5	6.0	2.1	19.1	64.2	6.2	2.9	19.0	..[g]
$[Et_4N][Fe(NO)S_4C_4Ph_4]$	61.7	5.8	4.0	18.3	62.0	5.8	4.3	18.1	158
$[Fe(NO)S_4C_4Ph_4]$	59.0	3.5	2.5	22.5	58.9	3.9	2.8	22.6	..[h]
$[Et_4N][Fe(NO)S_4C_4(CF_3)_4]$	28.7	3.0	4.2	19.2	28.9	3.2	4.1	19.4	129
$[Et_4N][Fe(py)S_4C_4(CF_3)_4]$	35.2	3.5	3.9	17.9	35.8	3.7	4.1	18.4	151
$[Ph_4As]_2[Fe(NO)S_4C_4(CF_3)_4]$	56.6	4.4	1.9	20.1	56.9	4.6	1.8	20.2	268[i]
$[Bu_4N][Fe(NO)(S_2C_6H_3CH_3)_2]$	56.6	7.6	4.4	20.1	56.9	7.7	4.8	20.2	147
$[Ph_4P][Fe(NO)(S_2C_6H_3CH_3)_2]$	62.2	4.4	1.9	...	61.9	4.3	2.2	...	177
$[Ph_4P]_2[Fe(NO)(S_2C_6H_3CH_3)_2]$	69.4	4.9	1.3	11.9	69.2	5.1	1.3	11.7	..[g]
$[Bu_4N][Fe(NO)(S_2C_6Cl_4)_2]$[d]	38.0	4.1	3.2	14.5	38.1	4.3	3.4	14.6	139
$[Bu_4N]_2[Fe(NO)(S_2C_6Cl_4)_2]$[e]	46.9	6.4	3.7	11.4	46.6	6.4	3.8	11.4	212[i]
$[Bu_4N]_2[Fe(S_2C_6Cl_4)_2]_2$	39.3	4.2	1.6	15.0	40.0	4.6	2.1	15.0	..[g]

[a] Carried out by the microanalytical laboratory of the department. [b] P: calcd 4.4; found 4.5%. [c] pyMe = N-methylpyridinium. [d] Cl: calcd 32.3; found 32.2%. [e] Cl: calcd 25.2; found 25.5%. [f] Conductivity measured in 10^{-4} *M* acetone solutions (in cm^2 ohm^{-1} mole^{-1}). Λ = 125–175 for 1:1 electrolyte, 225–350 for 2:1 electrolyte. [g] Not measured. [h] Nonconducting. [i] Solutions sensitive to serial oxidation.

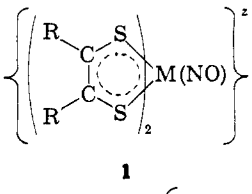
723 s, 693 s. (DMSO solution): 3068 w, 1719 w, 1690 w, 1448 w, 1395 w, 1334 w, 799 w, 756 s, 727 s.

$[(n\text{-}C_4H_9)_4N][Fe(NO)(S_2C_6Cl_4)_2]$ (KBr disk): 2962 m, 2935 m, 2870 m, 1537 m, 1483 s, 1460 m, 1453 w, 1371 s, 1326 s, 1287 w, 1257 s, 1157 s, 1142 s, 1100 s, 1082 m, 880 w, 841 w, 819 w, 742 w, 689 w.

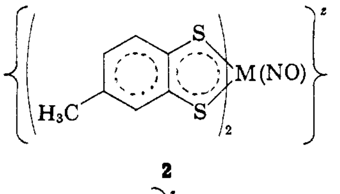
$[(n\text{-}C_4H_9)_4N]_2[Fe(NO)(S_2C_6Cl_4)_2]$ (KBr disk): 2962 s, 2936 m, 2870 m, 1624 vs, 1480 s, 1471 s, 1404 m, 1384 m, 1364 w, 1341 w, 1325 s, 1313 s, 1275 w, 1251 m, 1167 w, 1109 w, 1087 w, 1074 w, 1032 w, 927 w, 882 w, 866 w, 807 w, 788 w, 738 w, 679 s. (CH_2Cl_2 solution): 2968 s, 2936 m, 2877 s, 1819 vw, 1624 s, 1482 s, 1468 sh, 1383 w, 1369 w, 1527 s, 1317 s, 1251 w, 1153 w, 1109 w, 1089 w, 1073 w, 1029 w, 926 w, 882 w, 863 w.

Results and Discussion

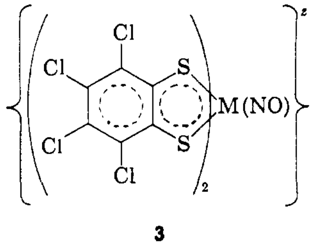
The complexes described in this paper are of types **1**, **2**, and **3**, where M = Fe and Co. In the iron complexes of type **1**, R may be CN, CF_3, or C_6H_5, and z may be +1, 0, −1, −2, or −3; in types **2** and **3**, z may be 0, −1, or −2. Cobalt complexes of types **1** and **2** have been detected where z = −1, −2, or −3. The wide variation in charge type z (from +1 to −3) is not experienced by all the complexes of type **1**, at least within the limits of our investigation, and some of the charge types of **1**, **2**, and **3** have not been isolated as crystalline solids. However, those complexes which have been isolated have been satisfactorily characterized by elemental analyses and conductivity measurements (Table I). The existence of the charge types which have not been isolated was established by voltammetric techniques, and some of the species so detected were generated electrochemically in solution.



1



2



3

Synthetic Studies. The most useful intermediates in the preparation of the mononitrosyls proved to be the monomeric monoanions, $[M(-S_4)]^-$, or the corresponding dimeric dianions, $[M(-S_4)]_2^{-2}$. The dimeric nature of some of the "monoanions" in solution and in the solid has recently been demonstrated,[12] but it is clear from magnetic studies[20] that some of the species which are dimeric in noncoordinating solvents are dissociated in polar solvents. Indeed, the interaction between the dimers and pyridine is so strong that the isolation of monomeric five-coordinate adducts, $[M(py)(-S_4)]^-$,[21,22] has been possible. Reaction of the monomers or dimers with NO in nonpolar or weakly coordinating solvents resulted in the formation of the five-coordinate monomeric mononitrosyls, $[M(NO)(-S_4)]^-$.

The monomeric nature of the neutral and dianionic iron complexes was established by direct molecular weight determinations of $[Fe(NO)S_4C_4Ph_4]^0$ (osmometrically) and by a single crystal X-ray structural analysis[23] of $[(C_2H_5)_4N]_2[Fe(NO)S_4C_4(CN)_4]$; the electronic and esr spectra clearly indicate that the dianions are similar electronically and structurally. The iron monoanions, and the one cobalt dianion to be isolated and characterized, were established as 1:1 and 2:1 electrolytes, respectively, by conductometric measurements and on the basis of voltammetric studies (see below); the cobalt monoanions are dicussed later in the text.

Monoanionic Species, $[M(NO)(-S_4)]^-$. The *iron* complexes were found to be stable to aerial oxidation and were not attacked by noncoordinating or weakly polar solvents. However, it was found that in DMF some of the complexes, particularly $[Fe(NO)S_4C_4$-

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(20) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 43 (1966).

(21) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *ibid.*, **86**, 2958, (1964).

(22) N. Connelly, J. Locke, J. A. McCleverty, and E. J. Wharton, to be published.

(23) R. Mason and A. I. M. Rae, private communication.

$(CN)_4]^-$, gradually lost NO and the isolation of the trisdithiolene, $[FeS_6C_6(CN)_6]^{-2}$,[24] was possible.

Nitric oxide was displaced from $[Fe(NO)S_4C_4(CN)_4]^-$ and $[Fe(NO)(S_2C_6Cl_4)_2]^-$ by treatment with pyridine, the five-coordinate adducts, $[Fe(py)(-S_4)]^-$, being formed. Small amounts of $[Fe(NO)S_4C_4(CN)_4]^{-2}$ were obtained when excess NO was passed into pyridine and acetone solutions containing the monoanion. The bis(perfluoromethyl) and toluenedithiolene nitrosyl complexes appeared to be stable to pyridine and, indeed, the latter nitrosyl could be generated by passing NO into solutions containing $[Fe(py)(S_2C_6H_3CH_3)_2]^-$.[20] If $[Fe(NO)S_4C_4(C_6H_5)_4]^-$ was refluxed in a mixture of pyridine and acetone for 24 hr, 20% yields of $[FeS_4C_4(C_6H_5)_4]_2^0$ could be obtained, and the same nitrosyl reacted with triphenylphosphine in refluxing acetone to give $[Fe(PPh_3)S_4C_4(C_6H_5)_4]^0$. There was no evidence for the reaction of triphenylphosphine with the other dithiolene nitrosyls, and we were unable to detect the existence of six-coordinate complexes of the type $[Fe(NO)(L)(-S_4)]^-$.

The *cobalt* monoanions, $[Co(NO)S_4]^-$, of types **1** and **2** were extremely unstable and seemed to exist in an equilibrium

$$[Co(-S_4)]^- + NO \rightleftharpoons [Co(NO)(-S_4)]^-$$

or

$$[Co(-S_4)]_2^{-2} + 2NO \rightleftharpoons 2[Co(NO)(-S_4)]^-$$

In the presence of excess NO, the nitrosyls exhibited a characteristic green color in noncoordinating or weak donor solvents. However, if NO was removed from the solutions, the complexes rapidly dissociated regenerating the nonnitrosylated species. The only complex which could be isolated was $[Co(NO)S_4C_4(CN)_4]^-$, the most satisfactory samples being obtained with the N-methylpyridinium cation, but even this salt gradually lost NO in the solid state over several days. Because of their instability, these complexes were not established unequivocally as monomeric 1:1 electrolytes but, in view of their over-all similarity to the iron species and their voltammetric behavior, it seems reasonable to represent them as five-coordinate monoanionic species.

Treatment of $[Co(NO)S_4C_4(CN)_4]^-$ with pyridine or triphenylphosphine resulted in the formation of the five-coordinate adducts, $[Co(L)S_4C_4(CN)_4]^-$; the bis(perfluoromethyl)dithiolene behaved similarly whereas the toluene- and diphenyldithiolene merely lost NO thereby regenerating the nonnitrosylated species.

Dianionic Species, $[M(NO)(-S_4)]^{-2}$. Prior to the beginning of our work in these nitrosyl systems, McDonald, Phillips, and Mower[25] reported the existence of $[Fe(NO)S_4C_4(CN)_4]^{-2}$ and $[Fe(NO)(S_2C_6H_4)_2]^{-2}$ which they detected by esr studies in solution. On attempting to repeat their work by using the stoichiometric amounts of Fe^{+2} salts, NO, and $Na_2S_2C_2(CN)_2$ or $Na_2S_2C_6H_3CH_3$, we found that the only nitrosyls formed were the diamagnetic monoanions, $[Fe(NO)(-S_4)]^-$. After some manipulation, however, we found that the dianions could be generated if excess sulfur ligand was present.[26] A more convenient synthesis of the dicyanodithiolene was devised whereby the monoanion was reduced by sulfite ion, and the bis(perfluoromethyl)dithiolene was prepared similarly. Borohydride reduction of $[Fe(NO)(S_2C_6H_3CH_3)_2]^-$ and $[Fe(NO)(S_2C_6Cl_4)_2]^-$ readily afforded the respective dianions. Although elemental analyses of the salts of the bis(perfluoromethyl)-, tetrachlorobenzene-, and toluenedithiolene nitrosyl dianions were satisfactory, the complexes were clearly magnetically impure and repeated attempts to purify them by careful recrystallization frequently made the situation worse (Table V). Sodium amalgam reduction of salts of $[Fe(NO)S_4C_4(C_6H_5)_4]^-$ afforded ill-defined solids which may have contained the expected dianion; attempts to prepare rigorously pure salts of this dianion were abandoned after considerable effort.

Only one *cobalt* dianion, $[Co(NO)S_4C_4(CN)_4]^{-2}$, was isolated and characterized. It could be obtained in several ways, *viz*, reaction of $Na_2S_2C_2(CN)_2$ with cobaltinitrite, treatment of $[CoS_4C_4(CN)_4]^{-2}$ with NO, or reaction of $[CoS_4C_4(CN)_4]_2^{-2}$ with nitrite ion. Attempts to prepare the analogous bis(perfluoromethyl)- and tolueneedithiolenes by reduction of the monoanions in the presence of NO, or by treatment of the dianions with NO, were unsuccessful. However, treatment of solutions containing $[CoS_4C_4(C_4H_5)_4]_2^0$ which had been reduced with borohydride ion (and presumably contained $[Co(-S_4)]^{-2}$ [18]) with NO afforded $[Co(NO)S_4C_4(C_6H_5)_4]^{-2}$ which could be isolated as impure tetraalkylammonium salts. The complex was readily decomposed by air.

Neutral Species, $[M(NO)S_4]^0$. $[Fe(NO)S_4C_4(C_6H_5)_4]^0$ was readily obtained by oxidation of the monoanion with iodine. An alternative synthesis[7] involved treatment of a suspension of $[FeS_4C_4(C_6H_5)_4]_2^0$ in chloroform with NO, but a purple complex was formed in addition to the brown monomeric mononitrosyl, and it was observed that, on standing in chloroform or dichloromethane, the brown monomer gradually changed into the purple material. We originally formulated the purple complex as $[Fe(NO)(S_2C_2(C_6H_5)_2)]_2^0$ [7] on the basis of elemental analyses and molecular weight determinations, and by analogy with $[Fe(NO)(S_2C_2(CF_3)_2)]_2^0$ prepared by King.[27] However, the latter complex was recently reformulated[28] as a mixture, one component of which was $[Fe_3(NO)_3(S_2C_2(CF_3)_2)_3]^0$, and a reinvestigation of our complex has lead to its reformulation[14,29] as $[Fe_2(NO)_2(S_2C_2(C_6H_5)_2)_3]^0$ which may be similar to a compound briefly mentioned by Schrauzer and his colleagues.[17]

Reaction of $[Fe(NO)S_4C_4(C_6H_5)_4]^0$ with excess triphenylphosphine afforded moderate yields of the known $[Fe(PPh_3)S_4C_4(C_6H_5)_4]^0$,[17] and treatment of this phosphine complex with excess NO in chloroform gave the purple species although there was some evidence for the transient existence of the neutral mononitrosyl.

Although there is voltammetric evidence (see below) for the existence of both $[Fe(NO)(S_2C_6H_3CH_3)_2]^0$ and $[Fe(NO)(S_2C_6Cl_4)_2]^0$, attempts to prepare the former by iodine oxidation were unsuccessful. However, we were able to obtain a green ether-soluble complex which obviously contained the sulfur ligand and NO, but details of this compound will not be re-

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(24) M. Gerloch, S. F. A. Kettle, J. Locke, and J. A. McCleverty, *Chem. Commun.*, 29 (1966).

(25) C. C. McDonald, W. D. Phillips, and H. F. Mower, *J. Am. Chem. Soc.*, **87**, 3319 (1965).

(26) The reducing ability of $[S_2C_2(CN)_2]^{-2}$ had already been observed in the reactions between the anion and π-$C_5H_5CoS_2C_2(CN)_2$ and $[NiS_4C_4(C_6H_5)_4]^0$ when $[CoS_4C_4(CN)_4]^{-2}$ and $[NiS_4C_4(C_6H_5)_4]^-$ were formed.

(27) R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

(28) R. B. King and F. T. Korenowski, *Chem. Commun.*, 771 (1966).

(29) J. Locke, J. A. McCleverty, E. J. Wharton, and C. J. Winscom, to be published.

ported in full until characterization is complete. We were unable to obtain neutral mononitrosyls of the iron dicyano-, bis(perfluoromethyl)-, and tetrachlorobenzenedithiolenes and of the cobalt dithiolenes.

Voltammetric Studies. The application of polarographic and voltammetric techniques to the study of dithiolene complexes is well established[20,30,31] and has proved singularly useful in the systematization of the synthetic chemistry of these complexes and of their stability toward oxidizing and reducing agents.

The results obtained from the nitrosyldithiolenes are given in Table II. Only those data obtained from voltammetry using a rotating platinum electrode in dichloromethane are quoted; earlier polarographic studies in DMF were useful in establishing the existence of one-electron redox reactions but were discontinued when it was found that some of the nitrosyls were decomposed by DMF. The majority of the waves were reversible and corresponded to one-electron processes. Most of the voltammetric work was carried out using monoanionic complexes. A comparison of the half-wave potentials obtained from these and the corresponding dianionic or neutral species (if they were available) revealed that the $E_{1/2}$ values for the reduction or oxidation reactions agreed to within 20 mv for any given metal–ligand system.

Table II. Voltammetric Data for Iron and Cobalt Nitrosyl 1,2-Dithiolenes[a]

	Complex	Couple	$E_{1/2}$[b]	Slope[c]	i_d/c[d]
1	$[Fe(NO)S_4C_4(CN)_4]^{-2}$ [e]	$-1 \rightarrow -2$	+0.03	62	−33[f]
		$-2 \rightarrow -3$	−1.34	72	33
2	$[Fe(NO)S_4C_4(CF_3)_4]^-$ [g]	$-1 \rightarrow -2$	−0.07	58	18
		$-2 \rightarrow -3$	−0.36	57	16
		$-1 \rightarrow 0$	+0.84	53	−17
3	$[Fe(NO)(S_2C_6Cl_4)_2]^-$ [h]	$-1 \rightarrow -2$	−0.24	64	21
		$-1 \rightarrow 0$	+0.74	58	−18
4	$[Fe(NO)(S_2C_6H_3CH_3)_2]^-$ [g]	$-1 \rightarrow -2$	−0.64	59	37[f]
		$-1 \rightarrow 0$	+0.27	56	−32
5	$[Fe(NO)S_4C_4(C_6H_5)_4]^-$ [g]	$-1 \rightarrow -2$	−0.83	58	20
		$-1 \rightarrow 0$	−0.02	66	−20
		$0 \rightarrow +1$	+0.71	56	−18
6	$[Co(NO)S_4C_4(CN)_4]^{-2}$ [e]	$-1 \rightarrow -2$	+0.16	86	−28[f]
		$-2 \rightarrow -3$	−1.32	69	31

[a] All results obtained in CH_2Cl_2 at 25°, 10^{-3} *M* in complex and 0.1 *M* in supporting electrolyte. Results quoted against a saturated calomel electrode containing 1 *M* aqueous LiCl solution. All results corrected for *iR* drop, and the estimated error in recording and reading voltammograms is $\leqslant 10$ mv. [b] In volts. Scan from +2.00 to −2.00 v. [c] Slope of plot of E_{obsd} *vs.* log $i(i_d - i)^{-1}$ for anodic waves, and of $-E_{obsd}$ *vs.* log $i(i_d - i)^{-1}$ for cathodic waves. For a reversible wave in either case, the slope is theoretically equal to $0.059/n$ v, where n is number of electrons involved in the electrolytic process. In this table, $n = 1$ and the slope for a reversible wave should be 59 mv. [d] In μa/mmole. [e] $(C_6H_5)_4P^+$ salt. [f] Diffusion current is proportional to the surface area of the Pt electrode in the solution. In 1, 4, and 6 the electrode was longer than in 2, 3, and 5. [g] $(C_2H_5)_4N^+$ salt. [h] $(n\text{-}C_4H_9)_4N^+$ salt.

For the iron complexes of types **1**, **2**, and **3**, the existence of neutral, monoanionic, and dianionic species was established chemically and confirmed voltammetrically. However, a second cathodic wave in the voltammograms of $[Fe(NO)S_4C_4(CN)_4]^-$ and $[Fe(NO)S_4C_4(CF_3)_4]^-$, and a cathodic wave in that of $[Co(NO)S_4C_4(CN)_4]^{-2}$ and the corresponding iron analog, was attributed to the formation of a trianionic species, $[M(NO)(-S_4)]^{-3}$. An anodic wave in the voltammogram of $[Fe(NO)S_4C_4(C_6H_5)_4]^0$ was observed and may be due to the generation of the monocation, $[Fe(NO)(-S_4)]^+$. However, neither the trianions nor the monocation have been isolated as yet.

Davison and Holm[32] have discussed certain empirical generalizations which can be made about the half-wave potentials obtained from dithiolene systems. Although their remarks are based on studies in acetonitrile *vs.* a standard calomel electrode, while our work was carried out in dichloromethane using an only slightly different cell, a voltammetric comparison of a standard dithiolene using their system and our system has revealed no serious differences in $E_{1/2}$ values.[33] Thus we have used Davison and Holm's empirical "rules" in understanding the chemical properties of the dithiolene nitrosyls.

It was suggested[32] that reduced species in couples less positive than *ca.* 0.0 v were readily oxidized by air, and this was certainly true for all of the iron dianions with the exception of $[Fe(NO)S_4C_4(CN)_4]^{-2}$ which appeared to be moderately stable to air in solution. Reduced species in couples within the range *ca.* 0.00 to *ca.* +0.40 v should be oxidized by iodine, and those in the range above *ca.* +0.40 v require more powerful one-electron oxidizing agents such as $[NiS_4C_4(CF_3)_4]^0$ [19] or $[FeS_4C_4(CF_3)_4]_2^0$.[16] Attempts to prepare $[Fe(NO)(S_2C_6H_3CH_3)_2]^0$ by iodine oxidation of the monoanion were unsuccessful as described previously, although some unidentified nitrosyl species was obtained. The oxidation of the bis(perfluoromethyl)- and tetrachlorobenzenedithiolene monoanions has not yet been attempted.

The use of *o*- or *p*-phenylenediamine for the reduction of oxidized species in couples within the range +0.20 to −0.12 v is recommended.[32] However, we found that amines occasionally caused the removal of NO from the monoanions, and therefore they were avoided whenever possible, but it was discovered that sulfite ion smoothly effected the reduction of the dicycano- and bis(perfluoromethyl)dithiolene monoanions to the dianions. Oxidized species in couples more negative than *ca.* −0.12 v were conveniently reduced by borohydride ion or sodium amalgam, but those species in couples more negative than *ca.* −1.00 v could not easily be prepared by conventional chemical methods. Thus the remaining dianions in the iron series were obtained, although the diphenyldithiolene was not isolated pure. From the voltammetric data, it should be possible to obtain $[Fe(NO)S_4C_4(CF_3)_4]^{-3}$ by borohydride reduction of the corresponding mono- or dianion, but we have not been successful as yet; the other trianions could be prepared by controlled-potential electrolysis.

The order of oxidative stability of the reduced species in the complex $[M(NO)(-S_4)]^0 + e^- \rightleftharpoons [M(NO)(-S_4)]^-$ and $[M(NO)(-S_4)]^- + e^- \rightleftharpoons [M(NO)(-S_4)]^{-2}$ is CN (highest $E_{1/2}$ value) > CF_3 > $S_2C_6Cl_4$ > $S_2C_6H_3CH_3$ >

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(30) (a) M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 4870 (1966); (b) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

(31) D. C. Olson, V. P. Mayweg, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **88**, 4876 (1966).

(32) A. Davison and R. H. Holm, *Inorg. Syn.*, in press; private communication.

(33) Usually, $E_{1/2}$ values obtained using a dropping mercury electrode are *ca.* 50 mv more positive than those obtained using a rotating Pt electrode; use of different solvents does not effect $E_{1/2}$ significantly within the accuracy of our measurements.

Table III. NO Stretching Frequencies of the Iron and Cobalt Nitrosyl 1,2-Dithiolenes

M	z	Ligand	Solid state[a]		Solution	
			$(C_2H_5)_4N^+$	$(C_6H_5)_4P^+$	$(C_6H_5)_4N^+$	$(C_6H_5)_4P^+$
Fe	−2	$S_2C_2(CN)_2$	1645	1633	1650[b]	1647[c]
		$S_2C_2(CF_3)_2$		1624[d]		1615[b]
		$S_2C_6Cl_4$	1624[g]		1624[g]	
		$S_2C_6H_3CH_3$		1620		~1600[e]
		$S_2C_2(C_6H_5)_2$	~1620			
Co	−2	$S_2C_2(CN)_2$		1617 (1589 sh)		1607 (1690 sh)
		$S_2C_2(C_6H_5)_2$	1600, 1630			
Fe	−1	$S_2C_2(CN)_2$	1867	1814	1840[f]	1857[b]
		$S_2C_2(CF_3)_2$	1829	1827	1832[c]	1820[c]
		$S_2C_6Cl_4$	1824[g]		1825[b,g]	
		$S_2C_6H_3CH_3$	1765[g]	1790[g]	1802[b]	1796[c]
		$S_2C_2(C_6H_5)_2$	1770		1777[b]	
Co	−1	$S_2C_2(CN)_2$	1672, 1700[h]		1730[h]	1724[c]
		$S_2C_2(CF_3)_2$			1712[c]	
		$S_2C_6H_3CH_3$			1655[c,g]	
		$S_2C_2(C_6H_5)_2$			1697[c]	
Fe	0	$S_2C_2(C_6H_5)_2$[i]			1802[b] 1805[c]	
Fe		$S_2CN(C_2H_5)_2$	1690		1714[b] 1720[c]	
Co		$S_2CN(C_2H_5)_2$	1624		1643[b] 1650[c]	

[a] KBr disk. [b] CH_2Cl_2. [c] $CHCl_3$. [d] $(C_6H_5)_4As^+$. [e] DMSO. [f] CH_3CN. [g] $(n\text{-}C_4H_9)_4N^+$. [h] $C_5H_5NCH_3^+$. [i] $\nu_{C=C} = 1390\ cm^{-1}$.

C_6H_5, very similar to the order observed by Olson and his co-workers[31] in planar and trigonal dithiolene complexes. The half-wave potentials for these reversible reactions can be correlated[31] with a ligand substituent effect. It may be predicted from these orders that the mono- and dianions of the $[Fe(NO)S_4C_4H_4]^z$ and $[Fe(NO)S_4C_4(CH_3)_4]$ systems will be less stable than the corresponding diphenyldithiolene species, in the order H > CH_3, and that it may be possible to isolate the cationic complexes, $[Fe(NO)(-S_4)]^+$, of either or both of these systems, without difficulty.

Infrared Spectral Studies. The NO stretching frequencies for the iron and cobalt complexes are given in Table III, and the other absorptions are recorded in the Experimental Section.

It can be seen that ν_{NO} depends on four factors: (1) on the over-all charge z, (2) on the nature of the ligand and particularly on the ligand substituents, (3) on the nature of the cation, and (4) on the medium in which the spectra were recorded.

The last two factors are the least important as far as this discussion is concerned. Cation effects have been observed by other workers,[34] and medium effects are common in metal nitrosyls and carbonyls.

The NO stretching frequencies fall within the range generally associated with metal-coordinated "NO^+."[5b] Those of the dianionic species occur between 1650 and 1620 cm^{-1}, those of the monoanions between 1870 and 1770 cm^{-1}, and $[Fe(NO)S_4C_4(C_6H_5)_4]^0$ at 1804 ± cm^{-1}. The M–N–O bond angle in nitrosyl bisdithiocarbamates of iron[35] and cobalt[36] (which are isoelectronic with the corresponding dithiolene dianions) vary between 135 and 170° and it has been suggested[37] that NO stretching frequencies within the approximate range 1700–1600 cm^{-1} are characteristic of such nonlinear M–N–O systems. It is therefore possible that the M–N–O bond angle in the dianionic dithiolenes is also bent.[23,38]

An increase in ν_{NO} as negative charge is removed from the $[M(NO)(-S_4)]^z$ coordination unit is to be expected, and the difference in ν_{NO} between the $z = -2$ and $z = -1$ species is *ca.* 170 cm^{-1} in the iron complexes and *ca* 120 cm^{-1} in the cobalt dicyanodithiolene complexes; the difference in ν_{NO} between the neutral and monoanionic diphenyldithiolene–iron complexes is only 25 cm^{-1}. The relative values of these differences is surprising and suggests to us that there is some significant difference in the electronic structure of the dianions on one hand and the monoanions and neutral species on the other.

A comparison of the NO stretching frequencies of the dianionic dithiolenes with the netural nitrosyl bisdithiocarbamates reveals that ν_{NO} in the charged complexes is somewhat lower than that in the neutral compounds. In our previous study[4,5a] of the spectra of the *cis*-dinitrosylbisdithiolene and -bisdithiocarbamate complexes of molybdenum and tungsten, we concluded, on the basis of the very small shift of ν_{NO} on addition of negative charge to the $[M(NO)_2(-S_4)]^z$ coordination unit, that the dithiolene ligand is a powerful π acceptor. In these new five-coordinate nitrosyls it is more difficult to establish this point, particularly in view of the unusual changes in ν_{NO} within each dithiolene nitrosyl series. However, the small shifts of ν_{NO} in the dianions, relative to the neutral dithiocarbamates, are not inconsistent with π-acceptor behavior of the sulfur ligand.

The type of ligand and the electronic nature of the substituent on the ligand ring system has a pronounced effect on ν_{NO} in both the mono- and dianionic series. As the relative acceptor ability of the dithiolene ligand decreases, so the extent of the back-donation to the NO

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(34) N. M. Sinitsyn and O. E. Zvyagintsev, *Dokl. Akad. Nauk SSSR*, **145**, 105 (1962).

(35) L. F. Dahl, private communication; P. G. Owston, private communication.

(36) P. R. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

(37) P. Gans, *Chem. Commun.*, 144 (1965).

(38) A single crystal X-ray study of $[(C_2H_5)_4N]_2[Fe(NO)S_4C_4(CN)_4]$ has confirmed that the Fe–N–O bond angle is bent.[23,38a]

(38a) NOTE ADDED IN PROOF. The Fe–N–O bond angle in this dithiolene nitrosyl appears to be 168° but cannot be determined with accuracy because of thermal motion of the O atom (A. I. M. Rae, private communication); a similiar situation occurs in $[Fe(NO)(S_2CNMe_2)_2]$ (P. G. Owston, private communication).

Table IV. Electronic Spectra of Iron and Cobalt Nitrosyl 1,2-Dithiolenes and Their Analogs

Complex	Solvent	Band maxima (intensity), cm^{-1}
$[Fe(NO)S_4C_4(C_6H_5)_4]^0$	CH_2Cl_2	12,000 (6000); 17,300 (2600 sh); 21,600 (4900 sh); 33,800 (23,000 sh)
$[Co(PPh_3)S_4C_4(C_6H_5)_4]^0$	CH_2Cl_2	11,700 (8860); 18,800 (4970); 22,400 (5490 sh); 32,800 (39,800)
$[Fe(NO)S_4C_4(CN)_4]^-$ [a]	CH_2Cl_2	7,100 (3300); 22,000 (3080 sh); 24,600 (3860 sh); 33,400 (31,300 sh); 35,200 (35,600)
$[Fe(NO)S_4C_4(CF_3)_4]^-$ [a]	CH_2Cl_2	7,500 (2380); 17,000 (4800 sh); 23,600 (2850 sh); 25,700 (3870); 33,800 (14,700)
$[Fe(NO)(S_2C_6Cl_4)_2]^-$	CH_2Cl_2	7,900 (6200); 19,700 (4500); 30,700 (31,800); 35,700 (46,600)
$[Fe(NO)(S_2C_6H_3CH_3)_2]^-$ [b]	CH_2Cl_2	7,500 (5590); 16,000 (1100 sh); 19,800 (4190); 31,950 (24,300); 38,200 (56,000)
$[Fe(NO)S_4C_4(C_6H_5)_4]^-$ [a]	CH_2Cl_2	6,500 (1500); 15,400 (910 sh); 21,600 (1700 sh); 26,000 (3300 sh); 32,200 (30,000)
$[Co(PPh_3)S_4C_4(CN)_4]^-$	Acetone	8,100 (1700); 14,580 (382); 20,120 (2470); 25,810 (8140)
$[Co(NO)S_4C_4(CN)_4]^-$ [c]	Acetone	7,300 (370); 11,950; 14,050; 21,500
$[Co(NO)S_4C_4(CF_3)_4]^-$	Acetone	7,400 (350); 12,700 (760 sh); 14,700 (2050); 19,800 (970 sh); 23,500 (2500)
$[Co(NO)(S_2C_6H_3CH_3)_2]^-$	Acetone	7,200 (380); 12,500 (1540 sh); 14,300 (2400 sh); 15,050 (3700); 28,400 (9200 sh)
$[Co(NO)S_4C_4(C_6H_5)_4]^-$	$CHCl_3$	8,200 (380); 14,300 (7900)
$[Fe(NO)S_4C_4(CN_4)]^{-2}$	CH_2Cl_2	14,600 (500); 23,700 (4400); 31,200 (17,800); 36,260 (27,000)
$[Fe(NO)S_4C_4(CF_3)_4]^{-2}$	CH_2Cl_2	14,700 (330); 19,100 (500 sh); 25,500 (2800); 34,900 (17,900 sh); 36,800(26,000)
$[Fe(NO)(S_2C_6Cl_4)_2]^{-2}$	CH_2Cl_2	14,500 (820); 24,600 (8700 sh); 30,600 (19,100 sh); 36,000 (22,400)
$[Fe(NO)(S_2C_6H_3CH_3)_2]^{-2}$	DMSO	14,400 (510), 20,200 (3400)
$Fe(NO)(S_2CN(C_2H_5)_2)_2$	$CHCl_3$	10,300 (20); 14,900 (540); 22,800 (2500 sh); 26,500 (8100); 30,600 (11,800)
$[Co(NO)S_4C_4(CN)_4]^{-2}$ [d]	Acetone	7,300 (67); 13,700 (400); 22,500 (4000)
$Co(NO)(S_2CN(C_2H_5)_2)_2$	$CHCl_3$	15,600 (380); 26,950 (11,800); 32,000 (17,000)
$[Fe(py)S_4C_4(CN)_4]^-$ [d]	Acetone	12,400 (114); 16,700 (1100 sh); 20,800 (4800); 22,600 (8300)
$[Co(py)S_4C_4(CN)_4]^-$ [b]	Acetone	9,090; 14,180; 22,100

[a] $(C_2H_6)_4N^+$ salt. [b] $(n\text{-}C_4H_9)_4N^+$ salt. [c] $C_5H_5NCH_3^+$ salt. [d] $(C_6H_5)_4P^+$ salt.

group increases, and ν_{NO} decreases. The order of increase of ν_{NO} is $CN > CF_3 > S_2C_6Cl_4 > S_2C_6H_3CH_3 > C_6H_5$, precisely the same as that observed for the $E_{1/2}$ values discussed previously. Similar electronic effects on the position of ν_{NO} have been observed in the spectra of the N,N′-bis(salicylidene)ethylenediaminecobalt mononitrosyl[39] and its ligand-substituted analogs.

An inconsistency in the order of ν_{NO} occurs in $[Co(NO)(S_2C_6H_3CH_3)_2]^-$, where the frequency is some 40 cm^{-1} lower than expected. The nonnitrosylated complex, $[Co(S_2C_6H_3CH_3)_2]^-$, is monomeric in all solvents unlike the other cobalt complexes of type **1**, and it is possible that the green nitrosyl is a true monomeric mononitrosyl whereas the other nitrosyls are dimers, $[Co(NO)(\text{-}S_4)]_2^{-2}$. However, this seems unlikely in view of the magnetic properties of these species in solution, the position of their NO stretching frequencies, and the voltammetric behavior of $[Co(NO)S_4C_4(CN)_4]^{-2}$. It is possible that the toluenedithiolene complex is high spin ($S = {}^3/_2$) whereas the others are low spin ($S = {}^1/_2$) and it might be expected that these differences in electronic structure would have some effect on ν_{NO}. However, the most plausible explanation in our view is that the nitrosyl toluenedithiolene, in solution, is a dianion $[Co(NO)(\text{-}S_4)]^{-2}$, thereby accounting for the lack of esr signals, the position of ν_{NO}, and the green color which would arise from a combination of the blue of the nonnitrosylated monoanion and the expected orange or yellow of $[Co(NO)(\text{-}S_4)]^{-2}$.

Electronic Spectral Studies. The positions and intensities of the major absorptions in the electronic spectra of the nitrosyl complexes, and some pyridine and triphenylphosphine analogs, are given in Table IV; no spectral assignments have been made.

Both the neutral diphenyldithioleneiron and monoanionic dithioleneiron complexes are characterized by the presence of intense absorptions in the visible and near-infrared regions, a feature strongly reminiscent of the oxidized nickel dithiolenes, $[NiS_4C_4R_4]^{0,-}$ [40] and the five-coordinate dithiolenephosphine complexes of iron and cobalt.[17] These intense bands are generally absent from the spectra of all of the cobalt nitrosyl complexes and from the iron dianions.

$[Fe(NO)S_4C_4(C_6H_5)_4]^0$ and $[Co(PPh_3)S_4C_4(C_6H_5)_4]^0$ are isoelectronic and spectral comparisons of the two reveal a probable similarity in electronic structure. Similar comparisons between the iron monoanions and $[Co(PPh_3)S_4C_4(CN)_4]^-$ and $[Co(Pyr)S_4C_4(CN)_4]^-$ do not disclose such a close resemblance in spectra although the electronic configurations may be similar. There is no likeness between the spectra of $[Fe(NO)S_4C_4(C_6H_5)_4]^0$ and $[Fe(py)S_4C_4(CN)_4]^-$ which is to be expected since the spin ground states of the two are different (the former has $S = {}^1/_2$ and the latter $S = {}^3/_2$).[24]

The electronic spectra of the series of monoanionic complexes, $[Fe(NO)(\text{-}S_4)]^-$, do not vary greatly with changes in the ligands indicating that, within the series, the electronic structure of the complexes is similar. This is also true for the series of complexes $[Fe(NO)(\text{-}S_4)]^{-2}$, $[Co(NO)(\text{-}S_4)]^-$, and $[Co(NO)(\text{-}S_4)]^{-2}$. However, there are obvious spectral differences between the isoelectronic $[Fe(NO)(\text{-}S_4)]^{-2}$ and $[Co(NO)(\text{-}S_4)]^-$, suggesting that the electronic structures of these are not alike. Also, the spectra of the iron dianions are comparable with those of the corresponding nitrosyl bisdithiocarbamates, whereas those of the analogous cobalt compounds are not.

Magnetic Data and Esr Spectra. The complexes $[Fe(NO)S_4C_4(C_6H_5)_4]$,^{0} $(Fe(NO)(\text{-}S_4)]^{-2}$, and $[Co(NO)(\text{-}S_4)]^-$ were paramagnetic and the magnetic moments,

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(39) A Earnshaw, P. C. Hewlitt, and L. F. Larkworthy, *J. Chem. Soc.*, 4718 (1965).

(40) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 87, 3585 (1965).

Table V. Magnetic Data and Esr Results from Iron and Cobalt Nitrosyl 1,2-Dithiolenes

Complex	Prepn[a]	Solvent	$\langle g \rangle$	$\langle A_N \rangle$, gauss	$\langle A_M \rangle$, gauss	μ_{eff}, BM
$[Fe(NO)S_4C_4(CN)_4]^{-2}$	C	$CHCl_3$	2.028	15.4		1.84[b]
	C	CH_2Cl_2	2.028	15.3		
$[Fe(NO)S_4C_4(CF_3)_4]^{-2}$	C	CH_2Cl_2	2.027	15.0		1.77[c]
	C	Acetone	2.026	15.7		
$[Fe(NO)(S_2C_6Cl_4)_2]^{-2}$	C	CH_2Cl_2	2.027	15.4		...[b]
$[Fe(NO)(S_2C_6H_3CH_3)_2]^{-2}$	CPE	CH_2Cl_2	2.028	13.1		2.62[b,d]
	C	DMSO	2.028	15.0		
$[Fe(NO)S_4C_4(C_6H_5)_4]^{-2}$	C	THF	2.026	15.4		...[e]
	CPE	CH_2Cl_2	2.026	13.9		
$[Fe(NO)S_4C_4(C_6H_5)_4]^0$	C	$CHCl_3$	2.009	...		1.94
$Fe(NO)(S_2CN(C_2H_5)_2)_2$	C	CH_2Cl_2	2.040	12.8		
$[Co(NO)S_4C_4(CN)_4]^-$	C	Acetone	2.063		31.9	1.55[f]
$[Co(NO)S_4C_4(CF_3)_4]^-$	C	Acetone	2.059		32.9	...[e]
$[Co(NO)S_4C_4(C_6H_5)_4]^-$	C	Acetone	2.050		29.4	...[e]

[a] C = chemical synthesis; CPE = controlled-potential electrolysis. [b] $(C_6H_5)_4P^+$ salt. [c] $(C_6H_5)_4As^+$ salt. [d] Values varied from 2–3.3 BM depending on method and number of crystallizations. [e] Not measured. [f] $C_5H_5NCH_3^+$ salt.

where measured, were generally consistent with the expected spin-doublet ground state (Table V). The high moments of some of the dianionic iron complexes were probably due to the presence of paramagnetic impurities in the samples measured; repeated recrystallizations did not help to improve the moments significantly.

The iron dianions, $[Fe(NO)(-S_4)]^{-2}$, in solution at room temperature, exhibited characteristic esr spectra which consisted of a triplet due to ^{14}N ($I = 1$) hyperfine interactions. The g factors were close to 2.027 and the nitrogen hyperfine splitting constants were *ca.* 15 gauss. These results are in general agreement with those obtained by McDonald, Phillips, and Mower.[25] Small solvent effects on $\langle A_N \rangle$ were detected but the values of the constant fell in the range 14–16 gauss.

The cobalt series, $[Co(NO)(-S_4)]^-$, also displayed esr signals in solution at room temperature. These consisted of eight lines due to hyperfine interaction with ^{57}Co ($I = {}^7/_2$); g factors of *ca.* 2.058 were observed and the metal hyperfine splittings averaged 30 gauss; no ^{14}N hyperfine splittings were detected, again suggesting a difference in electronic structure between the cobalt monoanions and iron dianions. No esr signals were detected in solutions believed to contain $[Co(NO)(S_2C_6H_3CH_3)_2]^-$, and the possible reasons for this have been discussed in the Infrared Spectral Studies section.

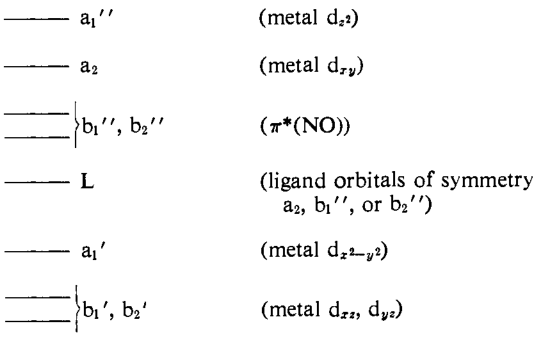

Figure 1. Proposed molecular orbital scheme for iron nitrosyl 1,2-dithiolene complexes: the important levels.

The esr spectrum of $[Fe(NO)S_4C_4(C_6H_5)_4]^0$ consisted of a single line with $\langle g \rangle = 2.009$, and ^{14}N splittings were not resolved. In DMF–$CHCl_3$ glasses, a threefold anisotropy of the g tensor was observed and $g_1 = 2.000$, $g_2 = 2.013$, and $g_3 = 2.021$. A detailed analysis and interpretation of these results is being prepared and will be presented shortly.[41]

Electronic Structures. Although several molecular orbital descriptions of the dithiolene complexes of nickel have been proposed,[30a,40,42] we do not present at this time a quantitative theory but consider a possible qualitative level-scheme which explains most of the gross features of the electronic properties of these new complexes.

Any molecular orbital scheme must explain the following features: (i) the observation of ^{14}N hyperfine splittings in $[Fe(NO)(-S_4)]^{-2}$, but their apparent absence in $[Fe(NO)(-S_4)]^0$ and $[Co(NO)(-S_4)]^-$; (ii) the shift of the g factor from *ca.* 2.027 in $[Fe(NO)(-S_4)]^{-2}$ to 2.009 in $[Fe(NO)(-S_4)]^0$, *i.e.*, the trend toward the free-electron value on oxidation; (iii) the marked shift in ν_{NO} on moving from $[Fe(NO)(-S_4)]^{-2}$ to $[Fe(NO)(-S_4)]^-$ compared with the smaller shift on moving from $[Fe(NO)(-S_4)]^-$ to $[Fe(NO)(-S_4)]^0$; (iv) the dependence of $E_{1/2}$ and ν_{NO} on the nature of the ligands; and (v) the occurrence of intense low-energy transitions in the electronic spectrum of $[Fe(NO)(-S_4)]^0$ and $[Fe(NO)(-S_4)]^-$, and their virtual absence in all other nitrosyl dithiolene complexes which we have prepared.

The orbitals of importance for the present discussion are indicated in Figure 1, where the labels refer to C_{2v} symmetry. The b_1', b_2', and a_1' levels, which are completely filled in all our complexes, are predominantly metal d_{xz}, d_{yz}, and $d_{x^2-y^2}$ in character, respectively. Next in energy above these we have placed a number of orbitals L which are primarily sulfur ligand in character. The exact number and form of these orbitals does not require specification for our qualitative discussion; the important feature of the scheme is that the orbital immediately below the b_1'' and b_2'' levels, which are predominantly π^*(NO) orbitals, be of this type. Previous experience has shown that orbitals of ligand character frequently have energies comparable to those of the metal d orbitals.[30a,40,42] The b_1'' and b_2'' levels are the highest orbitals to be occupied in any of our complexes. The remaining levels, a_2 and a_1'', which are always empty, are predominantly metal d_{xy} and d_{z^2} in character, respectively. With the exception of the inclusion of the L orbitals, this model is similar to that

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(41) N. M. Atherton and C. J. Winscom, to be published.

(42) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964).

proposed by Gray and Manoharan[43] for $[Fe(NO)(CN)_5]^{-2,-3}$ and related compounds.

According to our scheme, the configurations of our iron complexes are $\ldots (L)^2(b_1'',b_2'')^1$ for the dianions, $\ldots (L)^2$ for the monoanions, and $\ldots (L)^1$ for the neutral species.

The broad features of the scheme are applicable to all three differently charged types of complex, but there is one more detailed point which we must specify in principle. In the dianionic species, the near orbital degeneracy of the ground state arising from the configuration $\ldots (L)^2(b_1'',b_2'')^1$ will be relieved by a suitable distortion, corresponding to a bent Fe–N–O arrangement.[38] The monoanionic and neutral species in our scheme have orbitally nondegenerate ground states, and we anticipate a linear Fe–N–O system. Thus we expect to be able to correlate the properties of the neutral and single-charged complexes within the framework of a single level-scheme, the difference between the species being merely the addition of an extra electron. However, the dianions cannot be regarded as arising from the monoanion by placing an extra electron in the lowest unoccupied orbital of the level-scheme appropriate for the neutral molecule and monoanions. This distinction is important in our interpretation of certain properties of the complexes.

The interpretation of the g factors using this general orbital scheme is straightforward. In the dianions, spin–orbit coupling allows admixture of the excited configurations $(a_1')^1 \ldots (b_1'',b_2'')^2$, $(b_1'',b_2'')^0 \ldots (a_1'')^1$, and $(b_1'',b_2'')^0 \ldots (a_2)^1$, of which the first will be the most important because of the favorable energy denominator. The net result is a positive g shift. On the other hand, in the neutral complex it is reasonable to expect a near-cancellation of positive and negative contributions to the g factor. The latter situation would be analogous to that proposed by van Voorst and his co-workers[44] in explaining g in vanadocene. The ^{14}N hyperfine splitting in the dianions is assumed to arise by spin polarization of electrons in the s orbitals of the nitrogen by the spin density in the π^* orbitals of NO, the situation being analogous to that in $[Fe(NO)(CN)_5]^{-3}$.[43] In the neutral complex we expect much more spin density on the sulfur ligands, and if the uppermost singly occupied L orbital does not have a_1 symmetry, it is entirely reasonable that the ^{14}N hyperfine splitting should be zero or at least much smaller than in the dianions.

The marked changes in ν_{NO}, as summarized in (iii), are also simply understood in terms of the level-scheme. In the dianions the much higher population of the $\pi^*(NO)$ orbitals compared with the singly charged and neutral species would lead directly to a weakening of the NO bond, with concomitant decrease in the force constant and ν_{NO}. The change in population of the $\pi^*(NO)$ orbitals in going from the neutral complexes to the monoanions would be very small, and consequently there should be no great change in ν_{NO}, as observed.

The half-wave oxidation potentials for the monoanions are expected to show a linear correlation with the orbital energies of the highest occupied L level, and to this extent their dependence on the nature of the sulfur ligand can be readily understood in principle. However, the dependence on sulfur ligands of the half-wave oxidation potentials of the dianions is not so simply rationalized. We feel that the important point to make at this stage is that they are not expected to correlate simply with the orbital energy of (b_1'',b_2''), but rather with the energy difference between the gound states of the dianions and the monoanions. Assuming that the description of the dianions requires a modified MO scheme, by virtue of its nonlinear Fe–N–O arrangement, it is again reasonable to assume that this energy difference between the two ions in question is a function of the ligand substituent. A more detailed interpretation must await a more quantitative formulation of the theory.

Similar remarks apply to the interpretation of the optical spectra. Again, we do not feel able to go farther than to indicate that we expect some transitions to be common to both the neutral complexes and the monoanions, and the fact that the dianions behave differently is a further reflection of the fact that the finer details of the level-scheme must be different for the doubly charged species.

While the molecular orbital scheme appears to be moderately satisfactory in explaining the majority of the properties of the iron nitrosyldithiolenes, it is less satisfactory when applied to the corresponding cobalt complexes. Of course, it is quite possible that in the cobalt systems the relative ordering of the uppermost filled energy levels is different, and certainly the chemical evidence seems to indicate an electronic structure different from that of their iron analogs.

Considerable discussion about the nature of the oxidation state of the metal ions in oxidized dithiolene complexes has taken place. Using our tentative level scheme, it seems that the oxidation state of the iron in all our complexes is +2. This is justified by assuming that the b_1', b_2', and a_1' levels are filled and have pure metal character. Thus, the dianions can be described as $[Fe^{2+}(NO\cdot)(-S_4)^{-4}]$, where the two sulfur ligands are considered collectively as $(-S_4)^z$. The monoanions are $[Fe^{2+}(NO^+)(-S_4)^{-4}$ and the neutral species $[Fe^{2+}(NO^+)(-S_4)^{-3}]$. It is known that the 1,2-dicyanoethylene-1,2-dithiolate anion can be oxidized[45] to $[S_4C_4(CN)_4]^{-2}$ or $(-S_4)^{-2}$, and so we can predict the existence of $[Fe^{+2}(NO^+)(-S_4)^{-2}]$ or $[Fe(NO)(-S_4)]^+$, as a further oxidized species, and indeed, an example of this charge type has been detected voltammetrically. It is possible to add an electron to NO giving NO^-, and the predicted $[Fe^{+2}(NO^-)(-S_4)^{-4}]$, or $[Fe(NO)(-S_4)]^{-3}$, has also been identified. It does not seem likely to us that any other charge types will be found in the iron system. However, it must be emphasized that our assumption of pure metal, ligand, or $\pi^*(NO)$ character for these various energy levels is an oversimplification and the assignment of formal oxidation states must be viewed with caution.

Nomenclature. Throughout this paper and elsewhere[7,14] we have used the generic name "1,2-dithiolene" to describe ligands of the *cis*-1,2-disubstituted ethylenedithiol type, and their arene-12-dithiol analogs, when they are complexed to transition metals. The nomenclature is used only when the metal complex as a whole undergoes, or is capable of undergoing, electron-

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transfer reactions of the type described in this and other papers.[16,17,19,20,30b,31] By using this terminology we have sought firstly to avoid the use of particular ligand structures and metal valence formalisms which may be ambiguous, as in $[\mathrm{NiS_4C_4R_4}]^{0,-}$, or meaningless, as in $[\mathrm{VS_6C_6R_6}]^0$, and secondly to eliminate the use of confusing abbreviations such as MNT or BDT. Complexes which cannot engage in electron-transfer reactions of the type discussed above are referred to by the normal "dithiolate" nomenclature and by the use of formal oxidation numbers; *e.g.*, $[\mathrm{ZnS_4C_4(CN)_4}]^{-2}$ is described as the bis(*cis*-1,2-dicyanoethylene-1,2-dithiolate)zinc(II) anion.

It must be emphasized that the use of this terminology in no way represents a criticism, implied or real, of the existing discussion of the ground states of these unusual sulfur complexes.

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The Kinetics of the Rapid Interaction of Bis(histidinato)cobalt(II) with Oxygen

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Abstract: Bis(L-histidinato)cobalt(II), Co(L-h)$_2$, reacts rapidly with molecular O_2 in aqueous solution to give a deep brown solution containing [Co(L-h)$_2$]$_2$O$_2$. The kinetics of formation and decomposition of the brown species have been studied spectrally by flow methods. Kinetic data support the mechanism: Co(L-h)$_2$ + O$_2$ $\rightleftarrows$ Co(L-h)$_2$O$_2$ (k_1, k_{-1}) and Co(L-h)$_2$O$_2$ + Co(L-h)$_2$ $\rightleftarrows$ [Co(L-h)$_2$]$_2$O$_2$ (k_2, k_{-2}). The formation rate is independent of pH (8–11) and insensitive to 1 *M* KNO$_3$ addition. It was studied by using excess Co(L-h)$_2$ from 0.12 to 15.0 m*M*, and from the results $k_1 = 5 \times 10^7 \exp(-5600/RT)$. At 4.0°, $k_1 = 1.6 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_1k_2/k_{-1} = 5.5 \times 10^6\ M^{-2}\ \mathrm{sec}^{-1}$. Addition of EDTA^{4-}, $\mathrm{S_2O_4}^{2-}$, or low [H$^+$] to the brown solution removes rapidly Co(L-h)$_2$O$_2$ and/or Co(L-h)$_2$ and leads to an identical first-order decomposition rate constant, $k_{-2} = 6 \times 10^{17} \exp(-26{,}000/RT) = 10^{-2}\ \mathrm{sec}^{-1}$ at 4°. Addition of high [H$^+$] produces an intermediate which decomposes at similar rates to the brown species. The over-all association constant K_{12} ($= k_1k_2/k_{-1}k_{-2}$), $5.5 \times 10^8\ M^{-2}$ at 4°, compares well with that (3.5×10^8) M^{-2} obtained previously by manometric measurements and with our own determinations ($3.0 \times 10^8\ M^{-2}$). The behavior of the cobalt(II)–DL-histidine–O$_2$ system is more complex. The value of k_1 is very similar whether one uses L- or DL-histidine, but some differences reside in the decomposition behavior of the brown species even though K_{12} is very similar for the two systems.

Although a large variety of cobalt(II) complexes with amines, amino acids, and dipeptides have been shown to take up oxygen reversibly,[1] those of histidine and diglycine have been most thoroughly studied.[2–5] The cobalt(II)–histidine complex reacts readily with molecular O_2 to form an amber-colored species which is, however, rapidly decomposed with the release of oxygen, *e.g.*, by the addition of acid or by flushing the solution with nitrogen. The equilibrium involved has been very carefully studied[2] and the amber-colored species, shown to be diamagnetic,[2,6,7] contains a Co:h:O$_2$ ratio of 2:4:1 being probably a binuclear species with an –O–O– unit linking two Co(histidine)$_2$ residues.[5] We shall refer to this as the oxygenated species. No other oxygen-containing complex has been detected in the oxygenated solution.[2] Subsequent to the rapid reversible uptake of oxygen, there occurs a slow complex irreversible uptake of more oxygen leading eventually to dark pink cobalt(III) complexes. This slower oxygenation is being studied currently.[8] The present paper is concerned with the kinetics of formation and decomposition of the oxygenated species using a spectral stopped-flow apparatus. We have investigated mainly the behavior of L-histidine (with which the bulk of reported work is concerned) and then briefly the more complicated DL-histidine–cobalt(II)–oxygen system. These types of systems afford us an opportunity eventually to compare and contrast the behavior of the synthetic chelates with the reversible oxygen carriers of biological importance[9] although any analogy should not be over-emphasized.

Experimental Section

Materials. All chemicals used were reagent grade. The source of L- and DL-histidine (Mann Research Laboratories, Nutritional Biochemicals Corp.) had no effect on the results. Solutions of cobalt(II) nitrate were standardized by titration with EDTA using a murexide indicator.

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