plexing of copper(II) is well known, it is yet unknown for copper(I).[24]

A simpler polymeric structure for I can be envisaged in which copper is four-coordinate and in a tetrahedral environment. This structure consists of single chains of copper and chlorine atoms bridged by molecules of methyldiazene. Each copper atom is coordinated to two chlorine atoms and to two nitrogen atoms from different diazene molecules. Layers of this type are stacked together in the solid. Clearly, the larger number of diazene molecules in I poses no problem for proposing a reasonable crystal structure.

It is surprising that I cannot be obtained by the method of Diels and Koll[13] from the oxidation of aqueous methylhydrazine with cupric ion in the presence of chloride ion.[12] By anology with other systems,[12,13] methyldiazene should be produced in this reaction. The only evidence for this reaction found in the present study was the appearance of a small amount of a red-brown solid on the surface of the *unmixed* solution obtained by slowly adding a cupric sulfate solution to a nearly saturated sodium acetate solution containing some sodium chloride and methylhydrazine. This solid dissolved quickly and a yellow solution resulted which after ~15 min began to deposit metallic copper.[25] Methane was the only infrared-active gaseous product. Use of other buffer systems proved equally unsuccessful in yielding I.

Methyldiazene reacted rapidly with cupric ion in aqueous solution, but the final products depended upon the cupric salt used. With cupric chloride a reddish precipitate formed within seconds and redissolved slowly. This could be I, which was formed after reduction of some Cu(II) to Cu(I). The amount was too small to work with. With cupric sulfate a permanent reddish precipitate of cuprous oxide quickly formed.[25] Approximately one copper atom precipitated for every four molecules of methyldiazene present when the cupric sulfate was added. Thus, the failure to obtain I by the method of Diels and Koll could be explained by a rapid reaction of methyldiazene and cupric ion. However, the different products observed in the three reactions remain unexplained.

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[24] E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

[25] Identified by its X-ray diffraction powder pattern.

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Preparation and Oxygenation of Some Five-Coordinate Lewis Base Adducts of Iron Bis(1,2-dithiolenes)

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Triphenylphosphine oxide, triphenylarsine oxide, pyridine *N*-oxide, and halide ions cleave the dimers $Fe_2S_8C_8R_8^{2-}$ (R = CN, CF_3) to give adducts of the type (base)$FeS_4C_4R_4^-$. The isolation and physical properties of certain of these adducts, which have quartet ground states, are reported. Triphenylphosphine and triphenylarsine also cleave the dimers to give adducts which have been characterized in solution but not isolated. Exposure of these latter adducts to oxygen results in the oxidation of the bases to triphenylphosphine oxide and triphenylarsine oxide. No evidence for the formation of discrete oxygen complexes with any of these dithiolene complexes has been found. Cobalt dithiolene complexes are not effective in activating the oxidation of these bases.

Introduction

The ability of dithiolene complexes to undergo electron-transfer reactions has been extensively studied.[2] In addition dithiolene complexes have been shown to exert effects on the oxidation of other substrates. The neutral complexes $MS_4C_4(C_6H_5)_4$ (M = Ni, Pd, Pt) and $(C_4H_9)_3PCoS_4C_4(C_6H_5)_4$ have been shown to be effective as free-radical acceptors and hydroperoxide decomposition agents; consequently they act as autoxidation inhibitors.[3] In contrast iron dithiolenes have been observed to promote the oxidation of certain species. It has been reported that exposure of solutions of the ions $XFeS_4C_4R_4^{2-}$ (X^- = N_3^-, NCO^-; R = CN, CF_3) to air produces the corresponding $ONFeS_4C_4R_4^{2-}$ in

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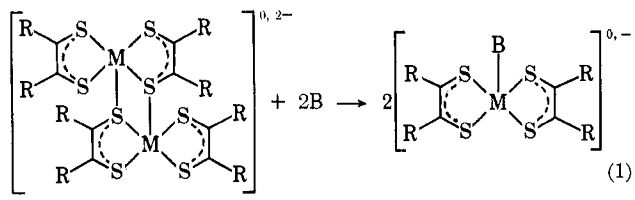
[1] University of California, Davis, Calif. 95616.

[2] J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968); G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968).

[3] C. Copping and N. Uri, *Discuss. Faraday Soc.*, **46**, 202 (1969); L. W. Fine, M. Grayson, and V. H. Suggs, *J. Organometal. Chem.*, **22**, 219 (1970).

small quantities.[4] Recently the reaction of triphenylphosphine with $Fe_2S_8C_8(CF_3)_8^{2-}$ and oxygen has been shown to result in the formation of triphenylphosphine oxide which is incorporated into the adduct $(C_6H_5)_3POFeS_4C_4(CF_3)_4^-$.[5]

The purpose of this article is twofold. Some additional information on the cleavage[4,6-12] of bis(dithiolene)-metal dimers by Lewis bases to form five-coordinate adducts (reaction 1) is reported. In addition, the results of synthetic studies on the scope and mechanism of oxidation of some group V bases are presented.



(1)

Experimental Section

Preparation of Compounds.—Commercial samples of triphenylphosphine, triphenylarsine, triphenylphosphine oxide, triphenylarsine oxide, and pyridine *N*-oxide were recrystallized before use. The dithiolene complexes were prepared *via* standard methods.[2]

$[(C_4H_9)_4N][(C_6H_5)_3AsOFeS_4C_4(CF_3)_4]$. 1. From Triphenylarsine Oxide.—A solution of 0.50 g (0.33 mmol) of $[(C_4H_9)_4N]_2[Fe_2S_8C_8(CF_3)_8]$ in 15 ml of acetone was added to a solution of 0.50 g (1.5 mmol) of triphenylarsine oxide in 20 ml of toluene. The solution was filtered, and the acetone was allowed to evaporate over a 24-hr period. The black, crystalline solid was collected by filtration, washed with toluene, and vacuum dried; mp 192–193°. *Anal.* Calcd: C, 47.02; H, 4.79; S, 11.95. Found: C, 46.70; H, 4.68; S, 11.85.

2. From Triphenylarsine.—A solution of 0.50 g (0.33 mmol) of $[(C_4H_9)_4N]_2[Fe_2S_8C_8(CF_3)_8]$ in 30 ml of acetone was added to a solution of 0.50 g (1.6 mmol) of triphenylarsine in 20 ml of toluene. The solution was filtered and allowed to evaporate over a 4-day period. The black, crystalline solid was collected by filtration. In order to free the product of some insoluble brown residue, it was dissolved in a minimum of acetone and filtered. Toluene (15 ml) was added to the filtrate which was then allowed to evaporate partially. The product was collected by filtration, washed with toluene, and vacuum dried. The melting point and infrared spectrum of the product were identical with those of the complex formed from triphenylarsine oxide.

$[(C_4H_9)_4N][(C_6H_5)_3POFeS_4C_4(CF_3)_4]$.—This complex may be obtained from triphenylphosphine oxide by the method described for the triphenylarsine oxide analog or from triphenylphosphine by evaporation of dichloromethane–toluene or acetone–toluene solutions as described previously.[5,6] The infrared and electronic spectra and melting points of the products obtained *via* either route are identical.

$[(C_2H_5)_4N][(C_6H_5)_3AsOFeS_4C_4(CN)_4]$. 1. From Triphenylarsine Oxide.—A solution of 0.45 g (0.50 mmol) of $[(C_2H_5)_4N]_2[Fe_2S_8C_8(CN)_8]$ in 25 ml of acetone was added to a solution of 0.38 g (1.2 mmol) of triphenylarsine oxide in 25 ml of acetone. *sec*-Butyl alcohol (75 ml) was added to the solution and the acetone was driven off by heating on a steam bath. The hot solution was filtered. Upon cooling, black needles were deposited. The product (0.50 g, 65%) was collected by filtration, washed with *sec*-butyl alcohol, and vacuum dried; mp 172–174°. *Anal.* Calcd: C, 51.78; H, 4.47; N, 8.88; S, 16.26. Found: C, 51.67; H, 3.97; N, 8.59; S, 16.88.

2. From Triphenylarsine.—An oxygen stream was bubbled through a solution of 0.50 g (0.55 mmol) of $[(C_2H_5)_4N]_2[Fe_2S_8C_8(CN)_8]$ and 1.20 g (3.9 mmol) of triphenylarsine in 30 ml of acetone for 10 hr. The solution was taken to dryness on a rotary evaporator and the resultant solid was extracted with three 30-ml portions of pentane. From the pentane extracts 0.85 g (2.8 mmol) of triphenylarsine was recovered. The residual solid was recrystallized from acetone–*sec*-butyl alcohol to yield 0.54 g (54%) of product; mp 171.5–173°. The infrared spectrum of this material was identical with that of a sample prepared from triphenylarsine oxide.

$[(C_4H_9)_4N][C_5H_5NOFeS_4C_4(CF_3)_4]$.—A solution of 0.50 g (0.33 mmol) of $[(C_4H_9)_4N]_2[Fe_2S_8C_8(CF_3)_8]$ in 30 ml of acetone was added to a solution of 1.0 g (4.8 mmol) of pyridine *N*-oxide in 50 ml of *sec*-butyl alcohol. The acetone was driven off by heating on a steam bath, and the hot solution was filtered. On cooling black crystals formed which were collected by filtration, washed with *sec*-butyl alcohol and ether, and vacuum dried; mp 120–120.5°. *Anal.* Calcd: C, 41.18; H, 4.89; N, 3.31. Found: C, 41.30; H, 4.81; N, 3.26.

$[(C_2H_5)_4N][C_5H_5NOFeS_4C_4(CN)_4]$.—This salt was prepared similarily to its perfluoromethyl-substituted analog; mp 169–170°. *Anal.* Calcd: C, 46.07; H, 4.39; N, 14.65. Found: C, 45.68; H, 4.26; N, 15.10.

$[(C_2H_5)_4N]_2[BrFeS_4C_4(CN)_4]$.—A solution of 0.45 g (0.50 mmol) of $[(C_2H_5)_4N]_2[Fe_2S_8C_8(CN)_8]$ and 0.21 g (1.0 mmol) of $[(C_2H_5)_4N]Br$ dissolved in a minimum of acetone was filtered. Ether was gradually added to the red solution to precipitate the product as black crystals. The product was collected by filtration and purified by dissolving in a minimum of acetone, filtering, and reprecipitating with ether; mp 163–165°. *Anal.* Calcd: C, 42.60; H, 5.96; Br, 11.81. Found: C, 42.49; H, 5.95; Br, 12.07.

$[(C_2H_5)_4N]_2[ClFeS_4C_4(CN)_4]$.—This salt was prepared *via* the route used for the bromo analog; mp 157–160°. *Anal.* Calcd: C, 45.60; H, 6.38; S, 20.29. Found: C, 45.74; H, 6.25; S, 20.50.

Attempts to prepare $[(C_2H_5)_4N]_2[IFeS_4C_4(CN)_4]$ by this same route were unsuccessful because of the greater degree of dissociation of the iodide adduct.

Oxidation of Triphenylphosphine. 1. In the Presence of $Fe_2S_8C_8(CN)_8^{2-}$.—Oxygen was slowly bubbled through a solution of 0.82 g (3.1 mmol) of triphenylphosphine and 0.22 g (0.48 mmol) of $[(C_2H_5)_4N]_2[Fe_2S_8C_8(CN)_8]$ in 35 ml of acetone for 5 hr. The solution was taken to dryness on a rotary evaporator and the resulting solid was triturated with 30 ml of pentane to dissolve any unreacted triphenylphosphine. The pentane solution was decanted and the solid was extracted with five 30-ml portions of boiling heptane. After concentrating the heptane solution to a volume of 60 ml and cooling, the white crystalline product was collected by filtration, washed with pentane, and air dried. A yield of 0.50 g (1.8 mmol, 57% based on triphenylphosphine) of triphenylphosphine oxide (identified by infrared spectrum and melting point) was obtained. The heptane-insoluble residue was dissolved in a minimum volume of acetone and filtered to remove a small quantity of brown, amorphous material. Isobutyl alcohol (20 ml) was added to the filtrate, and the acetone was distilled off by heating. From the cooled solution 0.11 g (50% recovery) of $[(C_2H_5)_4N]_2[Fe_2S_8C_8(CN)_8]$ was collected by filtration.

2. With $FeS_6C_6(CN)_6^{2-}$.—Oxygen was slowly bubbled through a solution of 0.51 g (0.41 mmol) of $[(C_6H_5)_4As]_2[FeS_6C_6(CN)_6]$ and 0.85 g (3.3 mmol) of triphenylphosphine in 40 ml of acetone for 6 hr. On working up the mixture as described above, 0.73 g (2.6 mmol, 81% based on triphenylphosphine) of triphenylphosphine oxide, 0.18 g (35% recovery) of $[(C_6H_5)_4As]_2[FeS_6C_6(CN)_6]$,

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[4] J. A. McCleverty, N. M. Atherton, N. G. Connelly, and C. J. Winscom, *J. Chem. Soc. A*, 2242 (1969).

[5] E. F. Epstein, I. Bernal, and A. L. Balch, *Chem. Commun.*, 136 (1970).

[6] A. L. Balch, *Inorg. Chem.*, **6**, 2158 (1967).

[7] C. H. Langford, E. Billig, W. I. Shupack, and H. B. Gray, *J. Amer. Chem. Soc.*, **86**, 2958 (1964).

[8] R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966).

[9] M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *ibid.*, **88**, 4870 (1966).

[10] G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *ibid.*, **88**, 4604 (1966).

[11] J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. J. Winscom, *ibid.*, **89**, 6082 (1967).

[12] E. Hoyer, W. Dietzsch, and H. Müller, *Z. Chem.*, **7**, 354 (1967).

TABLE I

ELECTRONIC SPECTRA[a]

Compd	ν_{max}, cm^{-1} (ϵ)
$(C_6H_5)_3PFeS_4C_4(CF_3)_4^-$ [b]	12,700 (150), 14,900 sh (540), 17,700 (2200), 22,700 (4300), 27,400 sh (6500)
$(C_6H_5)_3POFeS_4C_4(CF_3)_4^-$ [c]	8800 sh (50), 10,900 sh (95), 17,100 sh (1400), 20,200 (3300), 22,000 (4100), 24,500 (4100), 27,900 (7800)
$(C_6H_5)_3AsFeS_4C_4(CF_3)_4^-$ [b]	9300 (150), 17,100 (2400), 22,900 (4900), 30,800 (8200)
$(C_6H_5)_3AsOFeS_4C_4(CF_3)_4^-$ [c]	9700 sh (40), 11,400 sh (80), 17,500 sh (1300), 19,500 (3600), 22,300 (3200), 24,800 sh (3600), 27,800 (7200)
$(C_6H_5)_3PFeS_4C_4(CN)_4^-$ [b]	7000 (590), 11,500 sh (130), 14,400 (930), 16,900 (2500), 22,200 sh (8300), 23,800 (9030)
$(C_6H_5)_3POFeS_4C_4(CN)_4^-$ [b]	9300 sh (60), 12,100 (120), 16,700 sh (1100), 19,600 (4700), 20,600 sh (5000), 23,500 (6500), 27,100 (12,600)
$(C_6H_5)_3AsOFeS_4C_4(CN)_4^-$ [c]	9300 sh (50), 12,000 sh (110), 13,200 (130), 16,700 sh (980), 19,600 (3500), 21,200 sh (3100), 24,400 sh (5800), 27,100 (10,300)
$C_5H_5NFeS_4C_4(CF_3)_4^-$ [c]	13,100 (100), 17,500 sh (980), 22,200 (5000), 23,700 (6300), 28,500 (7900)
$C_5H_5NOFeS_4C_4(CF_3)_4^-$ [c]	11,600 (80), 17,500 sh (1200), 20,000 sh (3100), 21,900 (4700), 24,600 (4500), 28,600 (9600)
$C_5H_5NFeS_4C_4(CN)_4^-$ [c]	12,600 (120), 16,700 sh (1000), 18,700 sh (2600), 20,800 (5000), 22,500 (9500), 28,000 (13,000)
$C_5H_5NOFeS_4C_4(CN)_4^-$ [c]	13,400 (100), 16,700 sh (1300), 19,600 sh (4800), 20,500 (5500), 23,600 (6200), 27,700 (14,000)
$ClFeS_4C_4(CF_3)_4^{2-}$ [b]	9300 sh (60), 12,100 sh (130), 13,700 sh (160), 16,900 sh (1300), 19,500 (3900), 21,900 (3500), 25,000 sh (3000), 27,900 (7300)
$ClFeS_4C_4(CN)_4^{2-}$	6100 (130), 12,300 (390), 16,100 sh (1100), 19,100 (4700), 20,900 sh (3500), 23,900 (6500), 27,400 (11,200), 31,500 (14,200)
$BrFeS_4C_4(CN)_4^{2-}$ [b]	11,200 sh (190), 12,000 (200), 16,100 sh (1500), 19,000 (4600), 20,200 (4500), 23,500 (7000), 27,000 sh (10,200), 30,800 (13,400)
$IFeS_4C_4(CN)_4^{2-}$ [b]	11,300 (210), 16,400 sh (1700), 19,800 (5200), 23,300 (5900), 29,200 (14,000)

[a] Measured in dichloromethane solution. [b] Prepared in solution from $Fe_2S_8C_8R_8^{2-}$ and excess base. [c] Measured in the presence of excess base.

and some $[(C_6H_5)_4As]_2[Fe_2S_8C_8(CN)_8]$ were obtained. The recovery of $FeS_6C_6(CN)_6^{2-}$ was variable; in similar experiments sometimes only $Fe_2S_8C_8(CN)_8^{2-}$ could be obtained after reaction.

Physical Measurements.—Magnetic susceptibilities of solids were obtained using a Faraday balance as described previously.[6] Electronic spectra were recorded on a Cary 14 spectrophotometer. Solutions for spectral observation under oxygen-free conditions were prepared on a standard vacuum line with three freeze–thaw operations to remove oxygen from the solvent prior to dissolving the solid complexes. Infrared spectra in the 4000–500-cm^{-1} region were recorded on a Perkin-Elmer 421 spectrometer; in the region 500–290 cm^{-1} a Beckman IR5A spectrometer was used. Conductivities were measured with a Serfass conductivity bridge.

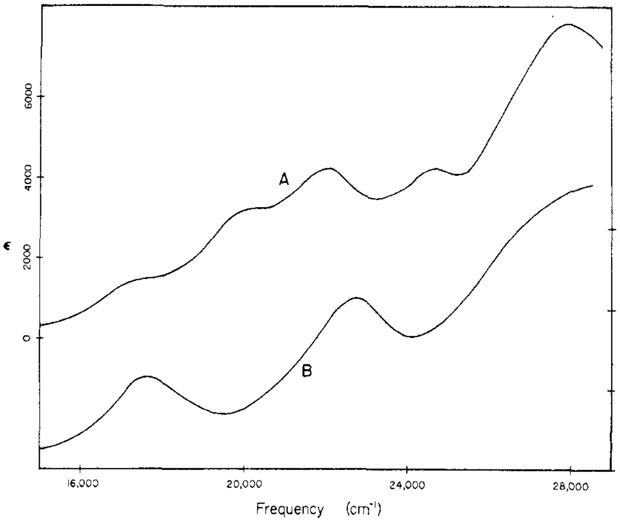

Figure 1.—Electronic spectra of (A) $(C_6H_5)_3POFeS_4C_4(CF_3)_4^-$ (left ordinate) and (B) $(C_6H_5)_3PFeS_4C_4(CF_3)_4^-$ (right ordinate) formed from $Fe_2S_8C_8(CF_3)_8^{2-}$ and excess of the appropriate base in dichloromethane solution.

Results

Cleavage Reactions.—The cleavage reaction 1 may be detected by changes in the electronic spectrum (and usually in the color) of the complex upon addition of an appropriate base, by changes in the electrochemical behavior of the complex in the presence of base, and in certain cases by isolation of the resulting adduct. Triphenylphosphine oxide and triphenylarsine oxide cleave the cyano- and perfluoromethyl-substituted bis-dithiolene dianionic iron dimers to yield adducts which are presumably five-coordinate monomers.[13,14] Triphenylphosphine and triphenylarsine also cleave these dimers to yield adducts which are distinctly different from those formed by their respective oxides. It is presumed that these adducts are also five-coordinate by analogy with the phosphine and arsine adducts previously isolated[4] and because of their facile polarographic oxidation to (base)$FeS_4C_4R_4$.[6] In addition, halide ions (Cl^-, Br^-, I^-), pyridine, and pyridine *N*-oxide also cleave these dimers. As reported previously[4,6,15] triphenyl phosphite ruptures the dimers, but the dimers are unaffected by triphenyl phosphate. The electronic spectra of these adducts are reported in Table I. The electronic spectra of $(C_6H_5)_3PFeS_4C_4(CF_3)_4^-$ and $(C_6H_5)_3POFeS_4C_4(CF_3)_4^-$ in solution are reproduced in Figure 1. Some physical data for those adducts which have been isolated are set out in Tables II and III. It is apparent that

(13) Although the magnetic susceptibilities of the neutral adducts $(C_6H_5O)_3PCoS_4C_4(CF_3)_4$[6] and $(C_6H_5)_3PCoS_4C_4H_4$[12] suggest that these species may be dimerized in the solid (but not in solution in the first example), there exists no evidence to suggest that any of the anionic adducts are dimerized. Both $(C_6H_5)_3AsFeS_4C_4(CF_3)_4$[14] and $(C_6H_5)_3POFeS_4C_4(CF_3)_4^-$[5] have been shown to be monomeric in the solid state. In agreement with the most recent work,[6,11] there is no evidence for addition of a second base to give six-coordinate adducts.

(14) E. F. Epstein and I. Bernal, to be submitted for publication.

(15) It has been stated[4] that $(C_6H_5O)_3PFeS_4C_4(CF_3)_4^-$ loses triphenyl phosphite on standing in the solid. We find that in the solid $(C_6H_5O)_3PFeS_4C_4(CF_3)_4^-$ is stable indefinitely as long as it is protected from the atmosphere; exposure of the solid to air causes reaction which does not simply produce triphenyl phosphate.

those species with magnetic susceptibilities indicative of a quartet ground state exhibit electronic spectra that are quite similar while the spectra of the phosphine and arsine adducts are notably different.

TABLE II

INFRARED SPECTRA (CM^{-1})[a]

$[(C_4H_9)_4N][(C_6H_5)_3POFeS_4C_4(CF_3)_4]$	3060 w, 2970 s, 2938 m, 2880 m, 1590 w, 1541 s, 1482 s, 1461 w, 1441 s, 1381 m, 1246 vs, 1160 vs, 1120 vs, 1073 w, 1027 w, 999 w, 895 s, 838 m, 758 w, 750 m, 725 s, 714 s, 693 s
$[(C_4H_9)_4N][(C_6H_5)_3AsOFeS_4C_4(CF_3)_4]$	3050 w, 2963 s, 2939 m, 2878 m, 1536 s, 1483 s, 1458 w, 1442 s, 1383 m, 1243 vs, 1162 vs, 1120 vs, 1134 w, 1023 w, 998 w, 908 s (ν(As–O)), 893 s, 835 m, 750 s, 744 s, 716 s, 692 s
$[(C_2H_5)_4N][(C_6H_5)_3POFeS_4C_4(CN)_4]$	3063 w, 2998 w, 2215 m, 2205 m, 1495 sh, 1484 s, 1481 sh, 1441 s, 1391 m, 1306 w, 1183 m, 1173 m, 1147 s, 1109 w, 1088 s, 1049 w, 1026 w, 1001 s, 858 s (ν(As–O)), 787 m, 753 m, 745 s, 741 m, 698 s
$[(C_4H_9)_4N][C_5H_5NOFeS_4C_4(CF_3)_4]$	3114 w, 2965 s, 2945 sh, 2876 m, 1590 s, 1482 s, 1383 m, 1245 vs, 1205 w (ν(N–O)?), 1195, w (ν(N–O)?), 1170 sh, 1160 s, 1125 vs, 1068 w, 1023 w, 1004 w, 923 w, 896 s, 885 sh, 838 m, 830 m, 819 w, 771 m, 718 s, 694 m, 679 m
$[(C_2H_5)_4N][C_5H_5NOFeS_4C_4(CN)_4]$	3108 m, 3086 w, 2995 w, 2211 m, 2201 s, 1481 s, 1470 sh, 1430 m, 1391 m, 1240 w, 1210 sh, 1203 s (ν(N–O)), 1174 s, 1146 m, 1107 w, 1039 w, 1023 w, 998 m, 834 sh, 826 s, 775 s, 683 s
$[(C_2H_5)_4N]_2[BrFeS_4C_4(CN)_4]$	3005 w, 2985 w, 2950 w, 2211 m, 2198 s, 1476 s, 1458 w, 1438 w, 1391 m, 1297 w, 1181 w, 1171 m, 1146 m, 1106 w, 1048 w, 1025 w, 1000 m, 856 w, 788 s, 505 w,[b] 347 br,[b] 335 sh[b]

[a] Recorded in KBr pellets. [b] Recorded in hydrocarbon mull.

TABLE III

MAGNETIC SUSCEPTIBILITY AND CONDUCTIVITY DATA

Compd	μ_{eff}[a]	Λ[b]
$[(C_4H_9)_4N][(C_6H_5)_3POFeS_4C_4(CF_3)_4]$	4.00	68
$[(C_4H_9)_4N][(C_6H_5)_3AsOFeS_4C_4(CF_3)_4]$	3.98	59
$[(C_2H_5)_4N][(C_6H_5)_3AsOFeS_4C_4(CN)_4]$	3.97	65
$[(C_4H_9)_4N][C_5H_5NOFeS_4C_4(CF_3)_4]$	4.00	63
$[(C_2H_5)_4N][C_5H_5NOFeS_4C_4(CN)_4]$	4.00	71
$[(C_6H_5)_4P][C_5H_5NFeS_4C_4(CF_3)_4]$	3.98[c]	. . .
$[(C_4H_9)_4N][C_5H_5NFeS_4C_4(CN)_4]$	3.90[c]	. . .
$[(C_2H_5)_4N]_2[ClFeS_4C_4(CN)_4]$	3.99	156
$[(C_2H_5)_4N]_2[BrFeS_4C_4(CN)_4]$	4.02	170

[a] Calculated from the Curie law, $\mu_{eff} = 2.84(\chi^{M}_{cor}T)^{1/2}$, for solid samples at 23°. [b] In cm^2 mol^{-1} ohm^{-1}; in $\sim 10^{-3}$ M nitromethane solution. [c] Data from ref 4.

The infrared spectra of the complexes are in general a superposition of the spectrum of the base on the spectrum of the parent complex. It has been possible to observe directly the X–O (X = P, As, N) stretch except in those cases, $(C_6H_5)_3POFeS_4C_4(CF_3)_4^-$ and $C_5H_5NOFeS_4C_4(CF_3)_4^-$, where these vibrations occur in the region of the strong C–F vibrations. In the case of $[(C_2H_5)_4N]_2[BrFeS_4C_4(CN)_4]$ the infrared spectrum is virtually identical with that of $[(C_2H_5)_4N]_2[Fe_2S_8C_8(CN)_8]$ except in the region below 400 cm^{-1}. In this case the bands from the dimer at 375, 350, and 325 cm^{-1} are replaced with a broad band at 347 and a shoulder at 335 cm^{-1} in the adduct. These bands are probably due to metal–sulfur stretching vibrations and differences are due to cleavage of the dimer in formation of the adduct. Similarly $[(C_2H_5)_4N]_2[ClFeS_4C_4(CN)_4]$ has only a broad band at 340 cm^{-1} due to the iron–sulfur stretch; the iron–chlorine stretch probably occurs below 290 cm^{-1}, the limit of our instrumentation.

The polarographic behavior of the adducts $(C_6H_5)_3EFeS_4C_4R_4^-$ (E = P, As, Sb, O_3P; R = CN, CF_3), which has been described in detail previously,[5] indicates a reversible, one-electron oxidation to the neutral complexes $(C_6H_5)_3EFeS_4C_4R_4$. In the case of the perfluoromethyl-substituted complexes, the neutral species have been isolated and their polarographic reduction has been demonstrated.[6] The triphenylphosphine oxide and triphenylarsine oxide adducts also undergo an apparent one-electron oxidation at voltages *ca.* 0.3–0.4 V more positive than the oxidation of their phosphine or arsine counterparts. These oxidative waves have not been examined in detail, but it has been noted that the half-wave potentials are dependent on the base concentration. Attempts to prepare neutral adducts $(C_6H_5)_3EOFeS_4C_4(CF_3)_4$ (E = P, As) from $Fe_2S_8C_8(CF_3)_8$ have been unsuccessful; only a mixture of unstable products has been obtained. The inability to isolate $(C_6H_5)_3EOFeS_4C_4(CF_3)_4$ leads us to believe that the polarographic oxidation of $(C_6H_5)_3EOFeS_4C_4(CF_3)_4^-$ may involve more than simple one-electron transfer. Nevertheless it is certain that the polarographic data in ref 6 are to be ascribed to the phosphine and arsine adducts themselves.

In contrast to the iron dithiolene dimers, the cobalt analogs exhibit no evidence of interaction with triphenylphosphine oxide, triphenylarsine oxide, or halide ions.

Apical Base Oxidations.—Exposure of solutions of the triphenylphosphine or triphenylarsine adducts to air or oxygen results in oxidation of the apical bases to their respective oxides. It has been possible to isolate $(C_6H_5)_3POFeS_4C_4(CF_3)_4^-$ and $(C_6H_5)_3EOFeS_4C_4(CN)_4^-$ (E = P, As) *via* this route; these products are identical with the adducts prepared directly from the oxides. In these reactions only about 1 mol of phosphine or arsine is oxidized per gram-atom of iron; if phosphine or arsine is present in excess, it can be recovered unchanged. It appears that the formation of a firmly bound adduct $(C_6H_5)_3EOFeS_4C_4R_4^-$ inhibits oxidation of additional phosphine or arsine. In the presence of $Fe_2S_8C_8(CN)_8^{2-}$ triphenylphosphine is also oxidized to the oxide but at least 40 mol of triphenylphosphine oxide is produced per mole of dimer. In this case the adduct $(C_6H_5)_3POFeS_4C_4(CN)_4^-$ does form in solution but its stability toward dissociation is low and consequently it has not been isolated. The tris complex $FeS_6C_6(CN)_6^{2-}$ shows similar ability to activate the oxygenation of triphenylphosphine; in this case some (and frequently a substantial amount) $Fe_2S_8C_8(CN)_8^{2-}$ is formed during the reaction. In all cases a significant quantity of a brown solid which is insoluble in organic solvents and water but soluble in acid is formed. This is probably a mixture of iron oxides and sulfides which results from decomposition of the dithiolene complexes. This decomposition occurs also in the absence of base. Since this decomposition is accompanied by the uptake of oxygen, it has thwarted our attempts to measure the stoichiometry of oxygen consumption during the oxidation of triphenylphosphine. It has not been possible to oxidize pyridine to pyridine *N*-oxide by oxygen in the presence of these iron dithiolene complexes.

Cobalt dithiolene complexes are not capable of similar promotion of oxidation of triphenylphosphine or triphenylarsine. The neutral complexes $(C_6H_5)_3ECoS_4C_4(CF_3)_4$ (E = P, As), which are isoelectronic with $(C_6H_5)_3EFeS_4C_4(CF_3)_4^-$, are unaffected by oxygen in the solid state and in dichloromethane solution. Likewise the anionic adducts $(C_6H_5)_3ECoS_4C_4R_4^-$ are not oxidized by oxygen in the solid or in solution under the same conditions used for oxidation of the bases in the presence of the iron dithiolenes.

Discussion

Acceptor Properties of Cobalt and Iron Dithiolenes.—It has been established for some time that, in forming adducts of the type $(base)CoS_4C_4R_4^-$, cobalt is acting as a soft-acid center.[6,16] In the same environment iron, however, appears to be a hard acid. Iron adducts are formed with a number of hard bases (halide ions, triphenylphosphine oxide, triphenylarsine oxide) which do not form adducts with the cobalt bis(dithiolenes). Semiquantitative evaluation of the equilibrium constants for reaction 1 indicates that triphenylphosphine and triphenylarsine form weaker adducts than do their respective oxides; the order of stability toward dissociation of the halide adducts $XFeS_4C_4R_4^{2-}$ is also $I^- < Br^- < Cl^-$. These stability trends are consistent with a hard-iron center.

The ability of the iron bis(dithiolenes) to form adducts with a greater variety of bases may also be related to the greater electron deficiency of the iron bis(dithiolenes) *vis a vis* their cobalt counterparts. Support for this idea comes from the observation that electron-withdrawing substituents on the dithiolene ligand increase the stability of the adducts. Thus, for example, it is reported[4] that $C_5H_5NFeS_4C_4(CN)_4^-$ and $C_5H_5NFeS_4C_4(CF_3)_4^-$ are stable toward base dissociation in solution whereas appreciable dissociation of $C_5H_5NFe(S_2C_6H_3\text{-}4\text{-}CH_3)_2^-$ occurs; numerous adducts of the types $(base)CoS_4C_4(CN)_4^-$ and $(base)CoS_4C_4(CF_3)_4^-$ have been prepared but $Co(S_2C_6H_3\text{-}4\text{-}CH_3)_2^-$ is resistant to adduct formation except by triethylphosphine.[8]

On the basis of their magnetic behavior the iron adducts fall into two categories. Those complexes with apical bases, such as phosphines, phosphites, arsines, phenyl isocyanide, and cyanide ion, which coordinate through soft donor atoms, have doublet ground states.[4,6] However the complexes in which the apical base coordinates through a hard donor atom (as is the case with amines, pyridine *N*-oxide, triphenylphosphine oxide, triphenylarsine oxide, halide ions, azide ion) exhibit quartet ground states.[4-12] It should be noted that the five-coordinate dithiocarbamato complexes $XFeS_2CNR_2$ (X = Cl, Br, I; R = alkyl) also have quartet ground states.[17] In contrast to the iron dithiolene adducts, all of the known cobalt adducts $(base)CoS_4C_4R_4^-$ have singlet ground states regardless of the nature of the apical donor.

Mechanism of Base Oxidations.—Although our studies on the mechanism of these oxidations are far from complete, several observations bearing on the mechanism have been made. The observation that certain metal complexes of molecular oxygen are effective in catalyzing the oxygenation of triphenylphosphine[18,19] and alkyl isocyanides[20] suggested that the iron dithiolene complexes might also form complexes with molecular oxygen. However no evidence for the existence of such complexes has been found. Solutions of $[(C_2H_5)_4N]_2[Fe_2S_8C_8(CN)_8]$ in acetone and *N,N*-dimethylformamide, of $[(C_4H_9)_4N]_2[Fe_2S_8C_8(CF_3)_8]$ in acetone and dichloromethane, and of the latter complex in the presence of an excess of triphenylphosphine, which generates $(C_6H_5)_3PFeS_4C_4(CF_3)_4^-$, in dichloromethane have been prepared under rigorous exclusion of oxygen. The electronic spectra of these oxygen-free solutions were recorded. The solutions were then exposed to oxygen at 1 atm pressure and shaken for from 5 to 10 min. The spectra of these oxygen-treated solutions exhibited no changes which could be ascribed to the formation of an oxygen adduct. In addition the polarography of the bis-dithiolene dimers and the base adducts is not affected by the presence of oxygen.

It is rather surprising that only the iron and not the cobalt dithiolene complexes are active in promoting the oxidations of triphenylphosphine and triphenylarsine. The polarographic half-wave potentials for simple one-electron oxidation of both the bis-dithiolene dimers and the bis-dithiolene adducts are more strongly dependent on the nature of the peripheral substituents than on the metal. Consequently the ease of oxidation of a pair of cobalt and iron complexes with similar substituents differs by less than 150 mV, but the cyano-substituted complexes are from 300 to 400 mV more difficult to oxidize than their perfluoromethyl-substituted counterparts.[4,6] It has been suggested that the ability to coordinate molecular oxygen is related to the ease of oxidation of the metal complex.[21] If this notion is correct and if coordinated oxygen were performing the oxidation of the apical bases, then similar behavior would be expected for both the cobalt and the iron dithiolenes and the activity of the complexes in promoting the oxidation of phosphines and arsines would be expected to be strongly dependent on the nature of the dithiolene substituents. Such behavior however is clearly not found.

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[16] R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

[17] R. H. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).

[18] G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, **6**, 92 (1967).

[19] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968).

[20] S. Otsuka, A. Nakamura, and Y. Tatsumo, *ibid.*, **91**, 6994 (1969).

[21] A. E. Martell and M. Calvin, "The Chemistry of Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1952, p 352.

Autoxidation of free phosphines has been demonstrated to be a radical chain process.[22-24] It may be that the iron complexes serve to initiate this process. The observation that certain amounts of the iron dithiolene complexes are destroyed during these reactions suggests that the activating agent may not be the parent complexes themselves. We have attempted the oxidation of triphenylphosphine in the presence of $FeCl_3$ in acetone and in the presence of $Na_2S_2C_2(CN)_2$. Traces of triphenylphosphine oxide and triphenylphosphine sulfide were obtained in the latter case, but neither reagent was nearly as effective in promoting oxidation on a synthetic scale as was $Fe_2S_8C_8(CN)_8^{2-}$ or $FeS_6C_6(CN)_6^{2-}$. Other compounds formed from the parent complexes may be agents that are active in promoting these oxidations.

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[22] S. A. Buckler, *J. Amer. Chem. Soc.*, **84**, 3093 (1962).

[23] M. B. Floyd and C. E. Boozer, *ibid.*, **85**, 984 (1963).

[24] However coordination of phosphines and arsine to Lewis acids markedly affects their oxidation. For example $(C_6H_5)_3AsAlCl_3$ is more rapidly oxidized by air to $(C_6H_5)_3AsO$ than is $(C_6H_5)_3As$ under similar conditions: D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 666 (1942). Aerial oxidation of coordinated phosphine in $CoCl_2(P(C_2H_5)_3)_2$ has been reported to produce only the phosphine oxide, whereas oxidation of free alkylphosphines produces approximately equal quantities of R_3PO and $R_2P(O)OR$: D. D. Schmidt and J. T. Yoke, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 5, 1969, No. INOR 203. What effect coordination has on the mechanism of the oxygenation reactions described herein is not clear, but coordination alone cannot be of overriding importance since the apical bases in the cobalt adducts are not activated.

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Octahedral Chromium(III) Complexes in Dipolar Aprotic Solvents. III.[1] Ion Association Studies in *N*,*N*-Dimethylformamide, *N*,*N*-Dimethylacetamide, and Dimethyl Sulfoxide by Conductance Measurements[2]

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Ion-pair association constants have been determined from conductance measurements for the association of chloride, bromide, iodide, perchlorate, and thiocyanate ions with a series of cations of the type *cis*- and *trans*-$CrXY(en)_2^+$, where "en" represents ethylenediamine or an *N*-methyl-substituted ethylenediamine, and X and Y represent monodentate monovalent negative ligands. The data have been treated by the equation of Fuoss, Onsager, and Skinner.[3] The solvents investigated are *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), and dimethyl sulfoxide (DMSO). In order to extend the comparison with our previous work on the analogous cobalt(III) complexes[4] some results are presented for selected rhodium(III) complexes. The results are presented together with limiting ionic conductances at 25°. The results confirm the previous conclusions regarding the importance of the dipolar nature of the complexes and the role of H bonding to the ethylenediamine nitrogen protons.[4] The association constants show remarkable independence of the identity of the metal ion and also show clearly that it is naive to overemphasize interionic electrostatic terms in comparing ion association constants, since in doing so one for the most part is emphasizing enthalpy terms associated with interionic interactions which, even when comparing these simple analogous systems, may not predominate over the corresponding modifications introduced in solvation energies.

Since the initial recognition by Taube and Posey[5] of the role of ion aggregates in substitution mechanisms of cationic octahedral complexes the importance of such fast ion association reactions as a prelude to rate-determining phenomena has been firmly established. As we have previously emphasized,[6] the weakness of ion association in aqueous systems of monovalent ions, the only ions for which precise conductance-based association constants are obtainable at the time, has made it difficult to compare the ion association constants, established as compatible with rate data, with independently established values. Ion association constants in water have been established through spectrophotometric methods based on the charge-transfer spectrum of the ion pair[7] but have given widely scattered values[8] and have been better applied either to systems involving highly charged cations, such as $Co(NH_3)_6^{3+}$ with halide ions,[9] or to ion pairs in poorly solvating solvents, such as tetramethylene sulfone,[6] than to the systems treated here.

The advantage of investigating the role of ion association in mechanisms by using dipolar aprotic solvents has

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[1] Part II: D. A. Palmer and D. W. Watts, *Aust. J. Chem.*, **21**, 2895 (1968).

[2] These results were presented in part at the XIIth International Conference of Coordination Chemistry, Sydney, Australia, Aug 1969.

[3] R. M. Fuoss, L. Onsager, and J. Skinner, *J. Phys. Chem.*, **69**, 2581 (1965).

[4] W. A. Millen and D. W. Watts, *J. Amer. Chem. Soc.*, **89**, 6858 (1967).

[5] H. Taube and F. A. Posey, *ibid.*, **75**, 1463 (1953).

[6] D. W. Watts, *Rec. Chem. Progr.*, **29**, 131 (1968).

[7] C. W. Davies, "Ion Association," Butterworths, London, 1962.

[8] L. G. Sillén and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964).

[9] (a) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953); (b) E. L. King, J. H. Esperson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).