V, Cr, Mo, W) have not been described before. Derivatives of the cationic species $[M(arene)_2]^+$ have always been prepared from aqueous solutions, or indirectly. For example, the iodide, the reineckate, and the picrate of the cation $[Cr(C_6H_6)_2]^+$ are isolated from its aqueous solutions.[3] $[Mo(C_6H_6)_2]I$ and $[W(C_6H_6)_2]I$ are obtained[5] by oxidation of the zerovalent complex with iodine.

No confirmation could be obtained that $V^0(arene)_2$ complexes can be formed by a disproportionation reaction of the type shown in eq. 3 involving the formation of V(V). The behavior of $[V(C_6H_3(CH_3)_3)_2]^+$ with water is best represented by a disproportionation of the type shown in eq. 4 followed by

$$V^{2+} + [V(arene)_2]^+ \longrightarrow V^{3+} + V^0(arene)_2 \qquad (9)$$

Reaction 9 becomes important only in alkaline medium, as a consequence of the enhanced reducing properties of V(II) in alkaline solutions.[10] In alkaline medium the over-all reaction can, therefore, be best represented as

$$3[V(C_6H_3(CH_3)_3)_2]^+ \longrightarrow 2V(C_6H_3(CH_3)_3)_2 + V^{3+} + 2C_6H_3(CH_3)_3 \qquad (10)$$

with, perhaps, to a small extent, a further reduction by V^{3+}.

$$[V(C_6H_3(CH_3)_3)_2]^+ + V^{3+} + H_2O \longrightarrow V(C_6H_3(CH_3)_3)_2 + VO^{2+} + 2H^+ \qquad (11)$$

The fact that the ratios $V(0)/V^{n+}$ in alkaline medium are lower than the theoretical value of 2 for eq. 10 can be explained by the competititive oxidation of the intermediate $V(OH)_2$ by H^+.

From the present study it appears that the chromium and vanadium systems are actually closely related, the only difference being that reaction 4 is much faster than (1). This explains the use of dithionite ions in the case of the synthesis of diarenechromium(0) complexes. The excellent yields reported[8] (as high as 98%) are to be attributed to the fact that reaction 1 is kinetically unfavored, enabling the reduction to be carried out exclusively by the dithionite. The dithionite, although used in a more recent preparation[23] of $V(C_6H_6)_2$, is probably not effective in this particular case because of the relatively high rate of reaction 4. The highest yields of dibenzenevanadium actually reported[23] are 46%. From the present study, it is seen that only two-thirds of the vanadium employed can be converted into $V^0(arene)_2$, corresponding to a maximum yield of 67%. Slightly higher yields could be obtained if conditions were found which suppress the spontaneous oxidation of $V(OH)_2$ by H^+ and if some advantage could be taken of the reduction by V(III) (eq. 11). There is no evidence, however, from the present study that reaction 11, although favored in principle by an alkaline medium, plays an important role.

The formation of uncomplexed metal ions in their highest oxidation states in the presence of the corresponding zerovalent complexes seems to be limited now to the case of molybdenum and tungsten, where $M(C_6H_6)_2$ and MO_4^{2-} in a molar ratio 5:1 were found[5] to be formed.

Acknowledgment.—The author is greatly indebted to Mr. Jean Moser and Mr. Robert Schopfer for the appreciated help in carrying out the experimental part of this work, to Miss I. Höflinger for measuring the infrared spectra and Dr. K. Noack for discussing them, and to Dr. H. D. Murdoch for reading the manuscript.

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Further Examples of Complexes Related by Electron-Transfer Reactions: Complexes Derived from Bis(trifluoromethyl)-1,2-dithietene

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A new series of four-coordinate bis chelate complexes of the general type $[MS_4C_4(CF_3)_4]^z$ has been prepared. This series is closely related to that previously described[1,2] containing $[MS_4C_4(CN)_4]^z$ complexes ($z = -1, -2$) in that its members undergo facile one-electron transfer reactions and those with $z = -1, -2$ are believed to have a planar structure. Complexes with $z = -2$, M = Pd, Pt, Co; $z = -1$, M = Pd, Pt, Co, Fe; and $z = 0$, M = Pt, Co, have been synthesized and supplement the nickel complexes with $z = 0, -1, -2$ obtained in earlier work.[1,2] The syntheses of all complexes are presented in detail. Chemical stabilities are discussed in terms of polarographic half-wave potentials. The results of magnetic susceptibility, electron spin resonance, nuclear magnetic resonance, and infrared spectral studies are presented and discussed in terms of probable electronic structures and chemical bonding in the complexes.

Introduction

Recent work in these laboratories[1,2] has demonstrated that complexes of the general type **1** undergo reversible and unusually facile electron-transfer reactions which have permitted the synthesis of a wide variety of complexes with total charge $z = 0, -1, -2$. The principal portion of the previous work has dealt with

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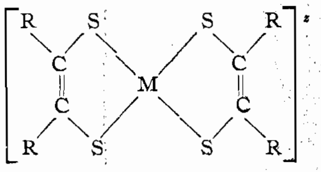
[1] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963).

[2] A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).



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complexes in the R = CN series containing M = Cu, Au, Ni, Pd, Pt, or Co. Oxidation of these bis(*cis*-1,2-dicyanoethylene-1,2-dithiolato) complexes with $z = -2$[3] by a variety of agents has afforded the unique series $[MS_4C_4(CN)_4]^-$ which has been examined by magnetic susceptibility and electron spin resonance studies. The Cu and Co complexes are diamagnetic whereas those of Ni, Pd, and Pt contain the metal in the doublet spin state and represent new magnetic species. Further oxidation in the cyano series to the $z = 0$ complexes could not be achieved.

The only known complexes with $z = 0$ are the nickel complexes with R = C_6H_5[4] and CF_3. The latter complex, together with the $z = -1$ and -2 reduction products, was synthesized in our previous work.[1,2] In view of the considerable stability associated with each member of the nickel series, a more general study of these trifluoromethyl complexes has been carried out in an attempt to assess the generality of these electron-transfer reactions and the stabilities of the products obtained. In addition to species containing nickel, complexes have now been obtained containing palladium, platinum, cobalt, and iron. The syntheses and characterization of these species are discussed herein together with certain results from nuclear and electron spin resonance and magnetic susceptibility studies. Detailed considerations of the e.s.r. and optical spectral results will be communicated separately.

Experimental

Preparation of Compounds.—Disodium *cis*-1,2-dicyanoethylene-1,2-dithiolate, $Na_2S_2C_2(CN)_2$, was prepared by the method of Bähr and Schleitzer.[5] Bis(trifluoromethyl)-1,2-dithietene was obtained by the gas phase reaction of sulfur and hexafluorobutyne-2 according to the procedure of Krespan.[6] The fraction boiling at 96–98° was used in the following preparations. The compound was freshly distilled before use.

All melting points are uncorrected.

$[(C_6H_5)_3P]_2NiS_2C_2(CF_3)_2$.—To a solution of 1.06 g. of bis(triphenylphosphine)nickel dicarbonyl in 20 ml. of dichloromethane was added 0.38 g. of $(CF_3)_2C_2S_2$ in 5 ml. of dichloromethane. The solution turned dark green with rapid evolution of carbon monoxide. After gas evolution was complete, the solution was concentrated to 10 ml. and the product crystallized on standing to give olive-green microcrystals. After washing with dichloromethane (2 ml.) and *n*-pentane (10 ml.), 0.70 g. (50%) of product was obtained; dec. pt. 235°.

Anal. Calcd.: C, 59.35; H, 3.74; S, 7.92; F, 14.08. Found: C, 59.42; H, 3.74; S, 8.14; F, 13.90.

$[(C_6H_5)_3P]_2PdS_2C_2(CF_3)_2$.—$(CF_3)_2C_2S_2$ (2.4 g.) was added to 12 g. of freshly recrystallized tetrakis(triphenylphosphine)palladium[7] in 500 ml. of dichloromethane. A blood red color developed immediately; the solution was allowed to stand for 2 hr., during which time the product was slowly deposited as pale pink crystals. After filtration and washing with dichloromethane, 6.4 g. (72%) of product was obtained, very sparingly soluble in common organic solvents.

Anal. Calcd.: C, 56.05; H, 3.53; S, 7.48; F, 13.30. Found: C, 55.60; H, 3.57; S, 7.64; F, 13.11.

$[(C_6H_5)_3P]_2PtS_2C_2(CF_3)_2$.—$(CF_3)_2C_2S_2$ (3.2 g.) was added to a solution of 4.5 g. of tris(triphenylphosphine)platinum[8] dissolved in 200 ml. of dichloromethane. The deep yellow color of the initial solution lightened upon standing for 2 hr. and lemon-yellow crystals were slowly deposited; 2.8 g. (65%) of product was collected.

Anal. Calcd.: C, 50.79; H, 3.20; S, 6.78; F, 12.05. Found: C, 50.71; H, 3.33; S, 6.88; F, 11.51.

$[(C_6H_5)_3P]_2NiS_2C_2(CN)_2$.—Bis(triphenylphosphine)nickel dibromide[9] (2.58 g.) and 0.66 g. of $Na_2S_2C_2(CN)_2$ were mixed as solids, and 50 ml. of acetone was added. The mixture was shaken until no more of the original nickel complex remained. The solution was filtered, and the slow addition of 50 ml. of water effected separation of the product as brown crystals. After filtration and washing with 50% aqueous acetone, 2.2 g. (89%) of air-dried product was obtained.

Anal. Calcd.: C, 66.41; H, 4.18; N, 3.87. Found: C, 66.19; H, 4.44; N, 3.88.

$[(C_6H_5)_3P]_2MS_2C_2(CN)_2$ M = Pd, Pt.—The two complexes were prepared by shaking 0.005 mole of the bis(triphenylphosphine)dichloro complex with 0.005 mole of $Na_2S_2C_2(CN)_2$ in 50 ml. of acetone for 1 hr. The resulting solid was filtered, washed with 50 ml. of water, 25 ml. of acetone, and twice with 10 ml. of *n*-hexane. The palladium complex was obtained in 88% yield as deep pink microcrystals; the platinum complex was isolated in 65% yield as brilliant yellow crystals slightly soluble in acetone.

Anal. Calcd. (M = Pd): C, 62.28; H, 3.92; N, 3.63. Found: C, 62.35; H, 4.13; N, 3.53. Calcd. (M = Pt): C, 55.87; H, 3.52; N, 3.26. Found: C, 56.04; H, 3.59; N, 3.30.

$[PtS_4C_4(CF_3)_4]$.—$[(C_6H_5)_3P]_2PtS_2C_2(CF_3)_2$ (8.9 g.) was refluxed in 250 ml. of benzene containing 7.2 g. of $(CF_3)_2C_2S_2$ for 18 hr. The deep purple solution was filtered from a very small amount of starting complex and the solvent removed *in vacuo*. The residual oily solid was dissolved in 20 ml. of benzene and treated with 200 ml. of *n*-pentane. After 5 min. standing the intense purple solution was decanted from a sticky oil. This procedure was repeated two or three times until the *n*-pentane solution was colorless. The residual red oil was treated with 30 ml. of 70% ethanol–water and filtered to remove triphenylphosphine sulfide. This solution was found to contain the anion $[PtS_4C_4(CF_3)_4]^-$ and its isolation is described below. The combined purple extracts were allowed to stand for 1 hr. while additional triphenylphosphine sulfide crystallized. The solvent was removed *in vacuo* to give oily purple crystals, which were dried on a porous plate and then subjected to vacuum drying at room temperature for 24 hr. In this way a small amount of a yellow malodorous oil was removed. After sublimation [110–130° (0.1 mm.)] onto a water-cooled probe, 3.1 g. (46%) of brilliant red-purple needles, pure enough for the reductions described below, was collected. An analytical sample was obtained by recrystallization from benzene; m.p. 174–175° (sealed tube); mol. wt. calcd. 647, found 645 (37°, benzene).

Anal. Calcd.: C, 14.84; H, 0.00; S, 19.81; F, 35.22. Found: C, 14.64; H, 0.04; S, 19.65; F, 35.37.

$[(C_6H_5)_4P][PtS_4C_4(CF_3)_4]$.—To the filtrate of the 70% ethanol-water solution was added an excess of tetraphenylphosphonium chloride in ethanol. Small red-brown crystals immediately precipitated. These were collected, washed with water, twice

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[3] H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

[4] G. N. Schrauzer and V. Mayweg, *ibid.*, **84**, 3221 (1962).

[5] G. Bähr and G. Schleitzer, *Ber.*, **90**, 438 (1957).

[6] C. G. Krespan, *J. Am. Chem. Soc.*, **83**, 3434 (1961).

[7] L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1186 (1957).

[8] L. Malatesta and C. Cariello, *ibid.*, 2323 (1958).

[9] L. M. Venanzi, *ibid.*, 719 (1958).

recrystallized from ethanol–water, and dried *in vacuo* overnight; 2.3 g. (26%) of product was obtained; m.p. 173.5–175°.

Anal. Calcd.: C, 38.95; H, 2.04; S, 13.00; F, 23.11. Found: C, 38.77; H, 2.09; S, 12.79; F, 23.25.

$[(C_6H_5)_4As][PtS_4C_4(CF_3)_4]$.—$PtS_4C_4(CF_3)_4$ (2.0 g.) was dissolved in a mixture of 25 ml. of acetone and 80 ml. of ethanol. The color changed over the course of 5 min. from blue-green to deep red-brown. To the solution was added 2.0 g. of tetraphenylarsonium chloride in 20 ml. of ethanol. Sufficient water was added dropwise to produce incipient crystallization. The solution was allowed to stand 1 hr., and the product was collected and purified, as was the corresponding tetraphenylphosphonium salt, to yield 1.15 g. (36%) of brown needles; m.p. 168–169°.

Anal. Calcd.: C, 37.29; H, 1.96; S, 12.44; F, 22.12. Found: C, 37.89; H, 2.15; S, 12.88; F, 22.36.

$[(C_6H_5)_4As]_2[PtS_4C_4(CF_3)_4]$.—$PtS_4C_4(CF_3)_4$ (2.0 g.) was shaken with 200 g. of 1% sodium amalgam in 70 ml. of tetrahydrofuran until the color changed to deep golden yellow. The solution was decanted and filtered into an aqueous solution of excess tetraphenylarsonium chloride in 150 ml. of water. An immediate precipitate of golden yellow plates occurred. The crude product was recrystallized from acetone–alcohol (1:9 v./v.) to yield 3.1 g. (70%); m.p. 240–241.5° dec. Solutions are moderately stable to aerial oxidation; the solid is attacked only very slowly by air over the course of several months.

Anal. Calcd.: C, 47.56; H, 2.85; S, 9.07; F, 16.12. Found: C, 47.37; H, 3.01; S, 8.84; F, 16.36.

$[C_9H_{10}N][PdS_4C_4(CF_3)_4]$.—$[(C_6H_5)_3P]_2PdS_2C_2(CF_3)_2$ (4.1 g.) and 3.25 g. of $(CF_3)_2C_2S_2$ were refluxed in 200 ml. of benzene for 3 hr. A transient purple color first developed and then the solution turned progressively more brown as the reaction proceeded. The solvent was removed *in vacuo* to leave a dark brown oil. The oil was treated with 50 ml. of 70% aqueous ethanol to remove triphenylphosphine sulfide upon filtration. Excess N-methylquinolinium iodide dissolved in the aqueous ethanol was added to the clear brown solution. Water was added slowly to cause precipitation of the crude product. The product was recrystallized from ethanol with considerable loss to afford 0.80 g. (24%) of pure product as red-brown needles; m.p. 245–247° dec.

Anal. Calcd.: C, 29.55; H, 1.46; N, 2.03; S, 18.56; F, 33.00. Found: C, 29.38; H, 1.43; N, 2.13; S, 19.14; F, 32.97.

$[(C_6H_5)_4As]_2[PdS_4C_4(CF_3)_4]$.—$[(C_6H_5)_3P]_2PdS_2C_2(CF_3)_2$ (4.8 g.) and 3.1 g. of $(CF_3)_2C_2S_2$ were allowed to react as above and the clear brown aqueous alcohol solution obtained was treated with 30 ml. of 20% alcoholic hydrazine solution added dropwise with stirring. No marked color change was observed with the evolution of N_2 gas. Excess tetraphenylarsonium chloride in 20 ml. of ethanol was added to this solution. The product separated slowly as needles in *ca.* 1–2 min. These needles were collected and washed once with cold 95% ethanol (25 ml.), twice with *n*-pentane (50 ml.), and dried *in vacuo* to give 3.05 g. (41%) of the pure product as pale green needles; m.p. 248–251° dec.

Anal. Calcd.: C, 50.75; H, 3.04; S, 9.68; F, 17.20. Found: C, 50.64; H, 3.20; S, 9.44; F, 17.10.

$[CoS_4C_4(CF_3)_4]$.—Dicobalt octacarbonyl (4.65 g.) dissolved in 200 ml. of *n*-pentane was added slowly to a stirred solution of 12.1 g. of $(CF_3)_2C_2S_2$ in 600 ml. of *n*-pentane under reflux conditions and in a nitrogen atmosphere. The golden yellow color of the solution rapidly darkened and carbon monoxide was briskly evolved. After addition was complete (45 min.) the solution was brown-purple in color. Further refluxing for 1 hr. produced a blue-black solution and no further gas evolution. The hot solution was filtered rapidly through Super-Cel; the resultant solution was reduced *in vacuo* to a volume of 200 ml. and allowed to stand overnight. The crystallized product (8 g.) was collected and washed twice with *n*-pentane (25 ml.). It did not melt below 250° and the infrared spectrum indicated the presence of a small amount of terminal carbonyl (2128, 2087 cm.$^{-1}$).[10] The product was boiled with carbon tetrachloride for 10 min. and the hot solution filtered to remove a black amorphous material. Evaporation of the filtrate to *ca.* 20 ml. and subsequent slow cooling yielded 5.3 g. of shiny black crystals, m.p. 184–187° (sealed tube), whose infrared spectrum showed the absence of bands associated with the carbonyl-containing impurity. Two further recrystallizations from carbon tetrachloride afforded 4.5 g. (32%) of pure product; m.p. 188.5–189.5° (sealed tube); mol. wt. calcd. 511, found 993, 1020 (37°, CCl_4).

Anal. Calcd.: C, 18.79; H, 0.00; S, 25.08; F, 44.59. Found: C, 18.48; H, 0.04; S, 24.83; F, 44.86.

$[(C_2H_5)_4N][CoS_4C_4(CF_3)_4]$ (A).—The procedure for the preparation of $CoS_4C_4(CF_3)_4$ was carried out as above to the point at which the crude crystallized product (8 g.) was collected. This material was treated with 60 ml. of 1:1 v./v. acetone–dimethylformamide and allowed to stand for 5 min. as the color changed to an intense green. Water (200 ml.) was added and the solution filtered through Super-Cel. To the resultant solution was added excess tetraethylammonium bromide in aqueous solution. The finely divided precipitate so obtained was collected on Super-Cel, washed with water and *n*-pentane, and eluted with acetone to give a clear green solution. Isobutyl alcohol (25 ml.) was added to this solution and most of the acetone removed by heating. On slow cooling 10.9 g. (63% based on cobalt carbonyl) of lustrous black plates was obtained; m.p. 267.5–270.5°.

Anal. Calcd.: C, 29.95; H, 3.14; N, 2.18; S, 19.99; F, 35.54. Found: C, 29.79; H, 3.29; N, 2.29; S, 20.17; F, 35.62.

(B).—The monoanion can also be obtained by reduction of pure $CoS_4C_4(CF_3)_4$ with acetone–dimethylformamide by the procedure described above; the yield is 78% based on the starting cobalt complex.

$[(C_2H_5)_4N]_2[CoS_4C_4(CF_3)_4]$.—In this preparation all operations were carried out in a nitrogen atmosphere. $[(C_2H_5)_4N][CoS_4C_4(CF_3)_4]$ (3.0 g.) in 70 ml. of degassed tetrahydrofuran was shaken for 10 min. with 200 g. of 1% sodium amalgam. The dark green color of the solution rapidly became deep orange. The solution was decanted from the amalgam and filtered rapidly into a solution of a large excess of tetraethylammonium bromide in 100 ml. of degassed 95% ethanol. Orange needle-like crystals formed immediately. The solution was cooled by pumping, and the product was collected, washed with 100 ml. of cold degassed alcohol, and recrystallized from acetone–ethanol. Bright orange crystals were obtained (1.85 g., 51%), dec. pt. 245°. The compound is immediately oxidized in solution but when dry can be handled for several hours in air without evident decomposition.

Anal. Calcd.: C, 37.35; H, 5.22; N, 3.63; S, 16.62; F, 29.54. Found: C, 37.05; H, 5.27; N, 3.65; S, 15.66; F, 29.97.

$[FeS_6C_6(CF_3)_6]$.—Iron pentacarbonyl (4 ml., 5.8 g.) and 14.0 g. of $(CF_3)_2C_2S_2$ were heated with gentle reflux in 600 ml. of *n*-pentane under a nitrogen atmosphere. During the first 3 hr. the solution slowly assumed a magenta color. Within the next 2 hr. of reflux the solution became intensely purple. Refluxing was continued for an additional 10 hr. to give an intensely blue-black solution. The warm solution was filtered to remove a small amount of insoluble material. The filtrate was allowed to stand 24 hr. in the absence of air at 5°. During this time large lustrous black crystals were deposited. After filtration and washing with *n*-pentane, 6.15 g. (28%) was collected; m.p. 189–190° (sealed tube).

Anal. Calcd.: C, 19.65; H, 0.00; S, 26.20; F, 46.57. Found: C, 19.50; H, 0.03; S, 26.05; F, 46.70.

$[(C_2H_5)_4N][FeS_4C_4(CF_3)_4]$.—$FeS_6C_6(CF_3)_6$ (2.5 g.) was dissolved in 30 ml. of acetone and the resultant green solution was diluted with 100 ml. of water. The solution was filtered through Super-Cell and to the filtrate was added 2.1 g. of tetraethylammonium bromide in 50 ml. of water. The very finely divided precipitate was collected on Super-Cel, washed first with water,

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[10] Reaction of $Co_2(CO)_8$ and $(CF_3)_2C_2S_2$ under radically different conditions (R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963)) leads to the compound $C_4F_6S_2CoCO$, the stronger bands of which are observable in the spectrum of the solid at this point.

and then washed repeatedly with *n*-pentane until the washings were colorless. The product was eluted with acetone and isolated as was the corresponding cobalt salt to give 1.6 g. (74%) of lustrous black crystals; m.p. 290–295° dec.

Anal. Calcd.: C, 30.10; H, 3.16; N, 2.19; S, 20.09; F, 35.71. Found: C, 30.64; H, 3.25; N, 2.16; S, 19.81; F, 34.75.

$[(C_6H_5)_4As][FeS_4C_4(CF_3)_4]$.—This compound was prepared in 70% yield by the same procedure as that used for the tetraethylammonium salt; m.p. 251–253°.

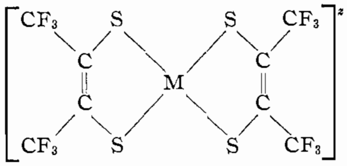
Anal. Calcd.: C, 43.11; H, 2.26; S, 14.39; F, 25.56. Found: C, 42.67; H, 2.23; S, 14.85; F, 25.29.

Infrared Spectra.—The following results were obtained in fluorolube (4000–1350 $cm.^{-1}$) and Nujol (1350–650 $cm.^{-1}$) mulls. $[NiS_4C_4(CF_3)_4]$: 1422 (m), 1377 (m), 1267 (w), 1222 (s), 1193 (s), 1179 (s), 1152 (w), 1055 (w), 928 (m), 858 (m), 732 (s), 721 (sh,m), 697 (m), 694 (m). $[PtS_4C_4(CF_3)_4]$: 1422 (m), 1376 (m), 1264 (w), 1230 (s), 1188 (s), 1149 (s), 1057 (m), 927 (w), 855 (m), 731 (s), 722 (sh, m), 701 (m), 697 (m). $[CoS_4C_4(CF_3)_4]$: 1466 (m), 1408 (m), 1383 (mw), 1370 (w), 1267 (w), 1229 (s), 1198 (s) 1175 (s), 1044 (m), 957 (vw), 917 (m), 859 (w), 738 (s), 727 (s), 697 (s). $[FeS_8C_8(CF_3)_8]$: 1517 (ms), 1433 (m), 1385 (w), 1368 (vw), 1220 (s), 1189 (m), 1170 (s), 1019 (m), 942 (mw), 891 (s), 853 (m), 732 (s), 717 (s), 693 (s), 683 (w).

Physical Measurements.—Magnetic susceptibility, electron spin resonance, and polarographic measurements were made as previously described.[2] Fluorine nuclear magnetic resonance spectra were obtained on a Varian V-4300 spectrometer operating at 40 Mc./sec. All measurements were referenced to benzotrifluoride as an internal standard to avoid bulk susceptibility corrections. Line positions were determined by an interpolation method using an audio oscillator monitored by a frequency counter. Infrared spectra were determined using a Perkin-Elmer 237 grating spectrometer. Molecular weight measurements were made at 37° with a Mechrolab osmometer calibrated with benzil. Optical spectra were recorded on a Cary Model 14 spectrometer.

Results and Discussion

The compounds described are of the general types **2** and **3**. Those of type **2** with $z = 0$, M = Pt, Co; $z = -1$, M = Pd, Pt, Co, Fe; and $z = -2$, M = Pd, Pt, Co, clearly represent an extension of our previous studies.[1,2] These studies have led to the isolation and characterization of series of planar complexes of type **1** containing transition metals stabilized in several valence states by unsaturated chelating ligands whose donor atoms are sulfur. Compounds of this type have been shown to undergo facile electron-transfer reactions. Type **3** complexes with R = CN or CF_3 have been isolated as intermediates in some preparations. These monochelated species are all crystalline solids, give nonconducting solutions in nitromethane, and do not readily undergo oxidation–reduction reactions. The composition of all new compounds has been firmly established by elemental analyses, molecular weights, and conductivities. Conductance data in nitromethane solution, when compared with our previous results[2] and those of others,[11] show that all salts function as uni-univalent or bi-univalent electrolytes.



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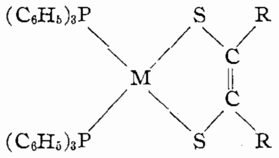

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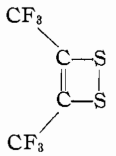
At present no direct evidence of the structures of any of the complexes of the R = CF_3 series can be given. However, the optical spectral properties of the dinegative anions of the CF_3 and CN series are very similar, particularly with respect to the ligand field absorptions. Inasmuch as it has been established from X-ray structural determinations that the complex anions in $[(CH_3)_4N]_2[NiS_4C_4(CN)_4]$[12a] and $[(n\text{-}C_4H_9)_4N]_2[CoS_4C_4(CN)_4]$[12b] are planar and that the salts $[(n\text{-}C_4H_9)_4N]_2[MS_4C_4(CN)_4]$ (M = Ni, Pd, Pt, Co) are isomorphous,[3] it is logically assumed that the dianions of the perfluoromethyl series are also planar. The monoanions are likewise assumed to be planar on the basis of spectral comparisons with the analogous cyano complexes, whose planar structures have been inferred from isomorphism studies.[2]

Synthetic Studies.—All complexes of the R = CF_3 series were obtained from the starting material bis(perfluoromethyl)-1,2-dithietene,[6] **4**. The particular advantage of this compound is that its use has allowed isolation in three series of complexes (Ni, Pt, Co) of the initial number of each series with $z = 0$.



4

The further members of the series are then obtained by reduction of these neutral complexes. Nickel tetracarbonyl[2] and dicobalt octacarbonyl react smoothly to yield the complexes **2** with $z = 0$. The preparation of the analogous platinum complex is less direct in the absence of a simple platinum carbonyl. However, reaction of **4** with the Pt(0) species, $[(C_6H_5)_3P]_3Pt$,[8] yields the desired product. The reaction proceeds in two stages. Two equivalents of **4** react in dichloromethane solution to give the intermediate **3** (M = Pt, R = CF_3), which has been isolated and definitely characterized. Further reaction of this compound in benzene with excess **4** yields bis(*cis*-1,2-trifluoromethylethylene-1,2-dithiolato)platinum and a significant amount of its monoanion. Reaction of **4** and $[(C_6H_5)_3P]_4Pd$[7] affords the corresponding intermediate, which upon further treatment with **4** under the same conditions as in the platinum reaction gives only $[PdS_4C_4(CF_3)_4]^-$.

The polarographic half-wave potentials set out in Table II reveal that the neutral complexes are uniformly quite strong oxidizing agents. Like the nickel complex[2] the platinum and cobalt complexes are reduced to their monoanions simply by treatment with a variety of basic solvents. In the preparation of the palladium monoanion from the intermediate **3** a trans-

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[11] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

[12] (a) R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 113 (1964); (b) J. D. Forrester, A. Zalkin, and D. H. Templeton, private communication.

TABLE I

CONDUCTIVITY AND MAGNETIC SUSCEPTIBILITY DATA[a]

		Solid		Solution		
Compound	Λ^c	$10^6\chi_{\text{corr}}^{\text{M}}$	$\mu_{\text{eff}}(\beta)^d$	$10^6\chi_{\text{corr}}^{\text{M}}$	Solvent	$\mu_{\text{eff}}(\beta)^d$
$[PtS_4C_4(CF_3)_4]$	...	Dia.^{b}	0	...	...	...
$[(C_6H_5)_4P][PtS_4C_4(CF_3)_4]$	63	1322	1.79	1302	Acetone	1.78
$[(C_6H_5)_4As][PtS_4C_4(CF_3)_4]$	64	1340	1.80	...	...	...
$[(C_6H_5)_4As]_2[PtS_4C_4(CF_3)_4]$	150	Dia.^{b}	0	...	...	...
$(C_9H_{10}N)[PdS_4C_4(CF_3)_4]$	75	...	...	1256	Acetone	1.73
$[(C_6H_5)_4As]_2[PdS_4C_4(CF_3)_4]$	150	Dia.^{b}	0	...	...	...
$[CoS_4C_4(CF_3)_4]^f$	...	Dia.^{b}	0	...	...	...
$[(C_2H_5)_4N][CoS_4C_4(CF_3)_4]$	85	Dia.^{b}	0	...	...	...
$[(C_2H_5)_4N]_2[CoS_4C_4(CF_3)_4]^e$	...	1772	2.06	...	...	...
$[(C_2H_5)_4N][FeS_4C_4(CF_3)_4]$	85	900	1.48	1363	Acetone	1.83
				6477	DMF	3.98
$[(C_6H_5)_4As][FeS_4C_4(CF_3)_4]$	70	794	1.39	...	...	...

[a] All data measured at ambient room temperature, 23–26°. [b] Accurate susceptibility not determined. [c] Cm.^{2} mole^{-1} ohm^{-1} in $\sim 10^{-3} M$ nitromethane solution. [d] Calculated from the Curie law, $\mu_{\text{eff}} = 2.84(\chi_{\text{corr}}^{\text{M}} T)^{1/2}$. [e] Measurements in solution not made because of rapid oxidation. [f] Insufficiently soluble for accurate measurement in solution.

ient intense violet color was noted in the first 30 sec. of reaction. This observation suggests that the neutral palladium complex is first formed and then quickly reduced by triphenylphosphine or triphenylphosphine sulfide, which was isolated from the reaction mixture, or by a species produced in the desulfurization of **4**. The neutral platinum complex, which is less easily reduced, still suffers some reduction under identical reaction conditions, presumably by the same process which effects complete reduction in the palladium system. As pointed out previously for the nickel complexes, the half-wave potentials for the platinum and cobalt couples $(M)^- \rightleftharpoons (M)^0 + e^-$ are considerably more positive ($\sim$0.4–0.8 v.) than those for the oxidation of $TCNE^{\cdot -}$ and $TCNQ^{\cdot -}$, the neutral forms of which are regarded as the strongest organic π-acids.[13]

Polarographic half-wave potentials are especially useful for the purpose of systematizing the chemical stabilities of complexes and suggesting that oxidant or reductant needed to effect a given electron-transfer reaction. In Table II are listed half-wave potentials for complexes obtained in this work, and, for purposes of comparison, the potentials measured previously for the R = CN series of complexes are included. With reference to the potentials certain generalizations relating to stabilities in solution can be made. All dianions in couples less positive than $\sim$+0.08 v. are readily oxidized, whereas all reduced species in couples more positive than this value are stable to aerial oxidation. The oxidized forms in couples more positive than $\sim$+0.20 v. are unstable to reduction by weakly basic solvents such as ketones and alcohols, while those in couples within the approximate range −0.12 to +0.20 v. are reduced by stronger bases such as aromatic amines. Oxidized forms in couples more negative than $\sim$−0.12 v. can be reduced by stronger reducing agents such as hydrazine or sodium amalgam. Finally, reduced forms in couples less positive than $\sim$+0.44 v. can be oxidized by iodine. Of all the complexes $[NiS_4C_4(CF_3)_4]$ is the most powerful one-electron oxidizing agent, and examples of its use in preparing monoanion complexes have been given previously.[2]

TABLE II

POLAROGRAPHIC HALF-WAVE POTENTIALS OF COMPLEXES IN ACETONITRILE SOLUTION

R	Couple	$E^{1/2}$, v.^{d}
$C_6H_5{}^a$	$(Ni)^{-2} \rightleftharpoons (Ni)^- + e^-$	$-0.74^{b,e}$
CF_3	$(Co)^{-2} \rightleftharpoons (Co)^- + e^-$	-0.398
CF_3	$(Pt)^{-2} \rightleftharpoons (Pt)^- + e^-$	-0.267
CF_3	$(Ni)^{-2} \rightleftharpoons (Ni)^- + e^-$	$-0.121^{c,e}$
CN	$(Co)^{-2} \rightleftharpoons (Co)^- + e^-$	$+0.050^e$
CF_3	$(Pd)^{-2} \rightleftharpoons (Pd)^- + e^-$	$+0.081$
CN	$(Pt)^{-2} \rightleftharpoons (Pt)^- + e^-$	0.210^e
$C_6H_5{}^a$	$(Ni)^- \rightleftharpoons (Ni)^0 + e^-$	$0.224^{b,e}$
CN	$(Ni)^{-2} \rightleftharpoons (Ni)^- + e^-$	0.226^e
CN	$(Cu)^{-2} \rightleftharpoons (Cu)^- + e^-$	0.330^e
CN	$(Pd)^{-2} \rightleftharpoons (Pd)^- + e^-$	0.440^e
CF_3	$(Co)^- \rightleftharpoons (Co)^0 + e^-$	0.535
CF_3	$(Fe)^- \rightleftharpoons (Fe)^0 + e^-$	0.71^f
CF_3	$(Pt)^- \rightleftharpoons (Pt)^0 + e^-$	0.819
CF_3	$(Pd)^- \rightleftharpoons (Pd)^0 + e^-$	0.963
CF_3	$(Ni)^- \rightleftharpoons (Ni)^0 + e^-$	$0.997^{c,e}$

[a] Measured in DMSO solution. [b, c] In each case the two waves possess nearly equal diffusion currents. [d] Obtained at ambient room temperature; potentials corrected for *iR* drop in polarographic cell; estimated error ±0.01 v. [e] Data from ref. 2. [f] Measured potentials are erratic with time; this value corresponds to the initial oxidation in a freshly prepared solution; oxidation product unknown.

The half-wave potentials show that for complexes of the type **1** with given M and *z* oxidative stability always decreases in the order R = CN > CF_3. In the case of the nickel complexes the order can be extended to CN > CF_3 > C_6H_5. The presence of the strongly electron-withdrawing groups cyano and perfluoromethyl obviously stabilizes species with the largest number of valence electrons, and their replacement by a poor electron-withdrawing group such as phenyl renders isolation of complexes such as $[NiS_4C_4(C_6H_5)_4]^{-2}$

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(13) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962). The potentials of the neutral nickel, platinum, and cobalt complexes strongly suggest that these compounds, like TCNE[14] and TCNQ,[13] might form charge-transfer complexes with organic π-bases. Extensive spectral studies of the nickel and platinum complexes and of the weaker electron acceptor $[NiS_4C_4(C_6H_5)_4]^0$ with relatively strong π-bases[14] in solution revealed no detectable charge-transfer complex formation.

(14) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

TABLE III

ELECTRON SPIN RESONANCE DATA[a]

Complex	Solution[b]		Glass[c]		
	$\langle g \rangle$	$\langle a \rangle$, gauss	g_1	g_2	g_3
$[NiS_4C_4(CF_3)_4]^-$	2.0618 ± 0.0002	. . .	1.996	2.044	2.137
$[PdS_4C_4(CF_3)_4]^-$	2.0238 ± 0.0002	7.7 ± 0.3 (Pd^{105})	1.955	2.049	2.065
$[PtS_4C_4(CF_3)_4]^{-}$[d]	2.039 ± 0.001	82 ± 7 (Pt^{195})	1.823	2.074	2.210
$[CoS_4C_4(CF_3)_4]^{-2}$	. . .	. . .	2.04 ± 0.02[e]		2.71 ± 0.01[e]

[a] All measurements made in 50% v./v. $CHCl_3$–DMF. [b] Room temperature data. [c] Results obtained at ~100°K. [d] Anisotropic hyperfine tensor for Pt^{195} interaction in the glass: $|a_1| = 118 \pm 5$, $|a_2| = 129 \pm 5$, $|a_3| = 0 \pm 7$ gauss. [e] Uncertainty due to large line width.

very difficult.[2] In this connection the recent isolation[15] of bis complexes derived from the divalent ions of copper, nickel, cobalt, and iron and toluene-3,4-dithiol as monoanions rather than dianions very likely is related to the fact that the parent ligand system contains no strongly electron-withdrawing groups. The reaction probably first generates the dianion which is spontaneously oxidized by air. One further stability trend is noticeable. As one proceeds from copper to the left in the first transition series the stabilities of the dianions decrease in the order Cu > Ni > Co >>> Fe. The iron dianions of the CF_3 and CN series have not been isolated. Attempted polarographic reduction of $[FeS_4C_4(CF_3)_4]^-$ in acetonitrile yielded no reduction wave up to −1.8 v. Further and more quantitative considerations of stability will be deferred until the structures of the complexes are established with greater certainty.

We regard the reactions of **4** with metal carbonyls to be, in effect, oxidation–reduction reactions whereby the metal attains, in a formal sense, the +4 oxidation state. The $z = -1$ complexes then formally contain M(III) and the $z = -2$ complexes M(II). The complexes can then be considered derivatives of the anion $(CF_3)_2C_2S_2^{-2}$, which is as yet unprepared. This formulation is to be compared with that of the $M(TDT)_2^-$ complexes (TDT = toluene-3,4-dithiolate) which are claimed to contain M(I) and two $TDT^{\cdot-}$ ligands whose spins are paired.[15] It has been suggested[16] that $[MS_4C_4(CN)_4]^-$ complexes have analogous formulation. We find no evidence in either the cyano or trifluoromethyl series that this formulation is to be preferred, and in several cases, *viz.*, $[MS_4C_4R_4]^-$, R = CN, CF_3, M = Ni, Pd, Pt, it is very probably incorrect. Evidence bearing on this point follows in the next section.

The reaction of **4** with iron pentacarbonyl in *n*-pentane gives purple-black tris(*cis*-1,2-ditrifluoromethylethylene-1,2-dithiolato)iron, $[FeS_6C_6(CF_3)_6]$. This complex is extremely reactive, is readily reduced and decomposed by basic solvents, and is sensitive to moist air. Treatment of the complex with aqueous acetone affords $[FeS_4C_4(CF_3)_4]^-$. This tris chelate complex represents one member of a series of complexes of the type $[MS_6C_6R_6]^z$ which, like the planar bis chelates, are interrelated by facile one-electron-transfer reactions. The properties of the tris iron complex will be discussed fully in forthcoming communications dealing with tris complexes of unsaturated sulfur ligands.[16]

Magnetic Susceptibility and Electron Spin Resonance Results.—The results of these studies are given in Tables I and III. As expected only the monoanions of the Pd and Pt series are paramagnetic and have a doublet ground state. Similar results have been obtained in Ni, Pd, and Pt complexes of the R = CN series and for $[NiS_4C_4(CF_3)_4]^-$, which has an average moment of 1.84 B.M. in the solid and 1.88 B.M. in solution.[2] Electron-nucleus hyperfine splittings due to Pd^{105} (22.2%, $I = 5/2$) and Pt^{195} (33.7%, $I = 1/2$) were readily detected and the coupling constants are given in Table III. The observation of the metal–nuclear hyperfine interaction, as well as the large deviations of the principal g values from the free electron value, indicate that in each case the unpaired electron is at least partially localized in the orbitals of the metal.

The most noteworthy feature of e.s.r. spectra of the Ni, Pd, and Pt monoanions is the considerable anisotropy of the g-tensor. Nearly identical anisotropies have been found in the corresponding $[MS_4C_4(CN)_4]^-$ complexes.[1] Now if the complexes $[NiS_4C_4R_4]^-$, for example, are to be regarded as containing Ni(I), the odd electron would most probably be in the σ^*-(b_{1g}) molecular orbital, which in D_{2h} symmetry consists mainly of the metal d_{xy} orbital. This electron configuration should give rise to near axial symmetry. In order to provide a thorough test of the axial symmetry of the g-tensor in a d^9 complex of this type, we have measured $[CuS_4C_4(CN)_4]^{-2}$ in 1% concentration in a single crystal of diamagnetic $[(n\text{-}C_4H_9)_4N]_2[NiS_4C_4(CN)_4]$. The measurements were made by rotating the magnetic field in three mutually perpendicular crystal planes. The data collected were treated by least squares and analyzed according to the procedure outlined by Schonland.[17] The following results were obtained: $g_1 = 2.023$, $g_2 = 2.026$, $g_3 = 2.086$. From the results of earlier work on planar Cu(II) complexes in single crystals of known structure,[18] we take $g_1 \cong g_2 = g_\perp$ and $g_3 = g_\parallel$. The near axial symmetry is verified and is commonly found in planar bis chelate Cu(II) complexes.[18,19] Comparison of

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(15) H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963).

(16) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, in preparation.

(17) D. S. Schonland, *Proc. Phys. Soc.* (London), **73**, 788 (1959).

(18) A. H. Maki and B. S. McGarvey, *J. Chem. Phys.*, **29**, 31, 35 (1958).

(19) D. Kivelson and R. Neiman, *ibid.*, **35**, 149 (1961); H. R. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962).

these g values with those of Table III demonstrates the pronounced rhombic symmetry of the g-tensor and, hence, the absence of the d^9 configuration in the Ni, Pd, and Pt monoanions.[20] Pronounced rhombic symmetry has also been found as a result of single crystal measurements on isoelectronic $[CoS_4C_4(CN)_4]^{-2}$.[21]

The paramagnetic resonance results for the $[CoS_4C_4(CN)_4]^{-2}$ complex[21] provide the strongest evidence to date that these low-spin d^7 complexes contain the unpaired electron in a delocalized $\pi^*_{1,2}(b_{2g}$ or $b_{3g})$ molecular orbital. The evidence is deduced from a comparison of the Co^{59} hyperfine interaction in $[CoS_4C_4(CN)_4]^{-2}$ with that in Co(II) phthalocyanine.[22] The largest principal components of the hyperfine tensors are 0.005 and 0.027 cm.$^{-1}$ for the two complexes, respectively. The greatly reduced Co^{59} interaction in $[CoS_4C_4(CN)_4]^{-2}$ is consistent with a significantly delocalized π-orbital. A possible energy ordering of the two highest molecular orbitals based on metal d-orbitals in D_{2h} symmetry is $\sigma^*(b_{1g}) > \pi^*_{1,2}(b_{2g}$ or $b_{3g})$. The order of the other three molecular orbitals, π^*_1 or π^*_2, $\pi^*(a_g)$, and $\sigma^*(a_g)$, has not yet been established experimentally. A rhombic g-tensor could also arise in D_{2h} symmetry from a configuration with the odd electron in the $\sigma^*(a_g)$ orbital, and it must be pointed out that this configuration has thus far been shown to be improbable *only* in $[CoS_4C_4(CN)_4]^{-2}$. The small value[1] of the Ni^{61} hyperfine interaction in $[NiS_4C_4(C_6H_5)_4]^-$ also tends, however, to suggest a delocalized $\pi^*_{1,2}$ odd electron for this complex. The recent assignment[12a] of the optical spectrum of $[NiS_4C_4(CN)_4]^{-2}$ based on an $\ldots(a_g)^2$ configuration is, of course, not necessarily inconsistent with a $\ldots(\pi^*_{1,2}{}^1)$ configuration for the monoanions in the event that this electronic structure should become firmly established. The energy separations of the four lowest MO's above may be sufficiently small such that the energy order could be altered upon addition of a single electron.

The $[CoS_4C_4(CF_3)_4]^{-2}$ complex is a further example of a spin-paired planar Co(II) species and is, therefore, very similar to $[CoS_4C_4(CN)_4]^{-2}$, which has recently been shown to have a doublet[21] rather than quartet[3] ground state. The observed magnetic moment of 2.06 B.M. is in reasonable agreement with the value of 1.98 B.M. required by the root mean square g value of 2.28. The existence of high-spin planar Co(II) complexes has still not been established.[23] The neutral complex $[CoS_4C_4(CF_3)_4]$ is a diamagnetic solid even though our formulation suggests the presence of Co(IV). In carbon tetrachloride solution the compound is apparently dimeric ($\bar{n}$ = 1.94, 2.00, 37°) but insufficiently soluble for an accurate magnetic susceptibility measurement. No e.s.r. signal in solution or in the solid could be detected. A dimer having strong metal–metal interactions may have a singlet ground state such as occurs in crystalline cupric acetate. Other multiplet states of the cobalt dimer must, however, be sufficiently high in energy that their thermal population at room temperature does not contribute perceptibly to the magnetic susceptibility.

Nuclear Resonance Results.—The failure to observe electron spin resonance absorption in $[FeS_4C_4(CF_3)_4]^-$ in several physical states, including a dilute glass at ~100°K., implies that in this complex the electronic spin-lattice relaxation time (T_{1e}) is short compared to that in $[NiS_4C_4(CF_3)_4]^-$, for example, in which spin resonance is readily detectable at room temperature.[1,2] Inasmuch as short electronic relaxation times are usually accompanied by long nuclear relaxation times,[25] the situation suggested that one of the two conditions (*viz.*, $T_{1e}^{-1} >> A$ expressed in frequency units) required[26] for observation of hyperfine contact interaction shifts in an n.m.r. spectrum might be satisfied. These interactions arise from $\vec{I} \cdot \vec{S}$ coupling with a coupling constant A. Accordingly, the F^{19} spectrum of this complex was examined in acetone and DMF solutions and broad resonances were detected in both cases. The chemical shift data are summarized in Table IV together with results for diamagnetic complexes.

TABLE IV

F^{19} NUCLEAR RESONANCE DATA[a]

Complex	Solvent	Chemical shift, c.p.s.[b]
$[NiS_4C_4(CF_3)_4]^{-2}$	CH_2Cl_2[d]	−337
	DMF	−346
$[NiS_4C_4(CF_3)_4]$	CH_2Cl_2	−238
$[PtS_4C_4(CF_3)_4]$	CH_2Cl_2	−247
$[CoS_4C_4(CF_3)_4]^-$	Acetone	−469
$[FeS_4C_4(CF_3)_4]^-$	Acetone ($s = {}^1/_2$)	−759 ± 50[c]
	DMF ($s = {}^3/_2$)	−1100 ± 50[c]
$(CF_3)_2C_2S_2$	CH_2Cl_2	−24

[a] Obtained at 22°. [b] Measured relative to benzotrifluoride as an internal standard; error <±1 c.p.s. unless otherwise stated. [c] Width at half height 180 c.p.s. [d] Contained 2% hydrazine to prevent oxidation.

For an assembly of complexes each of which has a

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[20] As part of the evidence for Ni(I) in $Ni(TDT)_2^{-1}$ it was stated that the powder of the $[(n\text{-}C_4H_9)_4N]^+$ salt gave two g values, $g_\perp = 2.045$, $g_\parallel = 2.193$.[15] We have found that powders of undiluted salts of $[NiS_4C_4(CN)_4]^-$ give either two or three g values, depending on the cation, but in dilute glasses three g values are always evident. Exchange interactions between magnetically inequivalent ions of a unit cell, if sufficiently strong, will result in averaging of the principal g values of a complex. Thus, an erroneous g-tensor may result from magnetically undiluted polycrystalline samples. We suggest that the apparent axial symmetry of the g-tensor of $[Ni(TDT)_2]^-$ in the polycrystalline $[(n\text{-}C_4H_9)_4N]^+$ salt arises from accidental averaging of the principal g values. Measurements of dilute glasses or magnetically dilute single crystal and polycrystalline samples are required to demonstrate the axial symmetry implied by the preceding notation.

[21] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 3049 (1963).

[22] J. F. Ingram, D. J. E. Ingram, and D. Schonland, *Discussions Faraday Soc.*, **26**, 72 (1958).

[23] Recently it has been claimed that the complex bis(*o*-hydroxyacetophenoneethylenediimine)cobalt(II) has a moment of 4.49 B.M. (22°).[24] We have prepared this compound in pure form and find that its moment is actually 2.37 B.M. (22°), demonstrating a doublet ground state. The corresponding Ni(II) complex is reported to have a moment of 3.55 B.M. (22°). Our results show this complex to be diamagnetic.

[24] S. N. Poddar, K. Dey, and S. C. N. Sarker, *J. Indian Chem. Soc.*, **40**, 489 (1963).

[25] R. E. Richards, *Discussions Faraday Soc.*, **34**, 74 (1962).

[26] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

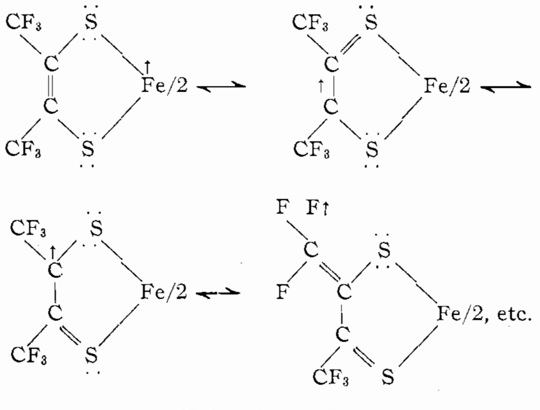
spin ground state S the isotropic hyperfine fluorine contact shifts are given by[27]

$$\frac{\Delta f}{f} = -A\left(\frac{\gamma_e}{\gamma_F}\right)\frac{g\beta S(S+1)}{3kT}$$

in which Δf is the contact shift in c.p.s., f is the spectrometer frequency, γ_e and γ_F the gyromagnetic ratios of the electron and fluorine, respectively, and A is the electron-nucleus coupling constant in gauss. The contact shifts were obtained from the relation $\Delta f = f_{\text{obsd}} - f_{\text{dia}}$ in which f_{dia} was approximated as -300 c.p.s. (*cf.* Table IV). The large deviation of the resonance frequency in $[CoS_4C_4(CF_3)_4]^-$, which we regard as containing Co(III), may be due to mixing of paramagnetic configurations with the singlet ground state by the applied magnetic field.[28] Examples of paramagnetic effects on F^{19} resonances in organo–transition metal compounds have been claimed.[29]

The total contact shift for the low-spin form in acetone is estimated as -460 c.p.s. and that for the high-spin form in DMF as -800 c.p.s. Ideally, these shifts could be utilized to calculate spin densities on the chelate ring carbon atoms from an extension of McConnell's relation $A = Q\rho_c$.[30] Coupling constants measured from proton[31] and fluorine[32] nuclear resonance have been extensively used to calculate absolute or relative spin densities. However, three conditions must be met before such calculations have validity: (i) the contact shifts from which A is calculated must have no appreciable contribution from pseudo-contact interactions[33]; (ii) the unpaired spin density must be delocalized through the π-system of the ligand; (iii) a reasonable value of Q, in this case Q_{CCF_3}, must be known. The observation of considerable anisotropy of the g-tensor in related complexes with $S = {}^1/_2$[1,2,21] (*cf.* Table III) suggests that pseudo-contact effects might be important in at least the low-spin form of $[FeS_4C_4(CF_3)_4]^-$. We have used the treatment of pseudo-contact shifts by McConnell and Robertson[33] to provide an order of magnitude estimate of the isotropic pseudo-contact contribution to the total contact shift for the low-spin form in acetone.[34] The result is $|\Delta f| \sim 30$ c.p.s. The pseudo-contact contribution is an order of magnitude less than the observed total shift, which is believed to be predominantly due to a Fermi contact interaction. The coupling constant A is calculated to be $+0.14$ gauss, neglecting any pseudo-contact contribution.

In $[FeS_4C_4(CF_3)_4]^-$ there is no direct means of deciding whether or not the unpaired spin is delocalized to the ligand *via* a predominantly π-bonding mechanism. However, in $[MS_4C_4R_4]^z$ complexes metal-ligand π-bonding appears necessary to an explanation of the e.s.r., infrared, and optical spectral results. Further, if the odd electron in the low-spin form is in a $\pi^*_{1,2}(b_{3g}$ or $b_{2g})$ orbital no direct spin transmission through the σ-system is possible. If the electron were primarily in such an orbital, the following valence bond structures could then contribute to spin delocalization, producing positive π spin densities at the ring carbons and, consequently, at the F^{19} nuclei. Taking Q_{CCF_3} as $+40$ gauss[35] in $A = Q_{CCF_3}\rho_c$ we find $\rho_c \simeq +0.003$ in the low-spin form. This order of magnitude for ρ_c is too low to be consistent with the presence of the unpaired spin in a strongly delocalized π-orbital. It is probably the correct order of magnitude, however, to be explained in terms of spin polarization of the ligand π-orbitals by the unpaired electron. This mechanism would also lead to the positive spin densities shown above.



Infrared Results.—The spectra of all compounds obtained in this work have been examined in the 4000–650 cm.$^{-1}$ region. Spectra of the neutral complexes $[MS_4C_4(CF_3)_4]$ are especially useful for the purpose of characterization, and band frequencies are tabulated in the Experimental section. Here we deal only with that absorption of highest frequency in each complex, all of which occur in the 1550–1400 cm.$^{-1}$ range. These absorptions are assigned to a perturbed C=C stretching mode on the simple basis that no other bond

(27) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **27**, 314 (1957).

(28) J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957).

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(31) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *ibid.*, **37**, 347 (1962); D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962); R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 379 (1964).

(32) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962); D. R. Eaton, A. D. Josey, and W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 2689 (1963).

(33) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(34) The pseudo-contact shift in c.p.s. is given by[33]

$$\frac{\Delta f}{f} = \frac{(3\cos^2\chi - 1)\beta^2 S(S+1)}{-27r^3kT}(g_\parallel + 2g_\perp)(g_\parallel - g_\perp)$$

with the simplifying assumption that the g-tensor is axially symmetric. The angle between the symmetry axis and the radius vector r from the metal to the fluorine atoms is χ. For this calculation it was assumed that the electron is localized on the metal; the radius vector was calculated from structural results on $[CoS_4C_4(CN)_4]^{-2}$.[12b] $|g_\parallel - g_\perp|$ was taken as one, a value comparable to the observed anisotropy in ferrihemoglobin azide.[22] The sign of the shift is indeterminate inasmuch as the sign of $(g_\parallel - g_\perp)$ is unknown. Because of the nature of the assumptions underlying this calculation, it is recognized that only the order of magnitude of the pseudo-contact shift could be expected. Because of the considerable uncertainty in the value of $|g_\parallel - g_\perp|$ for the high spin form, we make no firm estimate of the pseudo-contact contribution to the observed shift in this case. It is noted, however, that even if $|g_\parallel - g_\perp|$ is as large as 4, a significant fraction (dependent on the sign of $(g\ \ - g_\perp)$) of the observed shift remains and is presumably due to a true Fermi contact shift.

(35) The value of Q_{CCF_3}, like that of Q_{CCH_3},[31] is not a true constant but apparently depends on the exact position of substitution of a CF_3 group in a given molecule. We take this value of Q from results on $C_6(CF_3)_6^{\dot{-}}$ currently under study by M. Moulton of this laboratory.

in the complexes possessing double bond character, however large, would be expected to absorb in this range. Additionally, the bands in nearly all cases appear too intense to be overtone or combination frequencies and are not assignable to any $-CF_3$ group vibration. These absorptions lie below ~1360 cm.$^{-1}$.[36] For example, **4** exhibits a strong band at 1621 cm.$^{-1}$, which is assigned as a C=C stretch, and has no other strong absorptions above 1350 cm.$^{-1}$. The frequencies assigned to this vibration in all species are set out in Table V.

Table V

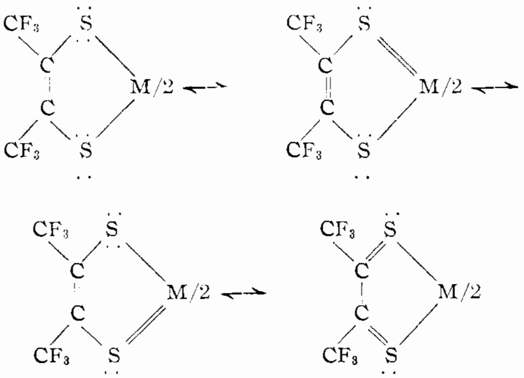
Perturbed C=C Frequency in Thietene Complexes[a]

Complex	Frequency, cm.$^{-1}$
$(CF_3)_2C_2S_2$ (neat)	1621
$[FeS_4C_4(CF_3)_4]^{-}$ [b]	1538
$[CoS_4C_4(CF_3)_4]$	1466
$[CoS_4C_4(CF_3)_4]^{-}$ [b]	1502
$[CoS_4C_4(CF_3)_4]^{-2}$ [b]	1515
$[NiS_4C_4(CF_3)_4]$	1422
$[NiS_4C_4(CF_3)_4]^{-}$ [b]	1502
$[NiS_4C_4(CF_3)_4]^{-2}$ [b]	1534
$[PdS_4C_4(CF_3)_4]^{-2}$ [c]	1513
$[PtS_4C_4(CF_3)_4]$	1422
$[PtS_4C_4(CF_3)_4]^{-}$ [c]	1493
$[PtS_4C_4(CF_3)_4]^{-2}$ [c]	1515
$[((C_6H_5)_3P)_2NiS_2C_2(CF_3)_2]$	1553
$[((C_6H_5)_3P)_2PdS_2C_2(CF_3)_2]$	1548
$[((C_6H_5)_3P)_2PtS_2C_2(CF_3)_2]$	1541

[a] Spectra of fluorolube mulls. [b] Measured as $(C_2H_5)_4N^+$ salt. [c] Measured as $(C_6H_5)_4As^+$ salt.

The most significant feature of the tabulated frequencies is that for a given metal the frequency increases as the negative charge on the complex increases. This effect is interpretable if the complexes are regarded as containing metals whose formal oxidation state increases from (II) to (IV) as z changes from -2 to 0 and if the ligand system has no strong tendency to back-accept charge from the metal *via* π-bonding. In metal carbonyl derivatives alkyl sulfides have a π-accepting tendency very similar to that of related phosphines and arsines.[37] The same conclusion has been drawn in this work (*vide infra*) with respect to the relative π-bonding tendencies of triphenylphosphine and $(CF_3)_2C_2S_2^{-2}$. Although the chelating ligand system has some tendency to back-accept, the net flow of charge in the π-system is believed to be from ligand to metal. This situation is the reverse of that in carbonyls, cyanides, isonitriles, etc., so that increased nuclear kernel charge[38] will increase, rather than decrease, metal-ligand π-bonding.

In the R = CN series structural results on $[NiS_4C_4(CN)_4]^{-2}$ and $[CoS_4C_4(CN)_4]^{-2}$ reveal the chelate ring C—C distances to be 1.30[12a] and 1.34 Å.,[12b] respectively, very near the normal C=C distance. The observed frequencies are highest in the dinegative perfluoromethyl complexes[39] for which similar structural results are anticipated. For these Ni, Pd, Pt dianions the electron configuration, implying no energy order, is $(\pi^*)^2(\sigma^*)^2(\pi^*_1)^2(\pi^*_2)^2$. The stable metal orbitals (d_{xz} and d_{yz}) capable of accepting electron density from the ligand π-system are then completely occupied. Removal of one or two electrons from these predominantly metal antibonding orbitals results in species with the possible configurations $(\pi^*_1)^2(\pi^*_2)^1$ and $(\pi^*_1)^2$, respectively, thereby increasing the availability of one of the two $d\pi$ orbitals for bonding. This situation would tend to increase ligand → metal charge transfer and can be represented by the following valence bond structures (omitting formal charges). In agreement with this argument the frequencies in all cases decrease in the order $z = -2 > -1 > 0$. The effect of a half-filled $d\pi$ orbital is small, the shifts being only ~10–30 cm.$^{-1}$. The further removal of an electron to give a vacant $d\pi$ orbital produces a much larger decrement in frequency (~40–80 cm.$^{-1}$).



An examination of the mixed complexes $[(C_6H_5)_3P]_2MS_2C_2(CF_3)_2$ shows that the carbon–carbon frequencies are 20–25 cm.$^{-1}$ higher than in the related dianions. If it may be assumed, as has been implicitly done in other discussions,[34] that sulfur and phosphorus are equally good σ-donors, it may be concluded that the ability of the $(CF_3)_2C_2S_2^{-2}$ ligand system to serve as a π-acceptor in these complexes is about equal to, or slightly greater than, that of triphenylphosphine.

Optical Spectral Results.—We defer a detailed consideration of the optical spectra of complexes prepared in this and earlier work[2] to a future communication. However, at present we note that a number of the observed transitions can be assigned with confidence as excitations to the $\sigma^*(b_{1g})$ orbital in D_{2h} symmetry or to $\sigma^*(b_1)$ in C_{2v} symmetry. The results to be considered are given in Table VI. The intensities are indicative of spin-allowed d-d transitions. The energies increase in the usual order Ni < Pd < Pt.

The most arresting feature of the results for the di-

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[36] See, *e.g.*, D. G. Weiblen in "Fluorine Chemistry," J. H. Simons, Ed., Vol. II, Academic Press Inc., New York, N. Y., 1954, Chapter VII.

[37] F. A. Cotton and F. Zingales, *Inorg. Chem.*, **1**, 145 (1962); H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4454 (1962).

[38] L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).

[39] The arguments which follow might equally well be applied to the $z = -1, -2$ complexes of the R = CN series. However, in this series the C=C frequencies are sufficiently low that they overlap those of the cations, thus making identification uncertain. This frequency lowering is anticipated upon comparing the C=C stretches in **4** (1621 cm.$^{-1}$) and *cis*-$(NC)(CH_3S)C{=}C(SCH_3)(CN)$ (1515 cm.$^{-1}$).[40]

[40] H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4756 (1962).

TABLE VI

LIGAND FIELD SPECTRAL DATA[a]

Complex	λ_{max}, cm.$^{-1}$	ϵ
$[NiS_4C_4(CF_3)_4]^{-2}$	12,900	18
$[PdS_4C_4(CF_3)_4]^{-2}$ [b]	16,950	40
$[((C_6H_5)_3P)_2NiS_2C_2(CF_3)_2]$	~15,200 (sh)	~70
$[((C_6H_5)_3P)_2PdS_2C_2(CF_3)_2]$	19,050	84
$[((C_6H_5)_3P)_2PtS_2C_2(CF_3)_2]$	25,320	141
$[((C_6H_5)_3P)_2NiS_2C_2(CN)_2]$	14,900	<100
$[((C_6H_5)_3P)_2PdS_2C_2(CN)_2]$	19,050	74

[a] Measured in dichloromethane solution unless otherwise noted. [b] Measured in DMF.

anions is the much reduced separation of $\sigma^*(b_{1g})$ and the next highest d-type orbital compared to the tetrahalo or tetracyano complexes.[41] A slightly smaller energy separation has already been observed in $[NiS_4C_4(CN)_4]^{-2}$.[12a] It is tempting to place $R_2C_2S_2^{-2}$ near the weak end of the spectrochemical series for planar complexes. However, this cannot be meaningfully done until d-orbital energy differences have been firmly established in a series of d^8 planar complexes. The designation of such energies requires consistent assignment of ligand field transitions, concerning which disagreement exists.[41,42] An overriding consideration may be that the ligand field is in fact quite strong due to significant covalency in the metal–ligand π- and σ-bonds. A particular feature of this ligand system could be the participation in relatively strong in- and out-of-plane π-bonding which promotes the $\pi^*_{1,2}$ (b_{2g} or b_{3g}) and $\pi^*(a_g)$ orbitals closer to $\sigma^*(b_{1g})$ than, for example, in $M(CN)_4^{-2}$ complexes. In these complexes in-plane π-bonding may be less important, and the out-of-plane π-orbitals (d_{xz} and d_{yz}) are believed to be the most stable metal orbitals.[41] These π-bonding effects could then account for the relatively small transition energies observed in the dianions. Although the ligand field may be weak in the sense of a spectrochemical series, it is believed that the metal–ligand bonds are quite robust.[44]

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[41] (a) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963); (b) H. B. Gray and C. J. Ballhausen, *ibid.*, **85**, 260 (1963).

[42] If the assignment of the lowest energy spin-allowed transition in MX_4^{-2} and $M(CN)_4^{-2}$ complexes is accepted to be $\pi^*(b_{2g}) \rightarrow \sigma^*(b_{1g})$,[41b] and if the analogous assignment, $\pi^*(a_g) \rightarrow \sigma^*(b_{1g})$, is made for the dianions, the following orbital energy differences Δ_1 are obtained: Ni, 16,400 cm.$^{-1}$, Pd, 19,400 cm.$^{-1}$. These values were calculated using $F_2 = 10F_4 = 1000$ cm.$^{-1}$ (Ni), 700 cm.$^{-1}$ (Pd). Comparison with other Δ_1 values [41b] gives the series $Br^- < Cl^- \lesssim (CF_3)_2C_2S_2^{-2} << CN^-$ for Pd. Taking the same assignment for type **3** complexes, the presence of triphenylphosphine increases Δ_1. In other complexes it has been found that $Cl^- < (C_6H_5)_3P$.[43]

[43] F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 1780 (1961).

[44] NOTE ADDED IN PROOF.—The structure of $[(n\text{-}C_4H_9)_4N][CuS_4C_4(CN)_4]$ has recently been completed and shows the monoanion to be planar.[12b] The ions $[MS_4C_4(CN)_4]^-$ form isomorphous crystals.[2] This result tends to confirm the general supposition that electron-transfer reactions between mono- and dianions involve planar species.

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Kinetics of Fast Electron-Transfer Reactions

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The temperature-jump method has been used to determine the rate constants for a series of rapid, "outer-sphere" oxidation–reduction reactions of the type

$$\mathrm{ox_1}^{2-} + \mathrm{red_2}^{2+} \underset{k_r\,(M^{-1}\,\mathrm{sec.}^{-1})}{\overset{k_f\,(M^{-1}\,\mathrm{sec.}^{-1})}{\rightleftharpoons}} \mathrm{red_1}^{3-} + \mathrm{ox_2}^{3+}$$

The symbol $\mathrm{ox_1}^{2-}$ represents $IrCl_6^{2-}$, $IrBr_6^{2-}$, or $RhCl_6^{2-}$. The symbol $\mathrm{red_2}^{2+}$ represents a substituted phenanthroline or bipyridine complex of iron(II) or ruthenium(II). It has been found that a diffusion-controlled limit of about 2×10^9 (M^{-1} sec.$^{-1}$) is approached when the equilibrium quotient is equal to or greater than unity. The rate of reaction for a given electron donor is then independent of the relative acceptor strength once the diffusional limit has been reached. Evidence was also found that steric restrictions can affect a diffusion-controlled electron-transfer reaction, causing the rate constant to fall somewhat short of the theoretical value.

As indicated by experiments utilizing the rapid mixing technique, electron transfer between large metal complexes is rapid.[1] The reactions are often so rapid that in many cases only the lower limits of rate constants are obtained. By applying the temperature-jump method it has been possible to determine the rate constants for electron-transfer reactions of the type

$$\mathrm{ox_1}^{2-} + \mathrm{red_2}^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{red_1}^{3-} + \mathrm{ox_2}^{3+}$$

where k_f (M^{-1} sec.$^{-1}$) and k_r (M^{-1} sec.$^{-1}$) are the bimolecular forward and reverse rate constants, respectively. The symbol $\mathrm{ox_1}^{2-}$ represents $IrCl_6^{2-}$, $IrBr_6^{2-}$, or $RhCl_6^{2-}$. The symbol red^{2+} represents a complex of iron(II) or ruthenium(II).

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[1] N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).