TABLE VI

SPECTRAL DATA

Fraction	$\lambda_{\max_1}$, mμ	ϵ_1	$\lambda_{\max_2}$, mμ	ϵ_2	$\lambda_{\max_3}$, mμ	ϵ_3	$\lambda_{\max_4}$, mμ	ϵ_4
I	256	31,800	348	12,800	524	21,400	556	22,000
II	256	32,400	348	13,000	524	21,600	556	22,400
III					522	22,000	556	22,600

X-Ray powder diagrams taken by Mr. E. Emerson of these laboratories indicated significant differences which were interpreted as due to different crystal structures. The combination of different chromatographic behavior and different crystal structure led us to the conclusion that these materials must be isomers.

(D) **Reaction of IV with (dien)Cr(CO)$_3$.**—At 30° 1 g of IV was slowly added to a stirred mixture of 1 g of (dien)Cr(CO)$_3$ in 20 ml of DMF. After 0.5 hr the mixture was precipitated into water. The solid was collected, washed with water, and dried. Analysis by paper electrophoresis showed a mixture of a cation (the desired product), two anions (unreacted IV and 2:1 complex), and a trace of a neutral dye.

The mixture (1.05 g) was separated on a Stubbings electrophoresis apparatus (Tauratron, Inc., Fogelsville, Pa.) specially constructed of CR-39 resin. The buffer system was 1:1 DMF–1-butanol containing 0.016 *M* lithium acetate and 0.016 *M* acetic acid. The sample was injected as a 10% solution in DMF at 2 ml/hr; the buffer flow rate allowed about 2 hr for separation at 700 v and 30 ma. The eluate samples were analyzed by paper electrophoresis, and the pure cationic samples were combined and evaporated. The residue was washed with water, centrifuged, and dried. Additional material was obtained from the supernatant liquid by making it strongly alkaline with NaOH, which precipitated the dye, and thorough washing with water. The total amount of dye was 0.25 g. The infrared and visible spectra of this material were the same as the spectra of compound **5** prepared from the chromic chloride complex.

(E) **Reduction of a Nitro Group in a Chromed Azo Dye (21) to Amine 22.**—The azo dye XVI was chromed by the triethylamine procedure described for dye XII (using chromic chloride, ethanol, triethylamine, and acetylacetone). A mixture of 5.2 g (0.0074 mole) of complex **21** and 150 ml of *p*-dioxane was hydrogenated using a teaspoonful of Raney nickel at 40 psi and room temperature for 3 hr. (It was found that 10% Pd on charcoal was ineffective.) Celite was added, the mixture was filtered, and the filtrate was poured into 1 l. of water. The dye was a fine suspension that was collected by slow filtration with fluted coarse paper. Vacuum drying at 50° gave 4.0 g (80%) of the amino compound **22**.

Anal. Calcd for $C_{30}H_{35}N_6O_7SCr \cdot H_2O$: C, 51.80; H, 5.30; Cr, 7.48; N, 12.11; S, 4.60. Found: C, 52.20; H, 5.47; Cr, 7.32; N, 10.56; S, 4.49.

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New Synthetic Studies on Four-Coordinate Complexes Derived from Bis(trifluoromethyl)-1,2-dithietene and Some Related Reactions

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A new synthetic route to complexes derived from bis(trifluoromethyl)-1,2-dithietene is described. New complexes of Cu and Au have been characterized, and a more convenient synthesis of the known Co, Ni, Pd, and Pt species is reported. A novel five-coordinate gold complex $[(C_6H_5)_3P \cdot AuS_4C_4(CF_3)_4]Cl$ has also been characterized. The desulfurization reactions of the neutral $[MS_4C_4R_4]$ species by triphenylphosphine to give four-coordinate $\{[(C_6H_5)_3P]_2MS_2C_2(CF_3)_2\}$ with M = Ni, Pd, and Pt are discussed. Polarographic studies of the $[MS_4C_4R_4]_z$ complexes with M = Co, Ni, and Cu are discussed in terms of the various electronic structures which have been proposed for these species. Evidence is presented which shows that certain of the cobalt complexes should be correctly formulated as dimeric dianions, *e.g.*, $[N(C_4H_9)_4]_2[CoS_4C_4(CN)_4]_2$, rather than, as previously assumed, monomeric monoanions.

The discovery of discrete one-electron-transfer reactions for both the bis-[2a] and the tris-[2b](*cis*-1,2-disubstituted ethylene-1,2-dithiolato[3])metal complexes has led to a continued interest in these and related systems. Much of the recent work has shown the remarkable versatility of this ligand system. In the bis complexes of the nickel group metals, a planar array of the four donor atoms is maintained in three apparent oxidation states[3,4] of the system. A planar structure was also found[5] for a characterized[6a] four-coordinate complex of copper in an $S = 0$ ground state. Metal-to-sulfur bonding between essentially planar units has been found[7] foı $[CoS_4C_4(CF_3)_4]_2$ which has the structure shown in Figure 1. In this dimeric species, the metal-to-sulfur

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[1] (a) NSF Student Participant, 1964; (b) Woodrow Wilson Fellow, 1964–1965; NSF Graduate Fellow, 1965–1967.

[2] (a) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963); (b) *ibid.*, **86**, 2799 (1964).

[3] This nomenclature, adopted to simplify electron bookkeeping, restricts us to an apparent or formal oxidation state of the metal only in a pedantic sense. However, these complexes are highly covalent and should properly be described in molecular orbital language. The electrons in the uppermost levels are associated with both ligand and metal. The degree of delocalization depends upon the metal and the total charge on the complexes. Such ambiguity between the concept of valence state and oxidation state arises quite often in transition metal chemistry, indicating that in many cases the ionic model and the valence bond descriptions do not provide a reasonable approximation to the bonding in such complexes.

[4] There is well-documented evidence that all three members of the nickel electron-transfer series are planar: (a) $[NiS_4C_4(CN)_4]^{2-}$, R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965); (b) $[NiS_4C_4(CN)_4]^-$, G. J. Fritchie, Jr., *Acta Cryst.*, **20**, 107 (1966); (c) $NiS_4C_4(C_6H_5)_4$, D. Sartain and M. R. Truter, *Chem. Commun.*, 382 (1966).

[5] J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1507 (1964).

[6] (a) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **2**, 1227 (1963); (b) H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963), reported the first characterized $S = 0$ complex of copper.

[7] J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).

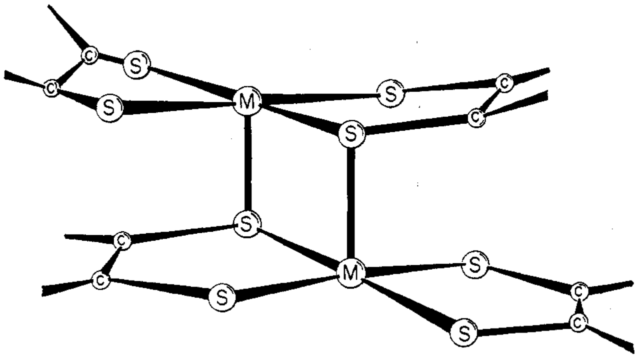

Figure 1.—Idealized structure for the dimeric species, based on that found[7] for $[CoS_4C_4(CF_3)_4]_2$.

distance between the two halves was only 0.22 A longer than that found in the chelate ring. This unit can undergo discrete one-electron-transfer reactions without disruption of the dimer.[8] A weaker metal-to-sulfur interaction of this type has also been proposed[9] to account for the antiferromagnetic behavior observed in the solid state for the $[MS_4C_4(CN)_4]^-$ ions of the nickel group chelates. Polarographic and spectral studies[6,10] have shown that the ring substituents have a pronounced effect on both the redox properties and the absorption spectra of the complexes. On the other hand, the characteristic esr spectrum of the $S = {}^1/_2$ complexes of the nickel group is virtually independent[2,6,10] of the precise nature of this substituent.

We describe here extensions of our work on these systems, which, in part, deal with a new synthetic procedure for obtaining *cis*-1,2-ditrifluoromethylethylene-1,2-dithiolato chelates. The reactivity of the neutral $[MS_4C_4R_4]$ complexes with triphenylphosphine and some related reactions is also considered. Certain preliminary results[11] have already been reported.

Experimental Section

Preparation of Compounds.—Bis(trifluoromethyl)-1,2-dithietene was prepared according to the procedure of Krespan.[12] It was carefully fractionated before use and the freshly distilled 96–98° fraction was used in the following preparations. All melting points are uncorrected.

$[(C_6H_5)_4As]_2[NiS_4C_4(CF_3)_4]$.—A solution of 1.75 g (7.8 mmoles) of $(CF_3)_2C_2S_2$ in 10 ml of benzene was added in one portion to 1.75 g (2.4 mmoles) of bis(triphenylphosphine)nickel dibromide in 60 ml of benzene. The solution darkened almost immediately. The solution was refluxed for 15 min, then the solvent was removed *in vacuo*. The residue was treated with 5 ml of benzene to give a viscous oil which was extracted with 100 ml of *n*-pentane. After standing, the slightly cloudy *n*-pentane extract was decanted and set aside. The residual oil was treated with 30 ml of 70% v/v ethanol–water, and the mixture was then allowed to stand for 30 min before it was filtered. The precipitate was recrystallized from ethanol–acetone–water to give 0.1 g of triphenylphosphine sulfide as white needles (mp 161–162°, mmp 161–162°). The filtrate was treated with 0.5 ml of hydrazine and the solution became orange immediately. It was then filtered and a solution of 2 g (4.8 mmoles) of $(C_6H_5)_4AsCl$ in 10 ml of ethanol was added. Crystallization was induced by dropwise addition of water and, upon standing, fine orange crystals separated. Recrystallization of this material from acetone–isobutyl alcohol gave 1.56 g (50%) of pure $[(C_6H_5)_4As]_2[NiS_4C_4(CF_3)_4]$ as orange needles (mp 234–235°, mmp 234–235°).

Anal. Calcd for $[(C_6H_5)_4As]_2[NiS_4C_4(CF_3)_4]$: C, 52.63; H, 3.34. Found: C, 52.64; H, 3.15.

The above procedure can be modified easily to give salts of the monoanion by elimination of the hydrazine reduction step. For example, $[(C_2H_5)_4N][NiS_4C_4(CF_3)_4]$ is produced in 49% yield by the addition of an aqueous $(C_2H_5)_4NCl$ solution to precipitate the complex prior to the reduction. The complex was recrystallized as previously described.[6]

Anal. Calcd for $[(C_2H_5)_4N][NiS_4C_4(CF_3)_4]$: C, 29.97; H, 3.14. Found: C, 29.66; H, 3.23 (mp 118.5–119°, mmp 119–120°).

The procedures outlined above work satisfactorily for the following known complexes. In each case the starting material was the corresponding bis(triphenylphosphine)metal dihalide.

$[(C_2H_5)_4N][CoS_4C_4(CF_3)_4]$.—Data for this complex are: mp 261–263°, mmp 261–263°; yield, 30% from $[(C_6H_5)_3P]_2CoCl_2$; reflux time, 5 hr. *Anal.* Calcd: C, 29.95; H, 3.14; N, 2.18. Found: C, 29.96; H, 3.11; N, 2.26.

$[(C_6H_5)_4As]_2[PdS_4C_4(CF_3)_4]$.—Data for this complex are: mp 250.0–251.5° dec, mmp 250–251.5°; yield, 60% from *trans*-$[(C_6H_5)_3P]_2PdCl_2$; reflux time, 20 min. *Anal.* Calcd: C, 50.75; H, 3.04. Found: C, 50.51; H, 3.13.

$[(C_6H_5)_4As][PtS_4C_4(CF_3)_4]$.—Data for this complex are: mp 167–168.5°, mmp 168–169°; yield, 42% from *cis*-$[(C_6H_5)_3P]_2PtCl_2$; reflux time, 12 hr. *Anal.* Calcd: C, 37.29; H, 1.96. Found: C, 38.88; H, 1.86.

In all cases triphenylphosphine sulfide was isolated as a byproduct of the reaction. In the platinum reaction small amounts (*ca.* 3–5%) of the neutral $PtS_4C_4(CF_3)_4$ were produced and extracted into the *n*-pentane layer.

The Recovery of 2,3,4a,6,7,8a-Hexakis(trifluoromethyl)-4a,8a-dihydro-*p*-dithiino[2,3-*b*]-*p*-dithiin from the Preparation of $[(C_6H_5)_4As]_2[NiS_4C_4(CF_3)_4]$.—When the pentane extracts from the preparation of $[(C_6H_5)_4As]_2[NiS_4C_4(CF_3)_4]$ were evaporated, small amounts of a pale yellow oil remained whose physical properties were identical with a known sample of 2,3,4a,6,7,8a-hexakis(trifluoromethyl)-4a,8a-dihydro-*p*-dithiino[2,3-*b*]-*p*-dithiin.[12] No evidence was obtained for the production of either tetrakis(trifluoromethyl)thiophene or tetrakis-2,3,5,6-(trifluoromethyl)-*p*-dithiin.

The Reaction of the Mercuric Salt of 1,2-Dimercapto-1,2-bis(trifluoromethyl)ethylene with Metal Salts.—A mixture of 1.5 g of $[HgS_2C_2(CF_3)_2]_n$, 1.1 g of LiCl, and 0.36 g of $NiCl_2 \cdot 6H_2O$ was allowed to stand in 70% v/v ethanol–water at room temperature for 5 days. After this time the mixture, which had become dark green, was filtered and the filtrate was treated with 1.34 g of $(C_2H_5)_4NCl$ in 10 ml of water. The precipitate of $[(C_2H_5)_4N][NiS_4C_4(CF_3)_4]$ was recrystallized and characterized as previously described.[6] The yield was 0.80 g (mp 116–117°, mmp 113–117°). Attempts to prepare lanthanide complexes by this procedure were unsuccessful.

$[(C_6H_5)_3P \cdot ClAuS_4C_4(CF_3)_4]$.—A solution of 3 g (13.9 mmoles) of $(CF_3)_2C_2S_2$ and 4 g (8.2 mmoles) of $(C_6H_5)_3PAuCl$ in 80 ml of benzene was refluxed for 20 min. The solution became deep orange after 1–2 min and deep green after 5–10 min. The resultant solution was evaporated to dryness *in vacuo* and the remaining solid was extracted with 300 ml of *n*-pentane. The pentane was decanted and the solid was then heated to boiling with 20 ml of dichloromethane. It was sealed and allowed to stand for 12 hr, during which time a large green crystalline mass (4.5 g) separated. The filtrate was treated with *n*-pentane to bring the solution to its cloud point and set aside. During 12 hr an additional 1.85 g of olive-green plates separated. A portion of the product was recrystallized from dichloromethane–*n*-pentane to give olive-green plates (mp 140–142°).

Anal. Calcd: C, 33.00; H, 1.59; S, 13.54; F, 24.07; Cl, 3.74. Found: C, 33.09; H, 1.59; S, 13.59; F, 23.98; Cl, 3.90.

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[8] A. L. Balch and R. H. Holm, *Chem. Commun.*, 552 (1966).

[9] J. F. Weiher, L. R. Melby, and R. E. Benson, *J. Am. Chem. Soc.*, **86**, 4329 (1964).

[10] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

[11] A. Davison and D. V. Howe, *Chem. Commun.*, 290 (1965).

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

$[(C_6H_5)_4As][AuS_4C_4(CF_3)_4]$.—A 1.03-g (1.1-mmole) sample of crude $[(C_6H_5)_3P{\cdot}ClAuS_4C_4(CF_3)_4]$ was dissolved in 32 ml of 70% v/v ethanol–water mixture. A solution of 0.55 g of $(C_6H_5)_4AsCl$ in 10 ml of ethanol was then added to this green solution. The addition of water, dropwise, caused the separation of green crystals which were collected and then recrystallized from 12 ml of 1:1 acetone–ethanol to which 1 ml of water was added to induce crystallization. The yield was 0.85 g (77%) of green plates (mp 179–181°) of $[(C_6H_5)_4As][AuS_4C_4(CF_3)_4]$. A subsequent crop (0.10 g) was obtained by the addition of more water to the mother liquor. *Anal.* Calcd: C, 37.22; H, 1.95; S, 12.42; F, 22.08. Found: C, 37.42; H, 2.02; S, 12.73; F, 22.70. $[(C_6H_5)_4As][AuS_4C_4(CF_3)_4]$ is obtained on 70% yield in one step from $(C_6H_5)_3PAuI$ utilizing the procedure described previously for the nickel and cobalt complexes.

The Reaction of $(C_6H_5)_3PAgI$ with $(CF_3)_2C_2S_2$.—Attempts to make silver complexes from $(C_6H_5)_3PAgI$ gave only $(C_6H_5)_3PS$ and AgI in quantitative amounts.

$[(C_6H_5)_4As][CuS_4C_4(CF_3)_4]$.—A solution of 2.0 g of $[(C_6H_5)_3PCuI]_4$ and 3.5 g of $(CF_3)_2C_2S_2$ in 40 ml of benzene was allowed to stand at room temperature for 60 min. (When the mixture is heated even for brief periods CuI is formed.) The solvent was removed *in vacuo* and the residue was treated with 50 ml of 70% v/v ethanol–water mixture. The solution was filtered to remove $(C_6H_5)_3PS$ and CuI and the filtrate was treated with a solution of 1.0 g of $(C_6H_5)_4AsCl$ in 10 ml of ethanol. A green precipitate slowly formed; this was collected and subsequently recrystallized four times from boiling isobutyl alcohol by the addition of an equal volume of cyclohexane. Upon standing, 1.6 g (40%) of long, olive-green needles were produced (mp 175–175.5°). *Anal.* Calcd: C, 42.74; H, 2.24; F, 25.35; S, 14.26. Found: C, 42.45; H, 2.19; F, 27.25; S, 14.95.

$[(C_6H_5)_4As]_2[CuS_4C_4(CF_3)_4]$.—The procedure is exactly analogous to that described above except that reduction to the dianion is achieved using 0.5 ml of hydrazine prior to precipitation with tetraphenylarsonium chloride. The complex was twice recrystallized from ethanol–water to which a drop of hydrazine had been added to prevent air oxidation of the dianion. The yield was 22% of brick red crystals (mp 198–200°). *Anal.* Calcd: C, 52.44; H, 3.14; F, 17.78; S, 10.00. Found: C, 52.54; H, 3.17; F, 18.81; S, 10.27.

$[(C_6H_5)_3P]_2NiS_2C_2(CF_3)_2$.—A solution of 3.5 g (13.5 mmoles) of triphenylphosphine in 30 ml of benzene was added in one portion to 2 g (4.9 mmoles) of $NiS_4C_4(CF_3)_4$ in 25 ml of the same solvent. The solution immediately became dark brown and an oil began to separate. The mixture was refluxed for 5 min and then allowed to stand for 2 hr. The solvent was removed *in vacuo*. The residual oil was dissolved in 10 ml of benzene and then slowly triturated with 60 ml of *n*-pentane. The benzene–pentane mixture was decanted from the resultant solid and set aside. The olive-green solid was purified by Soxhlet extraction with dichloromethane to give 1.60 g (51%) of pure $[(C_6H_5)_3P]_2NiS_2C_2(CF_3)_2$. *Anal.* Calcd: C, 59.35; H, 3.73. Found: C, 59.74; H, 4.15. The infrared spectrum of the compound prepared in this way was found to be identical with that of an authentic sample. The combined benzene–pentane extracts were evaporated almost to dryness and then refluxed with 25 ml of *n*-pentane. Upon cooling, 0.2 g of white needles of triphenylphosphine sulfide separated. These were collected and recrystallized (mp 161–162°, mmp 161–162°).

$[(C_6H_5)_3P]_2PtS_2C_2(CF_3)_2$.—This was prepared by a procedure similar to that used for the analogous nickel complex except that dichloromethane was used as a solvent. The product was identified by its infrared spectrum.

$PtS_4C_4(C_6H_5)_4$.—This complex was made by the published procedure[13] but was purified by Soxhlet extraction with dichloromethane prior to its subsequent reaction with triphenylphosphine.

$[(C_6H_5)_3P]_2PtS_2C_2(C_6H_5)_2$.—This complex, previously formulated as $[(C_6H_5)_3P]_2PtS_4C_4(C_6H_5)_4$, was made by the reaction of $PtS_4C_4(C_6H_5)_4$ with triphenylphosphine.[13] It was recrystallized five times. *Anal.* Calcd for $[(C_6H_5)_3P]_2PtS_2C_2(C_6H_5)_2$: C, 62.42; H, 4.19; S, 6.67; P, 6.44. Calcd for $[(C_6H_5)_3P]_2PtS_4C_4(C_6H_5)_4$: C, 63.82; H, 4.18; S, 10.65; P, 5.14. Found: C, 62.83, 63.07; H, 4.15; 4.03; S, 6.82; P, 6.54.

$(C_6H_5)_3PS(C_6H_5)_3PS_2C_2(CF_3)_2$.—A mixture of 2.26 g (10 mmoles) of triphenylphosphine in 40 ml of diethyl ether reacted immediately to give an intense orange solution. During 20 min bright yellow crystals separated. The product was collected by filtration and washed with 10 ml of 1:1 v/v *n*-pentane–diethyl ether, followed by 10 ml of *n*-pentane, and air dried. It weighed 2.7 g and was not recrystallized. The complex dissolves to give a yellow solution; this gradually fades and the decomposition product triphenylphosphine sulfide was isolated from the resulting clear solution. The yellow product does not melt sharply. It first decomposes and partially melts at 141–144°. It then solidifies and finally melts at 150–158°. It is best formulated as $(C_6H_5)_3PS(C_6H_5)_3PS_2C_2(CF_3)_2$. *Anal.* Calcd: C, 61.37; H, 3.86; F, 14.56; P, 7.91; S, 12.29. Found: C, 61.19; H, 4.08; F, 14.77; P, 7.97; S, 12.32.

In a similar experiment using triphenylarsine there was no evidence for adduct formation, but triphenylarsine sulfide (mp 165–166°) was isolated quantitatively. This represents a convenient synthesis of $(C_6H_5)_3AsS$ which, unlike $(C_6H_5)_3PS$, is not prepared easily by the direct reaction of the group V triaryl with sulfur.

Physical Measurements.—The polarographic data were obtained using a Heath-Built EUA-19-2 polarograph equipped with three electrodes. Additional details are given in the footnote to Table I. The conductivities were measured on a Serfass bridge using a cell calibrated with a 1 *M* aqueous potassium chloride solution. For the gold complexes described above, dichloromethane was used as the solvent. The following equivalent conductivities (ohm^{-1} cm^2 equiv^{-1}) were measured for 10^{-3} *M* solutions: $[(C_6H_5)_3PClAuS_4C_4(CF_3)_4]$, $\Lambda_e = 48.5$; $[(C_6H_5)_4As][AuS_4C_4(CF_3)_4]$, $\Lambda_e = 53.2$; and, for comparison, $[(C_4H_9)_4N]$-$NiS_4C_4(CF_3)_4$, $\Lambda_e = 40.7$. The first compound could be recovered unchanged from dichloromethane.

Table I

Polarographic Half-Wave Potentials[a] in Acetonitrile Solution for the Couple $ML_2^- + e^- \rightleftharpoons ML_2^{2-}$

	L		
M	$(C_6H_5)_2C_2S_2$	$(CF_3)_2C_2S_2$	$(CN)_2C_2S_2$
Co	−0.978	−0.24	+0.05
Ni	−0.824	−0.121	+0.226
Cu	...	−0.010	+0.333
Pt	−0.806	−0.267	+0.210
Au	...	*b*, *c*	−0.419

[a] Measured in volts with reference to sce using 0.05 *M* $[(n\text{-}C_3H_7)_4N](ClO_4)$ as supporting electrolyte. [b] No wave found in range 0 to −1.5 v. [c] Half-wave potential for the couple $ML_2^0 \rightleftharpoons ML_2^-$ occurs at +1.20 v.

The conductivities of other compounds of the type $[MS_4C_4R_4]^z$, etc., were measured in Spectrograde acetonitrile solution in the concentration range 10^{-2} to 10^{-4} equiv/l. Using the Onsager limiting law, $\Lambda_0 - \Lambda_e = (a\Lambda_0 + b)\sqrt{c} = A\sqrt{c}$, the value of Λ_0 was determined by extrapolation from a plot of Λ_e as a function of $\sqrt{c}$, where c is the equivalent concentration. The slope A was also determined. A theoretical value of A can be calculated from the limiting-law expression using the constants appropriate to acetonitrile.[14] For complexes formulated as 2:1 electrolytes, A depends also on the equivalent ionic conductivities, λ_0^+ and λ_0^-, in acetonitrile. The other ionic conductivities could then be determined by difference.

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(13) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483 (1965).

(14) (a) P. Walden and E. J. Birr, *Z. Physik. Chem.*, **144**, 269 (1929); (b) J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2529 (1965).

$[(C_4H_9)_4N]_2[CoS_4C_4(CN)_4]$: Λ_0, 188; A, 740 (calcd, 760)
$[(C_4H_9)_4N]_2[NiS_4C_4(CN)_4]$: Λ_0, 190; A, 790 (calcd, 770)
$[(C_4H_9)_4N]_2[CuS_4C_4(CN)_4]$: Λ_0, 187; A, 740 (calcd, 760)
$[(C_2H_5)_4N][NiS_4C_4(CN)_4]$: Λ_0, 169; A, 340 (calcd, 355)
$[(C_6H_5)_4As][CuS_4C_4(CF_3)_4]$: Λ_0, 145; A, 390 (calcd, 335)
$[(C_4H_9)_4N][Ni(tdt)_2]$: Λ_0, 145; A, 450 (calcd, 335)
$[(C_4H_9)_4N][Co(tdt)_2]$: Λ_0, 142; A, 460 (calcd, 335)
$[(C_4H_9)_4N]_n[\{CoS_4C_4(CN)_4\}_n]$: Λ_0, 166; A, 600 [calcd, 350 ($n = 1$); 715 ($n = 2$)]
$[(C_4H_9)_4N]_n[\{CoS_4C_4(CF_3)_4\}_n]$: Λ_0, 160; A, 530 [calcd, 345 ($n = 1$); 705 ($n = 2$)]
$[(C_2H_5)_4N]_n[\{CoS_4C_4(CF_3)_4\}_n]$: Λ_0, 184; A, 550 [calcd, 375 ($n = 1$); 730 ($n = 2$)]

Results and Discussion

Synthetic Studies.—We find that halotriphenylphosphine complexes react smoothly with bis(trifluoromethyl)-1,2-dithietene in benzene or dichloromethane to give bis(*cis*-1,2-ditrifluoromethylethylene-1,2-dithiolato) complexes. Since this procedure does not require the use of metal carbonyls, it has been possible to obtain the previously unknown complexes of copper and gold. This method has also provided a more convenient synthesis of the known cobalt, nickel, palladium, and platinum compounds. The bis(dithiolato) complexes were isolated as the salts of either the mono- or the dianions. In the platinum case, a small amount of $PtS_4C_4(CF_3)_4$ was also produced.

The mechanism of this reaction is not known with certainty but, at least in the nickel, palladium, and platinum cases, it does not proceed through the known[10] species $[(C_6H_5)_3P]_2MS_2C_2(CF_3)_2$ (M = Ni, Pd, and Pt). These complexes, which are extremely insoluble under the reaction conditions, were not detected in the reaction mixtures. In all of the reactions of this type triphenylphosphine sulfide was obtained together with trace amounts of 2,3,4a,6,7,8a-hexakis(trifluoromethyl)-4a,8a-dihydro-*p*-dithiino[2,3-*b*]-*p*-dithiin. Optimum yields were obtained with a (3.5–4.0):1 mole ratio of $(CF_3)_2C_2S_2$ to the metal triphenylphosphine complex. The reaction presumably involves the removal of the coordinated triphenylphosphine by the sulfur heterocycle to give triphenylphosphine sulfide and then subsequent reaction of the coordinatively unsaturated metal with $(CF_3)_2C_2S_2$ to give the dithiolate complex. It was found that triphenylphosphine reacts, at reflux temperature, with solutions of bis(trifluoromethyl)-1,2-dithietene to give triphenylphosphine sulfide quantitatively together with small amounts of the dithiin described above. At room temperature, however, an unstable adduct $(C_6H_5)_3P{=}S\cdot(C_6H_5)_3PS_2C_2(CF_3)_2$ is produced. The removal of the coordinated triphenylphosphine by $(CF_3)_2C_2S_2$ seems necessary because tetrahalometalates do not react to give bis(dithiolato) complexes.

Under aprotic conditions triphenylphosphinegold chloride reacts with bis(trifluoromethyl)-1,2-dithietene to give the easily reduced $(C_6H_5)_3PAuClS_4C_4(CF_3)_4$. This compound reacts with solvents containing O and N functional groups to give the $[AuS_4C_4(CF_3)_4]^-$ ion with loss of triphenylphosphine and chloride ion. It is insoluble in carbon tetrachloride and benzene, but it is readily soluble and gives a conducting solution in dichloromethane. It is recovered unchanged from the latter solvent. We formulate it as a five-coordinate, cationic gold complex $[(C_6H_5)_3PAuS_4C_4(CF_3)_4]Cl$. The stabilization of this unusual coordination number for gold is another striking demonstration of the remarkable versatility of the dithiolato ligand. This formulation prompted us to attempt the synthesis of the neutral isoelectronic platinum analog. The reaction of triphenylphosphine with $PtS_4C_4(CF_3)_4$ in a 1:1 mole ratio gave, however, a low yield of the known $[(C_6H_5)_3P]_2PtS_2C_2(CF_3)_2$ instead of the expected adduct. The use of excess triphenylphosphine gave essentially quantitative yields of this complex together with triphenylphosphine sulfide. Similarly $[(C_6H_5)_3P]_2NiS_2C_2(CF_3)_2$ was obtained from the corresponding reaction of triphenylphosphine and $NiS_4C_4(CF_3)_4$. This behavior is in direct contrast to that found[2,6,10] for weak aliphatic organic O or N functional bases, which rapidly reduce the neutral complexes to the monoanions. The two complexes $[(C_6H_5)_3P]_2MS_2C_2(CF_3)_2$ and $MS_4C_4(CF_3)_4$ (M = Ni and Pt) are readily converted into each other, depending upon the conditions. This is a reflection of the ability of triphenylphosphine to desulfurize the $(CF_3)_2C_2S_2$ fragment either when free or coordinated to a metal. These desulfurization reactions of the neutral dithiolato complexes are in direct contrast to the behavior reported by Schrauzer[13] for the reactions of $MS_4C_4R_4$ (M = Pd or Pt, R = CH_3 or C_6H_5) with triphenylphosphine which were claimed to form the six-coordinate complexes $[(C_6H_5)_3P]_2MS_4C_4R_4$. We have carefully reinvestigated these adducts and find them, instead, to be the expected four-coordinate complexes produced by a desulfurization reaction. The conclusions based on a semiempirical molecular orbital approach[13] rationalizing the six-coordinate complexes as having metals in effectively a +4 oxidation state must now be regarded with caution!

Polarographic and Conductivity Studies.—The relevant data from the polarographic studies are set out in Table I. This makes available a limited comparison of the ease of oxidation of complexes of cobalt, nickel, and copper as a function of the ligand substituent R. The data show that for a given R the ease of oxidation is Co > Ni > Cu, and that for a particular metal the ease of oxidation is markedly R dependent, R = C_6H_5 > CF_3 > CN.

Clearly, it is the nature of the ligand, rather than the metal, which is the dominant feature in these redox reactions. For the cobalt system the over-all process is $[(CoS_4C_4R_4)_2]^{2-} + 2e^- \rightleftharpoons 2[CoS_4C_4R_4]^{2-}$. In the nickel and copper cases the symmetries of the orbitals from which the electron is removed are clearly different. However, in both cases there is appreciable covalency[15] in these orbitals. In the copper case the electron is removed from a $\sigma^*(b_{1g})(xy)$ molecular orbital but at least for the complex $[CuS_4C_4(CN)_4]^{2-}$ the unpaired electron has been shown[15] to be extensively delocalized on the ligands. In the nickel case we have suggested[15] on the basis of a single-crystal esr study

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[15] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

that the highest filled level is an out-of-plane $\pi(b_{3g})(yz)$ orbital which is again appreciably covalent. Semiempirical molecular orbital calculations[16] of $[NiS_4C_4(CN)_4]$ ($z = -1, -2$) suggest that the highest filled orbital is an in-plane $\pi(a_g)(x^2 - y^2)$ which is mainly ligand in character. In both formulations the orbitals in question are strongly delocalized on the ligands and it is only the symmetry of the highest filled orbital which is in dispute.

Molar conductivities, usually for *ca.* 10^{-3} *M* solutions of salts of the bis(dithiolato)metal anions, have generally been taken as additional confirmatory evidence for the correctness of their formulations in the absence of X-ray structure determinations. However, it has recently become obvious that metal-to-sulfur interactions can occur between planar units (Figure 1) as in $[CoS_4C_4(CF_3)_4]_2$.[7] It has been pointed out[17] that molar conductivities measured at one concentration establish only the empirical formula, not the degree of polymerization; *e.g.*, such measurements cannot distinguish between [R][ML], a 1:1 electrolyte, and $[R]_2[M_2L_2]$, a 2:1 electrolyte. However, this ambiguity is removed by plotting the equivalent conductivity Λ_e or $\Lambda_0 - \Lambda_e$ as a function of $\sqrt{c}$. Such plots enable one to determine the nature of the electrolyte since 1:1 and 2:1 electrolytes have characteristically differing slopes. Plots of this type for the dithiolato complexes in acetonitrile in the concentration range 10^{-2} to 10^{-4} equiv/l. are shown in Figures 2 and 3. The significant feature of these results, see Figure 2, is that in solution the diamagnetic cobalt complexes should be properly formulated as salts of a dimeric dianion, *i.e.*, $[\{CoS_4C_4R_4\}_2]^{2-}$ (R = CF_3 and CN). These species presumably have the structure depicted in Figure 1. However, the related high-spin ($S = 1$) cobalt complex[18] with toluene-3,4-dithiol as a ligand has a curve which is almost coincident with that for the corresponding nickel complex of this ligand (Figure 3) and is clearly a 1:1 electrolyte. Our claim that some of the cobalt species are dimeric dianions in solution may seem, initially, to conflict with our earlier claim,[6a] based on X-ray powder data, that the complexes having the empirical formulas $[N(C_4H_9)_4][MS_4C_4(CN)_4]$ [M = Co, Ni, and Cu) are isomorphous. We have determined the unit cell dimensions and space group requirements of the cobalt complex using Weissenberg and precession photographs with a single crystal and Cu Kα radiation. It is monoclinic and has the dimensions $a = 15.27 \pm 0.03$ A; $b = 14.07 \pm 0.03$ A; $c = 27.72 \pm 0.04$ A; $\beta = 96.05 \pm 0.1°$. Reflections are absent unless $h + k + l = 2n$ and $h0l$ reflections are absent unless $l = 2n$. This is consistent with I2/c or Ic as the space group.

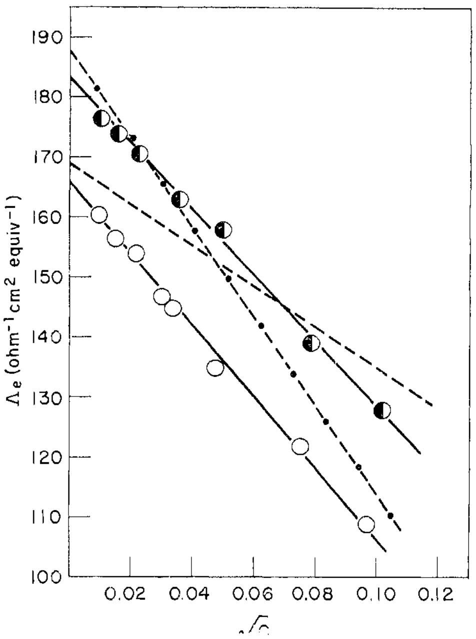

Figure 2.—The equivalent conductivities of 1:1 and 2:1 electrolytes in acetonitrile: ○, $[(n\text{-}C_4H_9)_4N]_2[CoS_4C_4(CN)_4]_2$; ◐, $[(C_2H_5)_4N]_2[CoS_4C_4(CF_3)_4]_2$; — · —, $[(n\text{-}C_4H_9)_4N]_2[CoS_4C_4(CN)_4]$; – – – –, $[(C_2H_5)_4N][NiS_4C_4(CN)_4]$.

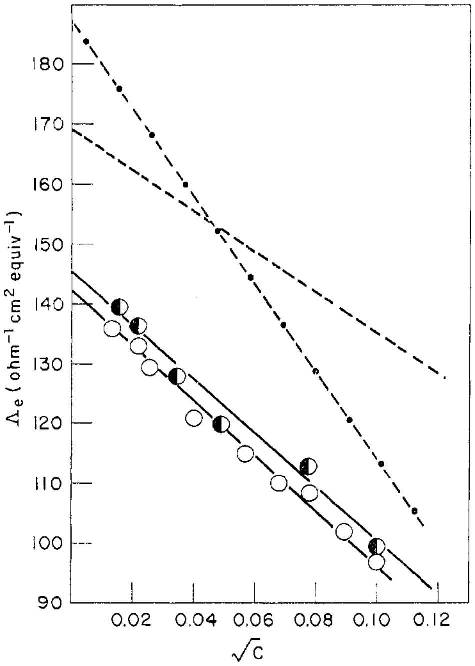

Figure 3.—The equivalent conductivities of 1:1 and 2:1 electrolytes in acetonitrile: ○, $[(n\text{-}C_4H_9)_4N][Co(tdt)_2]$; ◐, $[(n\text{-}C_4H_9)_4N][Ni(tdt)_2]$; — · —, $[(n\text{-}C_4H_9)_4N]_2[CoS_4C_4(CN)_4]$; – – – –, $[(C_2H_5)_4N][NiS_4C_4(CN)_4]$; tdt = toluene-3,4-dithiolate.

The copper[5] and cobalt complexes have the same systematic absences. They have similar unit cell dimensions but a visual comparison of the intensities of the $h0l$ levels in the Weissenberg photographs of both the copper and cobalt complexes shows significant differences. The copper complex[5] which was found to be I2/c has the anions stacked with their axes parallel to *a* and having relatively near neighbors (Cu–Cu distances of 4.026 and 4.431 A). A similar situation was found[4b] with a slightly different stacking of the anions in $[(C_6H_5)_3P(CH_3)][NiS_4C_4(CN)_4]$. Both arrangements lead to a reduction of the magnetic mo-

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[16] S. F. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964).

[17] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

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

ments for the nickel monoanions in crystalline samples.[6,9a] We are undertaking a complete structure determination of the cobalt complex to ascertain whether there is any pronounced dimerization present in the solid. However, even an arrangement similar to that in the copper case does not preclude the existence of dimeric dianions in solution. The apparent paradox of the different spin states of the cobalt species can now, at least qualitatively, be understood to be due to spin pairing in the dimer and is not simply due to a[18] smaller separation between the $\pi(yz)$ and $\pi(x^2 - y^2)$ orbitals in the toluene-3,4-dithiol complexes. The explanation of the diamagnetism of $[\{CoS_4C_4(CF_3)_4\}_2]$ and some of the related reactions associated with these dimeric units will clearly have to be postponed until the electronic structures of the dimeric units are understood.

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Substitution Reactions of Metallic Complexes of β,β′,β″-Triaminotriethylamine. II. Kinetics of Aquation of *cis*-Dibromo(triaminotriethylamine)cobalt(III) Ion[1]

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The kinetics of the aquation of *cis*-$[Co(tren)Br_2]^+$ have been investigated in 0.1 *M* $HClO_4$ at 20.0, 25.0, 30.0, 35.0, and 40.0°. The pseudo-first-order rate constant for the release of one bromide ion at 25.0° was found to be 2.81×10^{-2} sec.$^{-1}$ The primary aquation rate constant, k_1, is independent of the initial concentration of the complex over the range 5.0–7.5 m*M*, of pH from 1.0 to 6.0, and of ionic strength from 0.0038 to 1.60. The Arrhenius activation energy is 15.1 kcal mole^{-1} and ΔS^* is -14.8 cal deg^{-1} mole^{-1}. Added sulfate ion accelerates the aquation. A value for the secondary aquation rate constant, $k_2 = 1.55 \times 10^{-6}$, for the loss of the second bromide ion has also been determined.

Introduction

An extensive amount of kinetic data has been reported for substitution reactions in octahedral complexes for the type $[MA_4XY]^{1+ \text{ or } 2+}$ where M has been Co(III), Cr(III), or Ir(III) and A represents a nonreplaceable ligand, which may be monodentate or polydentate, including N- and/or C-substituted polyamines. The ligands X and Y, with X representing the replaceable group, may be F, Cl, Br, OH, H_2O, or NH_3, although most commonly X has been Cl, Br, or F.[2]

A recent study of the aquation of the $[Co(tren)Cl_2]^+$ ion (tren = β,β′,β″-triaminotriethylamine) showed its aquation rate to be greater than that of complex ions containing certain other organic amines.[1] It was assumed that the greater rate at which *cis*-$[Co(tren)Cl_2]^+$ aquated was attributable simply to steric strains produced by the peculiar geometry of the complex.[1] The purpose of the present investigation was to test this assumption by determining the rate constant and Arrhenius parameters for the first step of aquation of *cis*-$[Co(tren)Br_2]^+$ ion. In addition, we have also measured the second step of aquation for this cation.

The aquation reaction in 0.1 *M* acid solution takes place in two over-all steps

$$cis\text{-}[Co(tren)Br_2]^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-}[Co(tren)BrH_2O]^{2+} + Br^- \quad (1)$$

$$cis\text{-}[Co(tren)BrH_2O]^{2+} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} cis\text{-}[Co(tren)(H_2O)_2]^{3+} + Br^- \quad (2)$$

Reaction 1 proceeds at a much greater rate than forward reaction 2, so that no serious interference is caused by forward reaction 2 in the study of reaction 1. Under the conditions of the experiments reported here, equilibrium was not observed either in reaction 1 or 2.

Experimental Section

Preparation of Compounds.—β,β′,β″-Triaminotriethylamine trihydrochloride was synthesized according to a procedure outlined by Liu.[3]

***cis*-Carbonatotetraamminecobalt(II) Nitrate Hemihydrate.**—This compound was prepared by the method described by Schlessinger.[4]

***cis*-Dichloro(triaminotriethylamine)cobalt(III) Chloride.**—Described in a previous paper.[1]

***cis*-Dibromo(triaminotriethylamine)cobalt(III) Bromide.**—The new complex was prepared by adding a solution of 6.4 g of triaminotriethylamine trihydrochloride in 50 ml of water to 3.15 g

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(1) Part I: S. K. Madan, W. M. Reiff, and J. C. Bailar, Jr., *Inorg. Chem.*, **4**, 1366 (1965).

(2) For review see D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 78.

(3) C. F. Liu, Doctorate Dissertation, University of Illinois, 1957.

(4) G. Schlessinger, *Inorg. Syn.*, **6**, 173 (1960).