red spectrum showed no Re=O to be present. In fact, if one considers the precipitate to be $[Pt(NH_3)_4]_2[Re(SCN)_6]$, one finds that the rhenium content determined by the Russian workers (23.30% Re) is indeed in much better agreement with that calculated for the hexathiocyanate(IV) salt (23.31%).

These results show that the colored rhenium thiocyanate compounds produced by reduction of perrhenate are made up of rhenium(IV) and/or rhenium(V) hexathiocyanate species, depending on the amount of reducing agent used. An excess is clearly required for reproducible analytical use. No oxo species are formed unless in trace amounts in the acidity range considered here. In view of the fact that none of the previous workers in this field has given any direct evidence for the presence of oxygen in their compounds, it must be concluded that rhenium oxothiocyanates have not been observed as yet.

CONTRIBUTION NO. 2126 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

Cleavage Reactions of Cobalt and Iron Dithiolate Compounds. Five-Coordinate Complexes

BY A. L. BALCH

Received August 9, 1967

Synthetic and polarographic studies indicate that triphenylphosphine, triphenylarsine, triphenylstibine, and triphenyl phosphite (L) cleave the dimeric complexes $[MS_4C_4R_4]_2^z$ (M = Co, Fe; R = CF_3, z = 0, −1, −2; R = CN, z = −2) to yield monomeric, five-coordinate $[LMS_4C_4R_4]^z$. Polarography of the $[LMS_4C_4R_4]^z$ species indicates the existence of three complexes (z = +1, 0, −1) for M = Co and R = CF_3 and at least two (z = 0, −1) for M = Co and R = CN and for M = Fe and R = CF_3 or CN. In solution $LCoS_4C_4(CF_3)_4$ exhibits magnetic and esr properties consistent with a doublet ground state. In the solid $(C_6H_5)_3PCoS_4C_4(CF_3)_4$ is diamagnetic and presumably dimerized. Magnetic studies show that $LFeS_4C_4(CF_3)_4$ and $[(C_6H_5)_3PCoS_4C_4R_4]^-$ are diamagnetic whereas $[(C_6H_5)_3PFeS_4C_4(CF_3)_4]^-$ has an $S = {}^3/_2$ ground state. No evidence of these five-coordinate species adding further ligands has been found.

Introduction

A recent investigation[1] of the complexes $[MS_4C_4R_4]_n^z$ with M = Co or Fe and R = CF_3 has revealed that in dichloromethane solution an electron-transfer series embracing the members **1**–**4** exists. When R = CN

$$\underset{\mathbf{1}}{[M\text{–}S_4]_2^{0}} \longrightarrow \underset{\mathbf{2}}{[M\text{–}S_4]_2^{-}} \longrightarrow \underset{\mathbf{3}}{[M\text{–}S_4]_2^{2-}} \longrightarrow \underset{\mathbf{4}}{2[M\text{–}S_4]^{2-}}$$

only the three reduced species **2**–**4** have been detected. With $[CoS_4C_4(CF_3)_4]_2$[2] and $[FeS_4C_4(CN)_4]_2^{2-}$,[3] dimerization has been shown to occur through metal-to-sulfur bonds to give square-pyramidal coordination about each metal. This basic structure, depicted in Figure 1, is believed to persist throughout the electron-transfer series **1**–**3**. However the most reduced member **4** with M = Co and R = CN has been shown to have monomeric, planar geometry.[4]

The present study is concerned with the interaction of several potential two-electron donors with dimers **1**–**3**. Although addition—possibly stepwise—of donors to the intact dimers is feasible, previous studies indicate that cleavage of the dimers to give five- or six-coordinate complexes would be more likely. For example, it has been shown[5] that $[MS_4C_4(C_6H_5)_4]_n$ (M = Co, Fe) reacts with phosphines to yield monomeric [phosphine–$MS_4C_4(C_6H_5)_4$]. Reaction of $[CoS_4C_4(CN)_4]_2^{2-}$ with a variety of donors yields a variety of six- and apparently five-coordinate, monomeric species.[6] Five-coordination has also been observed in the novel gold dithiolato complex $[(C_6H_5)_3PAuS_4C_4(CF_3)_4]Cl$.[7]

Experimental Section

Preparation of Compounds.—Commercial samples of group V triaryls were recrystallized before use. Melting points are uncorrected.

$(C_6H_5)_3PCoS_4C_4(CF_3)_4$.—A solution of 0.263 g (1.00 mmole) of triphenylphosphine in 60 ml of dry pentane was added dropwise to a solution of 0.512 g (0.500 mmole) of $[CoS_4C_4(CF_3)_4]_2$[8] in 200 ml of dry pentane. The volume of the brown solution was reduced to 60 ml. The solution was filtered and cooled in a Dry Ice bath. The fine brown crystals which formed were collected by filtration and washed with pentane. Further purification was obtained by recrystallization from pentane followed by vacuum drying. The yield is 70–80%; mp 183–185°. *Anal.* Calcd: C, 40.37; H, 1.95; S, 16.58; P, 4.00; mol wt, 774. Found: C, 40.60; H, 2.00; S, 16.84; P, 4.08; mol wt, 757.

A similar procedure produced yields of 60–90% in the preparation of the following analogous compounds. For the iron compounds, $[FeS_4C_4(CF_3)_4]_2$[1] replaced its cobalt analog as starting material.

$(C_6H_5)_3AsCoS_4C_4(CF_3)_4$.—Brown crystals were obtained; mp 186.5–188°. *Anal.* Calcd: C, 38.29; H, 1.85; mol wt, 818. Found: C, 38.50; H, 2.05; mol wt, 785.

---

[1] (a) A. L. Balch and R. H. Holm, *Chem. Commun.*, 552 (1966); (b) A. L. Balch, I. G. Dance, and R. H. Holm, submitted for publication.

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

[3] W. C. Hamilton and R. Sprathy, *Acta Cryst.*, **7**, A142 (1966).

[4] J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1500 (1964).

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

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

[7] A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

[8] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **3**, 814 (1964).

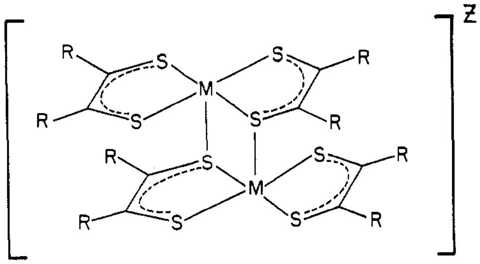

Figure 1.—Proposed structure for the $[MS_4C_4R_4]_2^z$ complexes.

$(C_6H_5)_3SbCoS_4C_4(CF_3)_4$.—Brown crystals which formed were recrystallized from heptane; mp 211–212°. *Anal.* Calcd: C, 36.13; H, 1.75; mol wt, 864. Found: C, 36.37; H, 1.66; mol wt, 856.

$(C_6H_5O)_3PCoS_4C_4(CF_3)_4$.—Fine green crystals were obtained; mp 103–104°. *Anal.* Calcd: C, 38.39; H, 1.90; S, 15.36; mol wt, 818. Found: C, 38.01; H, 1.84; S, 15.61; mol wt, 780.

$(C_6H_5)_3PFeS_4C_4(CF_3)_4$.—Green prisms were obtained; mp 125°. This complex is unstable in solution when exposed to strong sunlight. It also decomposes in the solid state without any visibly detectable change. The decomposed solid leaves a yellow residue upon dissolution in dichloromethane and is paramagnetic. All physical measurements were made on freshly prepared samples. *Anal.* Calcd: C, 40.53; H, 1.96; P, 4.02; mol wt, 770. Found: C, 40.10; H, 2.13; P, 3.85; mol wt, 721.

$(C_6H_5)_3AsFeS_4C_4(CF_3)_4$.—Black prisms were obtained; mp 158–159.5°. *Anal.* Calcd: C, 38.34; H, 1.86; mol wt, 812. Found: C, 38.72; H, 1.80; mol wt, 796.

$(C_6H_5)_3SbFeS_4C_4(CF_3)_4$.—Black prisms which formed were recrystallized from heptane; mp 171–173°. *Anal.* Calcd: C, 36.26; H, 1.76; mol wt, 861. Found: C, 36.39; H, 1.94; mol wt, 838.

$(C_6H_5O)_3PFeS_4C_4(CF_2)_4$.—Deep blue needles were obtained; mp 112–114°. *Anal.* Calcd: C, 38.15; H, 1.85; S, 15.67; P, 3.78; mol wt, 818. Found: C, 38.51; H, 1.80; 15.18; P, 3.61; mol wt, 805.

$[(C_4H_9)_4N][(C_6H_5)_3PCoS_4C_4(CF_3)_4]$.—A solution of 0.29 g (1.1 mmoles) of triphenylphosphine in 30 ml of dichloromethane was added to a solution containing 0.71 g (0.50 mmole) of $[(C_4H_9)_4N]_2[CoS_4C_4(CF_3)_4]_2$[7] in 125 ml of dichloromethane. Twenty milliliters of *sec*-butyl alcohol was added, and the solution was filtered. Most of the dichloromethane was removed by boiling the solution on a steam bath. On standing at room temperature for 24 hr, brown needles were deposited. The product was collected by filtration, washed with *sec*-butyl alcohol, and vacuum dried at 60°; mp 118–122°. *Anal.* Calcd: C, 49.65; H, 5.06; N, 1.38. Found: C, 49.76; H, 5.25; N, 1.65.

$[(C_4H_9)_4N][(C_6H_5)_3PFeS_4C_4(CF_3)_4]$.—A solution of 0.56 g (2.1 mmoles) of triphenylphosphine in 10 ml of acetone was added to a solution of 0.75 g (0.50 mmole) of $[(C_4H_9)_4N]_2[FeS_4C_4(CF_3)_4]_2$[1] in 10 ml of acetone. Twenty milliliters of toluene was added and the solution was filtered. The acetone was distilled off by heating on a steam bath. The red-brown prisms, which formed while the solution stood at room temperature for 48 hr, were collected, washed with toluene, and vacuum dried. The yield was 70%; mp 176–177.5°. *Anal.* Calcd: C, 49.80; H, 5.08; N, 1.38. Found: C, 49.60; H, 5.30; N, 1.74.

$[(C_4H_9)_4N][(C_6H_5)_3PCoS_4C_4(CN)_4]$.—This salt was prepared in the manner indicated by Langford, *et al.*;[6] mp 183–185°. *Anal.* Calcd: C, 59.77; H, 6.09; N, 8.30. Found: C, 59.95; H, 6.10; N, 8.31.

The Reaction of $[(C_2H_5)_4N][FeS_4C_4(CF_3)_4]_2$ with Triphenylarsine.—A solution of 0.1884 g (0.615 mmole) of triphenylarsine in 25 ml of dry dichloromethane was added dropwise to a stirred slurry of 0.702 g (0.612 mmole) of $[(C_2H_5)_4N][FeS_4C_4(CF_3)_4]_2$[1] in 25 ml of dry dichloromethane. The pale green solution darkened as the solution was stirred for 12 hr. The solution was filtered to remove black, crystalline $[(C_2H_5)_4N]_2[FeS_4C_4(CF_3)_4]$.[7] The crystals were washed with dichloromethane until the washings were colorless. The yield was 0.37 g or 97% based on reaction 2. Polarography of the product was identical with that of an authentic sample. *Anal.* Calcd: C, 30.10; H, 3.16. Found: C, 29.57; H, 3.45.

The combined dichloromethane filtrates were evaporated to yield green prisms. These crystals were recrystallized from pentane to give 0.406 g (82%) of $(C_6H_5)_3AsFeS_4C_4(CF_3)_4$. Polarography of this material was identical with that of the complex prepared from triphenylarsine and $[FeS_4C_4(CF_3)_4]_2$. *Anal.* Found: C, 38.76; H, 1.91.

Mass Spectra.—The composition of the new neutral compounds has been confirmed by the observation of the parent ions in their mass spectra. The *m/e* of the most intense peak in the parent ion multiplet is given: $(C_6H_5)_3PCoS_4C_4(CF_3)_4$, 773; $(C_6H_5)_3AsCoS_4C_4(CF_3)_4$, 817; $(C_6H_5)_3SbCoS_4C_4(CF_3)_4$, 863; $(C_6H_5O)_3PCoS_4C_4(CF_3)_4$, 821; $(C_6H_5)_3AsFeS_4C_4(CF_3)_4$, 814; $(C_6H_5)_3SbFeS_4C_4(CF_3)_4$, 860; $(C_6H_5O)_3PFeS_4C_4(CF_3)_4$, 818.

Physical Measurements.—Polarographic measurements were made using an ORNL Model 1988 polarograph equipped with a three-electrode configuration in conjunction with a rotating platinum electrode. The technique for obtaining polarograms in dichloromethane described previously[9] was modified[1b] by replacing $(n\text{-}C_4H_9)_4NPF_6$ with $(n\text{-}C_4H_9)_4NClO_4$ (0.500 *M*) as the supporting electrolyte in the reference compartment. Magnetic moments of solids were measured using a Faraday balance constructed from a 4-in. Varian magnet equipped with Heyding pole pieces[10] and a Cahn electrobalance; $HgCo(CNS)_4$ was employed as magnetic standard.[11] Magnetic moments in solution were measured by an nmr technique.[12] Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Molecular weights in chloroform solution were measured at 37° with a Mechrolab osmometer employing triphenylarsine as reference. A Picker MS-9 spectrometer was employed in the mass spectral studies. Esr spectra were recorded on a Varian spectrometer employing a Varian V-FR2503 field regulator. The microwave frequency was measured to ±1 Mc by a frequency meter and the magnetic field was calibrated by a Magnion nmr gaussmeter and frequency counter.

Results and Discussion

Synthetic Studies.—The reactions of the iron and cobalt complexes **1**, **2**, and **3** (R = CF_3) and **3** (R = CN) with the two-electron donors triphenylphosphine, triphenylarsine, triphenylstibine, and triphenyl phosphite (collectively referred to as L) follow analogous paths as discussed below. The potential donors diphenyl ether, diphenyl sulfide, and triphenylphosphine sulfide do not react with any of the dimeric complexes.

Treatment of $[MS_4C_4(CF_3)_4]_2$ with L results in cleavage of the dimer to produce the novel, five-coordinate $LMS_4C_4(CF_3)_4$ according to reaction 1. In contrast to

$$[MS_4C_4(CF_3)_4]_2 + 2L = 2LMS_4C_4(CF_3)_4 \qquad (1)$$

this the reaction with triphenylamine reduces $[MS_4C_4(CF_3)_4]_2$ to $[MS_4C_4(CF_3)_4]_2^{2-}$; similar reduction occurs with other nitrogen bases and some oxygen bases.[7] Reaction 1 also differs from the reaction of triphenylphosphine with $[MS_4C_4(CF_3)_4]$ (M = Ni, Pt); this reaction yields the substituted product $[(C_6H_5)_3P]_2MS_2C_2(CF_3)_2$.[7] The complexes $[MS_4C_4(CF_3)_4]_2$ are more susceptible to cleavage reactions than the related

---

[9] F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966).

[10] R. D. Heyding, J. B. Taylor, and M. L. Hair, *Rev. Sci. Instr.*, **32**, 261 (1961).

[11] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[12] D. F. Evans, *ibid.*, 2003 (1957).

$[MSC_4(C_6H_5)_4]_n$ species which are reported to be inert to triphenylarsine and triphenylstibine.[5]

Triphenylarsine reacts with $[(C_2H_5)_4N][FeS_4C_4(CF_3)_4]_2$ nearly quantitatively according to reaction 2. Both

$$2[Fe{-}S_4]^- + 2L = [Fe{-}S_4]_2^{2-} + 2[LFe{-}S_4] \qquad (2)$$

products have been isolated and shown to be identical with known samples of each product. On a smaller scale polarographic examination of the reaction of 2 moles of L with **2** (R = CF_3) indicates that the products are equimolar mixtures of $LMS_4C_4(CF_3)_4$ and $[M{-}S_4]_2^{2-}$. Thus reaction 2 appears to be a general one.

Addition of L to the dimeric dianions **3** produces marked color changes. Although the formation constants[13,14] for the products are rather low, it has been possible to isolate three complexes with the formulation $[LMS_4C_4R_4]^-$ (L = $(C_6H_5)_3P$: M = Co, R = CF_3 or CN; M = Fe, R = CF_3).

Polarographic Studies.—The polarography of dianionic species **3** also changes in the presence of added L. Figure 2 shows a typical case, the anodic[15] polarography of $[FeS_4C_4(CF_3)_4]_2^{2-}$ in the presence of varying amounts of triphenylphosphine. In the absence of triphenylphosphine the waves at +0.69 and +1.27 v correspond to the oxidations $[M{-}S]_2^{2-} \rightleftarrows [M{-}S_4]_2^- + e^-$ and $[M{-}S_4]_2^- \rightleftarrows [M{-}S_4]_2^0 + e^-$, respectively. Addition of triphenylphosphine creates a new wave at +0.30 v. The current of this wave eventually reaches a limiting value of approximately twice that of the wave at +0.69 v. Once this limiting current is reached, addition of further quantities of triphenylphosphine produces no changes at potentials less than +1.2 v.[16] The new wave is assigned to the oxidation of $[(C_6H_5)_3PFeS_4C_4(CF_3)]^-$ to $[(C_6H_5)_3PFeS_4C_4(CF_3)_4]$. The current is consistent with such a process, and a one-electron reduction of $[(C_6H_5)_3PFeS_4C_4(CF_3)_4]$ occurs at the same potential. Since no further changes in polarography occur with increased triphenylphosphine concentration, it appears that no other adducts are formed.

Concurrent with the growth of the wave at +0.30 v, the current of the wave at +0.69 v first increases and then decreases to zero. The initial increase can be accounted for by a kinetic component to the current. This kinetic current could result if some of the oxidation product, $[Fe{-}S_4]_2^-$, is converted to the electroactive species, $[Fe{-}S_4]_2^{2-}$, before the product can diffuse away from the electrode.[17] Reaction 2, if fast enough, can account for this transformation. The eventual decrease in the wave at +0.69 v results, of course, from the decreasing concentration of uncleaved $[Fe{-}S_4]_2^{2-}$.

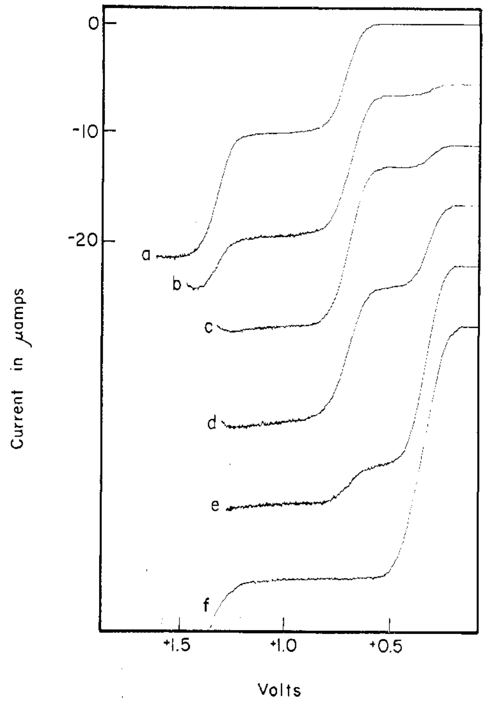

Figure 2.—Polarography of $[(C_4H_9)_4N]_2[FeS_4C_4(CF_3)_4]_2$ in the presence of $(C_6H_5)_3P$. Concentration of $[FeS_4]_2^{2-}$ is 1.00 m*M* throughout. $(C_6H_5)_3P$ concentration: a, 0; b, 0.61 m*M*; c, 1.28 m*M*; d, 5.78 m*M*; e, 25.1 m*M*; f, 47.4 m*M*. Current scale of successive polarograms is offset by ~5.5 μa.

Similar effects are observed on adding L to each of the four dianions **3**. Only one new wave was observed in each case; the data for this wave, which is assigned to the $[LM{-}S_4]^- \rightarrow [LM{-}S_4]^0$ oxidation, are set out in Table I. Reduction of authentic $[LM{-}S_4]^0$ (if available) occurs at the same potential as the oxidation of the corresponding adduct.

Polarography of $[LCoS_4C_4(CF_3)_4]^0$ reveals a one-electron oxidative wave which presumably produces

Table I

Polarographic Data for $[LMS_4C_4R_4]^z$

M	R	L	$(z = -1) \rightleftarrows (z = 0) + e^-$ $E_{1/2}$[a], v	$(z = -1) \rightleftarrows (z = 0) + e^-$ i_d/C,[b,c] μa/mmole	$(z = 0) \rightleftarrows (z = +1) + e^-$ $E_{1/2}$, v	$(z = 0) \rightleftarrows (z = +1) + e^-$ i_d/C, μa/mmole
Fe	CF_3	$(C_6H_5)_3P$	+0.30	23	None	
		$(C_6H_5)_3As$	+0.47	23	None	
		$(C_6H_5)_3Sb$	+0.41	24	None	
		$(C_6H_5O)_3P$	+0.37	23	None	
Fe	CN	$(C_6H_5)_3P$	+0.69	21	*d*	
		$(C_6H_5)_3As$	+0.77	*e*	*d*	
		$(C_6H_5)_3Sb$	+0.70	*e*	*d*	
Co	CF_3	$(C_6H_6)_3P$	+0.41	23	+1.50	22
		$(C_6H_5)_3As$	+0.46	22	+1.50	24
		$(C_6H_5)_3Sb$	+0.40	23	+1.50	24
		$(C_6H_5O)_3P$	+0.52	24	+1.56	24
Co	CN	$(C_6H_5)_3P$	+0.77	20	*d*	
		$(C_6H_5)_3As$	+0.75	20	*d*	
		$(C_6H_5)_3Sb$	+0.73	20	*d*	

[a] For R = CF_3 the reported values are the mean of the values observed for the oxidation of $LMS_4C_4(CF_3)_4^-$ and for the reduction of $LMS_4C_4(CF_3)_4$. In all cases these values differ by less than 0.04 v. [b] For R = CF_3 these values refer to the reduction of $LMS_4C_4(CF_3)_4$. For R = CN they refer to the oxidation of $LMS_4C_4(CF_3)_4^-$. [c] For comparison the one-electron oxidation $NiS_4C_4(CN)_4^{2-} \rightarrow NiS_4C_4(CN)_4^-$ gives i_d/C = 21 μa/mmole. [d] Presence of excess ligand obscures the region above +1.2 v. [e] Low solubility precludes determination.

---

(13) Spectral studies in dichloromethane solution indicate that for each complex **3** the order of stability of the adduct $[LMS_4C_4R_4]^-$ is L = $(C_6H_5)_3P$ > $(C_6H_5)_3As$ > $(C_6H_5)_3Sb$. Only one adduct appears to be formed. No spectral changes are observed with $(C_6H_5)_3N$. These results agree with the results obtained in acetone solution by Langford, *et al.*,[6] and indicate, as they pointed out, the unusual soft character[14] of the metal in these species.

(14) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 35 (1963).

(15) The cathodic polarography of **3** in the presence of L appears to involve only the couple $2e^- + [M{-}S_4]_2^{2-} \rightleftarrows 2[M{-}S_4]^{2-}$. No clean reduction waves assignable to a reduction $e^- + [LM{-}S_4]^- \rightleftarrows [LM{-}S_4]^{2-}$ have been observed.

(16) Electroactive behavior of *free* L at *ca.* +1.2 v precludes observation of the behavior of the metal complexes in this region.

(17) A. A. Vlcek, *Progr. Inorg. Chem.*, **5**, 211 (1963).

$[LCoS_4C_4(CF_3)_4]^+$. No corresponding oxidation of $[LFeS_4C_4(CF_3)_4]^0$ was observed. It was impossible to search for $[LMS_4C_4(CN)_4]^+$ since polarography of $[LMS_4C_4(CN)_4]^-$ required the presence of excess L,[16] and the corresponding neutral compounds were not prepared.

Examination of the half-wave potentials for the $[LM-S_4] + e^- \rightleftarrows [LM-S_4]^-$ couple reveals several interesting features. Comparison with the potentials (set out in Table II) for the reduction of $[M-S_4]_2^0$ and $[M-S_4]_2^-$ reveals that reduction of both of these species is easier than reduction of $[LM-S_4]^0$. This is not unreasonable. The $[M-S_4]_2^0$ and $[M-S_4]_2^-$ species may be viewed as electron-deficient species. Cleavage of the dimer results in donation of an additional two electrons to each (former) half of the dimer. Thus cleavage may be viewed as a form of reduction. The resulting monomers, enriched by the donor electrons, less readily accept a further electron. The half-wave potential connecting the neutral and anionic five-coordinate species varies only slightly and irregularly with changes in L. However, a large shift is observed on going from the R = CF_3 to the R = CN series. Such shifts are typical in dithiolato complexes and reflect the essential involvement of the ligand in the electron-transfer process.

TABLE II

POLAROGRAPHIC DATA FOR DIMERIC COMPLEXES[a]

	$E_{1/2}$, v	
Compound	$e^- + (z = 0) \rightleftarrows (z = -1)$	$e^- + (z = -1) \rightleftarrows (z = -2)$
$[CoS_4C_4(CN)_4]_2^z$	[b]	+1.03
$[CoS_4C_4(CF_3)_4]_2^z$	+1.24	+0.56
$[FeS_4C_4(CN)_4]_2^z$	[b]	+1.06
$[FeS_4C_4(CF_3)_4]_2^z$	+1.27	+0.69

[a] Abstracted from ref 1b. [b] Not observed.

Physical Properties of the Five-Coordinate Compounds.—Each of the $LMS_4C_4(CF_3)_4$ compounds is monomeric in chloroform solution. A square-pyramidal structure (Figure 3) similar to that proposed[5] for the [phosphine–$MS_4C_4R_4$] (R = H, C_6H_5) complexes is also likely for these compounds. Each set of four complexes with a common metal ion exhibits similar electronic spectra (Table III). Addition of further L to solutions of these species does not perturb their electronic spectra. The iron compounds are diamagnetic. In solution the cobalt species exhibit magnetic moments (Table IV) and esr spectra (Table V) consistent with an $S = {}^1/_2$ ground state. Hyperfine splitting from ^{59}Co as well as from ^{31}P in the case of $(C_6H_5O)_3PCoS_4C_4(CF_3)_4$ is observable at room temperature. Similar results have been briefly reported[5] for the [phosphine–$CoS_4C_4R_4$] (R = H, C_6H_5) species. Both the cobalt hyperfine splitting and the g-tensor anisotropy are unusually low for a paramagnetic cobalt-containing species[18–20] and indicate extensive delocalization of the unpaired electron throughout the complex.

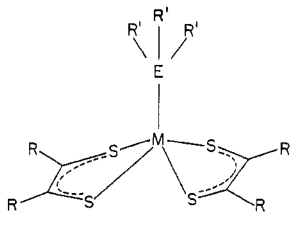

Figure 3.—Proposed structure for $[(C_6H_5)_3EMS_4C_4(CF_3)_4]$ (E = P, As, Sb, O_3P).

In the solid state $(C_6H_5O)_3PCoS_4C_4(CF_3)_4$, unlike the other $[LCoS_4C_4(CF_3)_4]^0$ species, is diamagnetic. Since the monomer is an odd-electron molecule, diamagnetism implies that association exists in the solid. We suggest the dimerization similar to that found in $[CoS_4C_4(CF_3)_4]_2$ is the most likely form of association. The proposed structure is shown in Figure 4. Similar be-

TABLE III

MAJOR SPECTRAL BANDS OF $[LM-S_4]^0$ COMPOUNDS[a]

Compound	Spectra
$(C_6H_5)_3PCoS_4C_4(CF_3)_4$	13,600 (3.58), 21,700 (3.59), 24,100 (3.59), 28,600 (3.82)
$(C_6H_5)_3AsCoS_4C_4(CF_3)_4$	13,500 (3.56), 21,100 (3.69), 23,800 (3.65), 28,400 (3.89)
$(C_6H_5)_3SbCoS_4C_4(CF_3)_4$	13,400 (3.56), 19,800 (3.41), 22,900 (3.69), 29,00 (3.94)
$(C_6H_5O)_3PCoS_4C_4(CF_3)_4$	13,600 (3.68), 23,800 (3.75), 29,400 (3.82)
$(C_6H_5)_3PFeS_4C_4(CF_3)_4$	16,400 (3.85), 22,200 (3.63), 26,800 (3.98)
$(C_6H_5)_3AsFeS_4C_4(CF_3)_4$	16,400 (3.90), 22,700 (3.65), 26,200 (4.01)
$(C_6H_5)_3SbFeS_4C_4(CF_3)_4$	16,200 (3.91), 22,200 (3.53), 26,300 (4.08)
$(C_6H_5O)_3PFeS_4C_4(CF_3)_4$	16,800 (4.00), 20,800 (3.47), 23,800 (3.60), 28,700 (3.99)

[a] Position given in cm^{-1}; log of molar extinction coefficients are in parentheses; spectra measured in dichloromethane solution.

TABLE IV

MAGNETIC SUSCEPTIBILITY DATA

Compound	μ_{eff}, BM[a]
$(C_6H_5)_3PCoS_4C_4(CF_3)_4$	1.75
$(C_6H_5)_3AsCoS_4C_4(CF_3)_4$	1.73
	1.71 (CH_2Cl_2 soln, 35°)
$(C_6H_5)_3SbCoS_4C_4(CF_3)_4$	1.79
$(C_6H_5O)_3PCoS_4C_4(CF_3)_4$	Dia
	1.70 (CH_2Cl_2 soln, 35°)
$(C_6H_5)_3PFeS_4C_4(CF_3)_4$	Dia
$(C_6H_5)_3AsFeS_4C_4(CF_3)_4$	Dia
$(C_6H_5)_3SbFeS_4C_4(CF_3)_4$	Dia
	Dia (CH_2Cl_2 soln, 35°)
$(C_6H_5O)_3PFeS_4C_4(CF_3)_4$	Dia
$((C_4H_9)_4N)[(C_6H_5)_3PCoS_4C_4(CF_3)_4]$	Dia
$((C_4H_9)_4N)[(C_6H_5)_3PCoS_4C_4(CN)_4]$	Dia
$((C_4H_9)_4N)[(C_6H_5)_3PFeS_4C_4(CF_3)_4]$	3.97

[a] Data refer to solids at 25° unless stated otherwise; diamagnetic susceptibilities not accurately determined.

---

(18) For comparison $g_{xx} = 2.798$, $g_{yy} = 2.025$, and $g_{zz} = 1.977$ and $A_{xx} = 5.0 \times 10^{-3}$ cm^{-1}, $A_{yy} = 2.8 \times 10^{-3}$, and $A_{zz} = 2.3 \times 10^{-3}$ in $[CoS_4C_4(CN)_4]^{2-}$.[19] With $[CoS_4C_4(CF_3)_4]^{2-}$, $g_1 = 2.71$ and $g_2 = 2.04$.[20] For both species a Co(II) formulation is reasonable whereas with the $[LCo-S_4]$ species an assignment of metal oxidation state is less meaningful.

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

(20) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 819 (1964).

TABLE V

ESR PARAMETERS FOR $[LCoS_4C_4(CF_3)_4]^0$

L	$\langle g \rangle$ [a]	$\langle A \rangle$ for Co,[a] gauss	$g_{\parallel}$[b]	$A_{\parallel}$[b] for Co, gauss
$(C_6H_5O)_3P$	2.0165	26.4[c]	2.0160	62.95
$(C_6H_5)_3P$	2.0192	28.83	2.0193	74.99
$(C_6H_5)_3As$	2.0197	31.15	2.0248	80.74
$(C_6H_5)_3Sb$	2.0302	*d*	2.0497	81.28

[a] Obtained in chloroform solution. [b] Obtained from frozen toluene solution at ~100°K. Perpendicular components insufficiently resolved. [c] ^{31}P hyperfine splitting of 9.3 gauss. [d] Complex solution spectrum not yet interpreted.

havior has been noted with the nickel group dithiolate anions $[MS_4C_4(CN)_4]^-$. These species are monomeric, $S = {}^1/_2$ species in solution. However, in the solid state metal-to-sulfur interactions between planar anions results in antiferromagnetic behavior and a diamagnetic ground state.[21,22]

The monoanions $[(C_6H_5)_3PCoS_4C_4(CF_3)_4]^-$ and $[(C_6H_5)_3PCoS_4C_4(CN)_4]^-$ [6] are diamagnetic. The magnetic moment of $[(C_4H_9)_4N][(C_6H_5)_3PFeS_4C_4(CF_3)_4]$ indicates an $S = {}^3/_2$ ground state with very little orbital contribution. Several other five-coordinate iron complexes with quartet ground states are known; these include $[(R_2NCS_2)_2FeX]$ (R = alkyl; X = Cl, Br, I),[23] which are known to have square-pyramidal geometry,[24] and $[(C_4H_9)_4N][C_5H_5NFe(S_2C_6H_3CH_3)_2]$.[25]

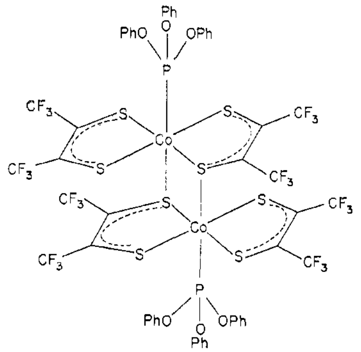

Figure 4.—Proposed structure for $(C_6H_5)_3PCoS_4C_4(CF_3)_4$ in the solid state.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Dr. F. Ann Walker for the esr measurements.

---

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

[22] C. J. Fritchie, *Acta Cryst.*, **20**, 107 (1966).

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

[24] B. F. Hoskins, R. L. Martin, and A. H. White, *Nature*, **211**, 627 (1966).

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

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH, PENNSYLVANIA 15213

Stereochemistry of β-Diketone Complexes of Cobalt(III). II. Preparation and Properties of Coordination Compounds with Two Unsymmetrical 1,3-Diketone Ligands[1]

BY L. J. BOUCHER

Received July 17, 1967

Cobalt(III) complexes of two unsymmetrical β-diketones, 1-methoxy-2,4-pentanedione and 2,4-hexanedione, have been studied. Coordination compounds of the types sodium dinitrobis(β-diketonato)cobaltate(III), nitropyridinebis(β-diketonato)cobalt(III), and ethylenediaminebis(β-diketonato)cobalt(III) iodide have been synthesized. The ultraviolet, visible, infrared, and nuclear magnetic resonance spectral properties of the complexes have been measured. The configuration of the third series of complexes is necessarily *cis* while that of the first two series is assumed to be the same as that of an analogous acetylacetone complex, *i.e.*, *trans*. Chemical and spectral evidence is consistent with this assignment. Both the *cis* and *trans* complexes can exist as additional geometrical isomers (with respect to the unsymmetrically substituted β-diketones). Proton magnetic resonance spectra suggest that the materials isolated are mixtures of all of the possible isomers.

Although substitution, isomerization, and racemization reactions of transition metal complexes have been extensively studied,[2] surprisingly little is known about the reactions of transition metal complexes of weak field bidentate ligands. Archer has suggested that complexes of β-diketones might show reaction pathways substantially different from those already observed.[3] These anionic ligands form coordination compounds of reduced positive charge that contain no acidic protons, and nuclear magnetic resonance (nmr) spectroscopy can be used in studying stereochemical changes in the reactions of their complexes.[4] The isomerization and racemization reactions of some tris(β-diketonato)cobalt-

---

[1] Part I: L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).

[2] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967.

[3] R. D. Archer in "Werner Centennial," Advances in Chemistry, No. 62, American Chemical Society, Washington, D. C., 1967, p 452.

[4] R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).