CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Metal Complexes of Substituted Dithiophosphinic Acids.
V. Complexes of Manganese, Iron, and Cobalt

BY R. G. CAVELL,* E. D. DAY, W. BYERS, AND P. M. WATKINS

Received August 25, 1971

Substituted dithiophosphinate complexes of the general formula $M[S_2PX_2]_n$ have been prepared and characterized for the substituents X = CF_3, CH_3, and C_6H_5 (M = Fe^{3+}, Co^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}), X = OC_2H_5 and F (M = Co^{3+}, Co^{2+}, Zn^{2+}), and X = F (M = Hg^{2+}) where n is the valence of the metal ion in all cases. The trivalent complexes are monomeric and six-coordinated (D_3) whereas the divalent complexes are both monomeric and polymeric depending on the substituent X and the physical state of the complex. All divalent complexes appear to possess pseudotetrahedral coordination of the metal by four sulfur atoms. The results of thermogravimetric and mass spectral studies are presented and discussed. Temperature-dependent magnetic susceptibility studies reveal Curie–Weiss behavior for all paramagnetic complexes. The Fe(II) complexes are high spin with moments typical of tetrahedral coordination. Visible and ultraviolet spectral studies, interpreted on a ligand field model, permit the ordering of the ligands into the spectrochemical series according to X: F $\sim$ OC_2H_5 > CH_3 $\sim$ C_6H_5 $\sim$ CF_3. Metal–sulfur infrared frequencies of the M^{3+} complexes follow the same trend with X but the M^{2+} complexes do not. Oxygen for sulfur substitution occurs in many cases during preparation but is not in general stoichiometric. In one case a stoichiometric complex $CoS_3OP_2(CH_3)_4$ was isolated and characterized.

Introduction

Recent review articles[1–4] have summarized the established chemistry of dithio acid systems, including the dithiophosphinates with which we are concerned. A wide variety of coordination geometries is displayed by the 1,1-dithio acids, which is, in general, quite different from that of their oxygen analogs.[4] In a continuation of our investigations of the chemistry of the metal dithiophosphinates $M[S_2PX_2]_n$[5–8] we have studied the complexes where $n = 3$, M = Fe or Co; and $n = 2$, M = Mn, Fe, Co, Zn, Cd, or Hg with X = CH_3, C_6H_5, or CF_3 for all M, OC_2H_5 and F for M = Co(II), Co(III), and Zn(II), as well as $Hg[S_2PF_2]_2$. Most of the fluoro-substituted complexes were first reported elsewhere[9] while this work was in progress and many of the alkoxy complexes have been known for some time.[10–12] Recently many of the alkyl-substituted dithiophosphinates ($R_2PS_2^-$, where R is C_2H_5 and higher homologs in most cases but a few R = CH_3 complexes have been made)[13,14] and phenyl-substituted dithiophosphinates[15,16] of the metals in the group considered here have been reported. A recent brief report of $R(F)PS_2^-$ (R = CH_3, C_2H_5) complexes of some of the present metals has also appeared.[17] We now report our investigations of thermochemical, magnetic, and spectroscopic properties of these dithiophosphinates basing our analysis on the available structural data. The metal M(II) complexes are of special interest because the complexes are undoubtedly tetrahedral and analogous to the first substantiated[18] tetrahedral $Fe^{II}S_4$ system formed by $[(CH_3)_2P(S)]_2N^-$.

Experimental Section

Air-sensitive X = F and CF_3 compounds were handled in a conventional vacuum system lubricated with Apiezon N stopcock grease. Very volatile, air-sensitive compounds were prepared in the grease-free apparatus described elsewhere.[8] Transfers of air-sensitive compounds were carried out in nitrogen-filled drybags. Syntheses of $HS_2P(CF_3)_2$,[19] HS_2PF_2,[20] $NaS_2P(CH_3)_2 \cdot 2H_2O$,[5] and $NH_4S_2P(C_6H_5)_2$[5] have been described elsewhere.

Infrared spectra were obtained on Perkin-Elmer 421 or 457 and Beckman IR-11 instruments. Electronic spectra were measured with a Cary 14 spectrometer equipped with the Cary 1411 diffuse-reflectance attachment operated in type II mode. Where possible the spectra were resolved as previously described.[5] Magnetic susceptibilities were obtained by the Faraday method over the temperature range 90–300°K using a cryostat of our own construction. The magnetic field was calibrated with $HgCo[NCS]_4$ prepared as described.[21] Mass spectra were obtained with an AEI MS-9 mass spectrometer operating at 70 eV with samples introduced by means of the direct-probe sample-insertion device. X-Ray powder photographs were taken with a Philips Debye–Scherrer powder camera, Type PW 1024. Thermogravimetric analyses were carried out under vacuum using the Du Pont Model 950 thermogravimetric analyzer as a module attachment to the Du Pont 900 differential thermal analyzer. Chlorocarbon solvents were dried and deoxygenated by vacuum distillation from P_4O_{10}. Analytical data are presented in Table I.

Syntheses. A. Salts. (i) $\mathbf{NH_4S_2P(OC_2H_5)_2}$ was prepared by bubbling ammonia gas into an ethanolic solution of $HS_2P(OC_2H_5)_2$ obtained by dissolving P_4S_{10} in ethanol. The product was precipitated as white lustrous flakes on addition of ether to the hot solution and was washed with ether.

(ii) $\mathbf{NaS_2P(OC_2H_5)_2}$ was prepared by addition of $NaOCH_3$ to an ethanolic solution of the acid obtained as in part (i). After filtration and evaporation to near dryness on a rotary evaporator,

---

[1] W. Kuchen and H. Hertel, *Angew. Chem., Int. Ed. Engl.*, **8**, 89 (1969).

[2] J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

[3] D. Coucouvanis, *ibid.*, **11**, 233 (1970).

[4] R. Eisenberg, *ibid.*, **12**, 295 (1970).

[5] R. G. Cavell, W. Byers, and E. D. Day, *Inorg. Chem.*, **10**, 2710 (1971).

[6] R. G. Cavell, E. D. Day, W. Byers, and P. M. Watkins, *ibid.*, **10**, 2716 (1971).

[7] R. G. Cavell, E. D. Day, W. Byers, and P. M. Watkins, *ibid.*, **11**, 1591 (1972).

[8] R. G. Cavell, W. Byers, E. D. Day, and P. M. Watkins, *ibid.*, **11**, 1598 (1972).

[9] F. N. Tebbe and E. L. Muetterties, *ibid.*, **9**, 629 (1970).

[10] C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

[11] C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2017 (1962).

[12] C. K. Jørgensen, *Inorg. Chim. Acta Rev.*, **2**, 65 (1968).

[13] W. Kuchen and A. Judat, *Chem. Ber.*, **100**, 991 (1967).

[14] W. Kuchen, A. Judat, and J. Metten, *ibid.*, **98**, 3981 (1965).

[15] (a) R. N. Mukherjee, V. V. Krishna Rao, and J. Gupta, *Indian J. Chem.*, **4**, 209 (1966); (b) R. N. Mukherjee, A. Y. Sonsale, and J. Gupta, *ibid.*, **4**, 500 (1966).

[16] A. Muller, V. V. Krishna Rao, and G. Klinksiek, *Chem. Ber.*, **104**, 1892 (1971).

[17] H. Roesky, *Angew. Chem.*, **80**, 844 (1968).

[18] (a) A. Davidson and E. S. Switkes, *Inorg. Chem.*, **10**, 837 (1971); (b) M. R. Churchill and J. Wormald, *ibid.*, **10**, 1778 (1971).

[19] A. A. Pinkerton and R. G. Cavell, *J. Amer. Chem. Soc.*, **93**, 2384 (1971).

[20] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 281 (1969); R. W. Mitchell, M. Lustig, F. A. Hartman, J. K. Ruff, and J. A. Merritt, *J. Amer. Chem. Soc.*, **90**, 6329 (1968); H. W. Roesky and E. L. Muetterties, *Inorg. Chem.*, **9**, 831 (1970).

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

TABLE I

ANALYTICAL DATA FOR $M(S_2PX_2)_n$ COMPOUNDS[a]

M	X	% M	% C	% H	% P	% S
Mn(II)	CH_3	17.84 (18.00)	15.96 (15.74)	4.14 (3.96)	20.48 (20.29)	42.22 (42.01)
	C_6H_5	9.73 (9.92)	51.98 (52.08)	3.54 (3.64)	11.07 (11.19)	22.90 (23.17)
Fe(II)	CH_3	17.85 (18.24)	15.54 (15.69)	3.81 (3.95)	19.78 (20.23)	42.23 (41.89)
	C_6H_5	10.65 (10.07)	51.86 (51.99)	3.87 (3.64)	10.74 (11.17)	23.86 (23.13)
Fe(III)	C_6H_5		53.65 (53.79)	3.98 (3.76)	11.68 (11.56)	23.67 (23.93)
Co(II)	CH_3		15.68 (15.53)	4.12 (3.91)		
	C_6H_5		51.86 (51.70)	3.83 (3.62)		
	OC_2H_5		20.86 (22.38)	4.63 (4.70)		28.00 (29.98)
$CoOS_3P_2(CH_3)_4$			16.34 (16.39)	4.13 (4.13)		
Co(III)	CH_3		16.61 (16.59)	4.13 (4.18)	21.06 (21.39)	
	C_6H_5		53.74 (53.59)	3.87 (3.75)		
	OC_2H_5		23.30 (23.45)	5.00 (4.92)		
Zn(II)	CH_3		15.47 (15.22)	3.92 (3.83)		
	C_6H_5		50.99 (51.11)	3.71 (3.58)		
	OC_2H_5		20.99 (22.05)	4.65 (4.63)		28.59 (29.43)
Cd(II)	CH_3		13.36 (13.24)	3.56 (3.34)		
	C_6H_5		47.16 (47.18)	3.40 (3.30)		
Hg(II)	CH_3		10.73 (10.65)	2.84 (2.68)		
	C_6H_5		41.32 (41.23)	2.82 (2.88)		
Na	OC_2H_5		22.76 (23.07)	4.50 (4.84)		
NH_4	OC_2H_5	6.84 (6.89)[b]	22.56 (23.64)	6.94 (6.94)		33.08 (31.55)

	X = CF_3		X = F
	% CF_3[c]	m/e	m/e
Mn(II)	26.4 (26.5)	520.7535 (520.7547)	320.7672 (320.7675)
Fe(II)	26.8 (26.4)	521.7500 (521.7515)	321.7659 (321.7648)
Fe(III)		754.6628 (754.6598)	
Co(II)	26.4 (26.3)	524.7526 (524.7498)	324.7620 (324.7626)
Co(III)		757.6613 (757.6581)	457.6765 (457.6773)
Zn(II)	26.3 (26.3)	529.7460 (529.7467)	329.7580 (329.8585)
Cd(II)		579.7175 (579.7202)	
Hg(II)		667.7886 (667.7872)	467.8002 (467.8002)

[a] Entries are observed values followed by theoretical values in parentheses. [b] Nitrogen analysis. [c] Calculated from HCF_3 evolved on basic hydrolysis of compound, assuming 1 mol of HCF_3 evolved/mol of P present.[19]

ether was added and the white product was washed well with ether and dried at 70° in an oven.

B. Complexes.—The preparation of the air-stable X = CH_3 and C_6H_5 compounds involved mixing of concentrated aqueous solutions of the metal and ligand salts, the resultant precipitates being filtered off and washed with ethanol or 2-propanol and then ether. Final purification (if necessary) was achieved by fractional sublimation under vacuum.

(i) **$Fe[S_2P(CH_3)_2]_2$ and $Fe[S_2P(C_6H_5)_2]_2$.**—Gaseous SO_2 was bubbled into a hot solution of 5 mmol of $FeSO_4 \cdot 7H_2O$ in 50 ml of water for 15 min to reduce any Fe(III) present. The solution was then reduced to half-volume by boiling to remove excess SO_2 and subsequently mixed (in a nitrogen atmosphere) with 25 ml of a freshly boiled methanolic solution of the respective ligand salt. On standing and cooling, the X = C_6H_5 complex crystallized out of solution as tiny pale yellow clusters of crystals. The mustard yellow X = CH_3 compound could only be precipitated by reduction of the solution volume to 5 ml by removal of solvent under reduced pressure. Both complexes were washed with cold, oxygen-free water and dried under vacuum (yields were 30–50%). When dry, the X = CH_3 compound proved remarkably resistant to aerial oxidation (even for several days) in contrast with the X = C_6H_5 complex which rapidly turned green and then black. Solutions of either complex were particularly susceptible to oxidation which, with their limited solubility, precluded recrystallization from solvents and the obtaining of reliable solution spectra. Green (oxidized) solutions of the methyl complex were unstable, depositing a tan material while fading.

(ii) **$Fe[S_2P(C_6H_5)_2]_3$** was prepared by mixing concentrated aqueous solutions of $FeCl_3 \cdot 6H_2O$ and $NH_4S_2P(C_6H_5)_2$. The resultant black[15a] (deep green) precipitate was washed with water and 2-propanol and then dried under vacuum.

(iii) **$Co[S_2P(CH_3)_2]_3$ and $Co[S_2P(C_6H_5)_2]_3$**[16] were prepared by mixing concentrated aqueous solutions of $Na_3Co(NO_2)_6$ and the respective ligand salt. The brown products were extracted into dichloromethane from which they were precipitated by evaporation of the solvent, washed quickly with cold 2-propanol, and dried.

(iv) **$CoOS_3P_2(CH_3)_4$.**—Attempted preparations of the green complex $Co[S_2P(CH_3)_2]_2$ in alcohol, acetone, or acetonitrile produced precipitates of varying shades of blue. A crystalline, blue material was prepared by mixing hot 25-ml ethanolic solutions containing 5 mmol of cobalt halide hexahydrate and 10 mmol of $NaS_2P(CH_3)_2 \cdot 2H_2O$, respectively. Halide contamination in the crystals was minimized (<3%) by use of cobalt bromide. Carbon and sulfur analyses on the blue crystals gave a C/S mole ratio of 1.36 (theoretical ratio for $CoOS_3P_2(CH_3)_4$ is 1.33). The halide salt contamination was effectively removed by subjecting the blue crystalline product to Soxhlet extraction into C_2H_5OH, CH_3OH, CH_2Cl_2, or $CHCl_3$. The infrared spectrum and C/S mole ratio was not affected by this treatment. Recrystallization could not be effected from these solvents because of the low solubility of the complex. The infrared spectrum of the complex showed peaks at 1422 (w), 1415 (w), 1399 (w), 1298 (w), 1285 (m), 1100 (w, sh), 1058 (s), 947 (m), 934 (m, sh), 901 (s), 861 (m, sh), 855 (m), 849 (w, sh), 745 (w), 716 (s), 593 (m, sh), 578 (s), 550 (m), 488 (m), 428 (m), 363 (m), 326 (m), 315 (m, sh), 253 (w), 215 (w, sh), and 205 (m) cm^{-1}. Preparations involving strictly anhydrous salts and solvents yielded only the green complex $Co[S_2P(CH_3)_2]_2$.

(v) **$Co[S_2P(OC_2H_5)_2]_2$** was prepared as lustrous, flat, blue needles by consecutively adding the ligand salt to a concentrated, freshly boiled aqueous solution of $CoCl_2 \cdot 6H_2O$, extracting the complex into freshly boiled CH_2Cl_2, and rapidly removing the solvent under vacuum. Surface Co(III) compounds and water-soluble species were readily removed by successively washing with acetone, water, acetone again, and finally ether. No halide was detected in the solid products.

(vi) **$Co[S_2P(OC_2H_5)_2]_3$** was prepared by adding $CoCl_2 \cdot 6H_2O$ to an ethanolic solution of the acid and allowing aerial oxidation of Co(II) to occur. The brown product obtained by concentration of the solution was recrystallized from dichloromethane–2-propanol (1:1 by volume).

(vii) **$Zn[S_2P(OC_2H_5)_2]_2$.**—Concentrated aqueous solutions of $ZnCl_2$ and either $NH_4S_2P(OC_2H_5)_2$ or $NaS_2P(OC_2H_5)_2$ were mixed and subsequently extracted with CH_2Cl_2. The product was obtained as large white flakes by concentration of the CH_2Cl_2 solution and was recrystallized twice from benzene.

(viii) **$M[S_2PF_2]_n$.**—These complexes were prepared essentially as described[9] working on a 0.1-g scale without solvents and purification was effected by fractional sublimation. In several cases partial reduction of the acid to SPF_2H and H_2S was detected. $Co[S_2PF_2]_3$ was prepared by introducing oxygen gas at ~500 Torr pressure to a mixture of HS_2PF_2 and $Co[S_2PF_2]_2$ or a mixture of Co metal and HS_2PF_2. The apparatus described elsewhere[8] proved convenient for preparation and purification.

(ix) **$M[S_2P(CF_3)_2]_n$.**—The $n = 2$ complexes with M = Mn, Fe, Co, Zn, Cd, and Hg were prepared by the direct reaction of excess $HS_2P(CF_3)_2$ with the metal in a sublimer fitted with a cold water cooled finger. After completion of the reaction, volatile components (excess $HS_2P(CF_3)_2$, $(CF_3)_2PSH$, H_2S, H_2) were removed and the solid products sublimed under vacuum by heating to 70°. Final purification was by fractional sublimation. All the products were moisture sensitive. The Co(III) and Fe(III) complexes were prepared similarly to the F analog as well as by reaction of the M(II) complex with $[S_2P(CF_3)_2]_2$.[19] Parameters obtained from the ^{19}F nmr spectra (chemical shifts *vs.* $CFCl_3$) for the Zn-group metals are as follows: $Zn[S_2P(CF_3)_2]_2$, ϕ 70.1 ppm, $J_{PF} = 108$ Hz; $Cd[S_2P(CF_3)_2]_2$, ϕ 69.5 ppm, $J_{PF} = 109$ Hz; $Hg[S_2P(CF_3)_2]_2$, ϕ 69.7 ppm, $J_{PF} = 107.5$ Hz.

Reaction between cobalt metal and an approximately 1:1 molar mixture of $(CF_3)_2P(S)SH$ and $(CF_3)_2P(S)OH$ gave a blue solid of low vapor pressure (20–200°). No green volatile $Co[S_2P(CF_3)_2]_2$ was observed to sublime from the blue material. The principal mass spectral peaks were found at *m/e* 1077, 1009, 860, 844, 769, 668, 662, 584, 525, 509, 464, 414, 399, 292, 76, 69, and 63, the presence of peaks at *m/e* greater than 524 indicating a polymeric structure. The infrared spectrum is quite distinct from that of $Co[S_2P(CF_3)_2]_2$ but the stoichiometry is unknown.

$Co[S_2P(CF_3)_2]_2$ is readily soluble in CH_2Cl_2, CCl_4, and C_6H_6 but reacts with methanol to give a white precipitate and with acetonitrile to give a yellow solution from which unidentified yellow-green crystals were obtained.

(x) **$Fe[S_2P(CF_3)_2]_2 \cdot CH_3NHCHO$.**—No immediate reaction was observed between a molar excess of $HS_2P(CF_3)_2$ and $FeCl_2 \cdot xH_2O$; however, a yellow solution slowly formed after addition of acetonitrile. After removal of the volatile components, a yellow solid was sublimed (70° *in vacuo*) onto a water-cooled finger, leaving a black, intractable residue. The yellow material appeared to be stable in air. The mass spectrum showed a parent ion which was mass measured at *m/e* 580.7899 (calcd for $Fe[S_2P(CF_3)_2]_2 \cdot C_2H_5NO^+$, *m/e* 580.7885). The major fragment appeared at *m/e* 522 which corresponds to $Fe[S_2P(CF_3)_2]_2^+$. The infrared spectrum contained bands attributable to acetamide.

Thermogravimetric Analyses.—All the $M[S_2PX_2]_2$ complexes sublime under vacuum with the exception of the $X = OC_2H_5$ complexes where decomposition occurs. The thermogram of $CoOS_3P_2(CH_3)_4$ showed a single structureless weight break at 182° leaving a black residue of CoO [(weight of residue)/(weight of sample): found, 0.129, 0.124; calcd for $CoO/2CoOS_3P_2(CH_3)_4$, 0.128].

Of the M(III) complexes, $Co[S_2P(OC_2H_5)_2]_3$, $Co[S_2PF_2]_3$, and $Co[S_2P(CF_3)_2]_3$ sublime under vacuum at 154, 50, and 80°, respectively, without decomposition while $Co[S_2P(CH_3)_2]_3$, $Co[S_2P(C_6H_5)_2]_3$, and $Fe[S_2P(C_6H_5)_2]_3$ under vacuum produced thermograms showing two distinct weight breaks, leaving no residue but depositing the corresponding M(II) complex and a white material in cooler parts of the apparatus. The first weight break is presumed to be due to loss of the corresponding "diligand" L_2 (where $L_2 = [S_2PX_2]_2$) and the thermograms were analyzed accordingly: $Co[S_2P(CH_3)_2]_3$, dec pt 130°, calcd for $^1/_2L_2/CoL_2$, 0.406 (found, 0.407); $Co[S_2P(C_6H_5)_2]_3$, dec pt 238°, calcd for $^1/_2L_2/CoL_2$, 0.309 (found, 0.311); $Fe[S_2P(C_6H_5)_2]_3$, dec pt 208°, calcd for $^1/_2L_2/FeL_2$, 0.312 (found, 0.310).

Results and Discussion

The series of dithiophosphinates $M[S_2PX_2]_n$ ($n = 3$, M = Fe, Co; $n = 2$, M = Mn, Fe, Co, Zn, Cd, Hg) can be prepared by the metathetical reaction

$$MCl_n + n(Na, NH_4)S_2PX_2 \longrightarrow M[S_2PX_2]_n + n(Na, NH_4)Cl \quad (1)$$

(where $X = CH_3$[1] or C_6H_5[15,16] for all metals and $X = OC_2H_5$ for M = Co(II), Co(III), and Zn(II)) or by the oxidation–reduction reaction

$$M + 2HS_2PX_2 \longrightarrow M[S_2PX_2]_2 + H_2 \quad (2)$$

(where X = F, CF_3; $n = 2$). The M(III) complexes $Fe[S_2P(CF_3)_2]_3$, $Co[S_2P(CF_3)_2]_3$, and $Co[S_2PF_2]_3$ were prepared from the acids and the metals in a manner analogous to eq 2, but allowing the reaction to occur in the presence of molecular oxygen, since the acids appear to be capable of oxidizing the present series of metals only to the divalent state.

Although dialkyldithiophosphinate complexes are generally readily soluble in organic solvents,[1] the M(II), $X = CH_3$, C_6H_5 complexes proved too insoluble in all common organic solvents for molecular weight determinations. The polymeric nature suggested by this limited solubility has now been established for the green complex $Co[S_2P(CH_3)_2]_2$.[22] The superimposability of the X-ray powder patterns of the remaining M(II), $X = CH_3$ compounds of the first-row transition metals suggests that these complexes are isomorphous. A more detailed single-crystal X-ray structural analysis of the blue compound $CoOS_3P_2(CH_3)_4$ obtained while attempting to prepare the cobalt(II) dithiophosphinate complex in ethanol according to eq 1 (*vide infra*) showed that it is also isostructural with the green Co(II) complex with the lack of systematic intensity differences between the two complexes suggesting that one oxygen atom replaces one sulfur in the CoS_4 unit in a random fashion to form the blue complex.[23]

The structure of $Co[S_2P(CH_3)_2]_2$ consists of infinite independent chains of Co atoms linked by alternating pairs of ligand bridges and arranged along a twofold screw axis as shown in Figure 1.[22] This structure is similar to that observed for $R_2PO_2^-$ complexes[24,25] but is in notable contrast with the reported[26] structure of $Zn[S_2P(C_2H_5)_2]_2$ (and the apparently isomorphous complex $Co[S_2P(C_2H_5)_2]_2$) which consists of two crystallographically nonequivalent discrete dimeric units (I) in

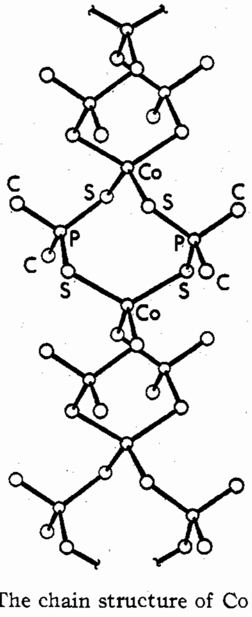


Figure 1.—The chain structure of $Co[S_2P(CH_3)_2]_2$.

---

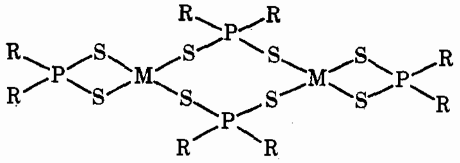
(22) M. J. Bennett and R. H. Sumner, unpublished results.

(23) M. J. Bennett and R. M. Tuggle, personal communication.

(24) M. Calligaris, A. Ciana, S. Meriani, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc. A*, 3386 (1970).

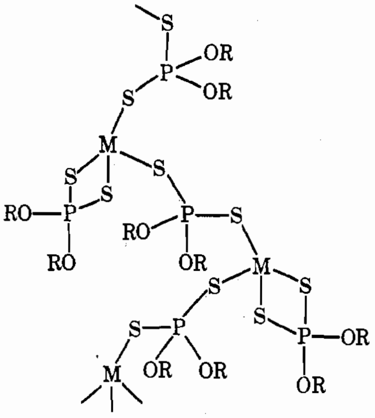
(25) B. P. Block, *Proc. Symp. Coord. Chem.*, 241 (1969).

(26) M. Calligaris, G. Nardin, and A. Ripamonti, *J. Chem. Soc. A*, 714 (1970).



I

which each metal is chelated by one dithiophosphinate ligand and bound to the other member of the dimer by two ligand bridges. The bridged portion of the dimer may be compared with one link of the infinite chain found in $Co[S_2P(CH_3)_2]_2$. The $X = OCH(CH_3)_2$ complexes of Zn(II) and Cd(II) also contain the dimers illustrated in I.[27] A different type of linkage arrangement is found in $Zn[S_2P(OC_2H_5)_2]_2$[28] and $Hg[S_2P(OCH(CH_3)_2)_2]_2$[29] where each metal atom is tetracoordinated by sulfur atoms from one chelating ligand and two branching bridging ligand groups with the result that infinite zigzag chains are formed as represented by II.



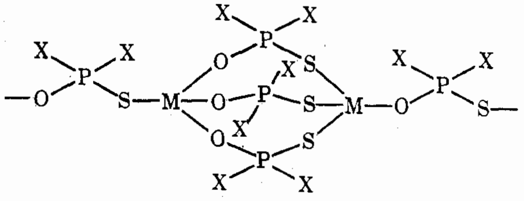
II

Thus three different polymeric structures are presently known for the metal(II) dithiophosphinate complex system. The relative importance of the electronic properties of the metal and the influence of the electronic and steric effects of the substituents governing the adoption of a specific structure are not yet clear because of the limited range of structural examples available. In the case of CH_3- and C_2H_5-substituted Co(II) complexes the electronic effects of the substituents must be rather similar suggesting that the difference in structures is due to the bulk of the alkyl substituent.

Powder patterns of the Co(III) and V(III),[6] $X = CH_3$ complexes are nearly superimposable with that of $Cr[S_2P(CH_3)_2]_3$ which is known to have D_3 molecular point group symmetry in the crystal.[5,22] The ready solubility of all of the M(III) complexes in halocarbon solvents and the absence of mass spectral fragments of mass greater than the molecular parent ion suggests that the Fe(III) and Co(III) complexes are monomeric in solution, as are the Cr(III)[5] and V(III)[6] complexes. It is also likely that all have the same structure. The mass spectral evidence must be assessed with caution since $Co[S_2P(CH_3)_2]_2$, which is known to be polymeric in the solid state,[22] gives a mass spectrum indicative of the presence of monomeric units only.

Reactions Involving Oxygen for Sulfur Substitution.—Preparations of M(II), $X = CH_3$ complexes (M = Mn, Fe, Co, Zn, Cd, Hg) in aqueous solutions or from the hydrated salts in polar organic solvents according to eq 1 yielded products which generally showed a broad infrared absorption of variable intensity in the region 1020–1080 cm^{-1} and a sharp absorption of lesser intensity at 550–520 cm^{-1} in addition to the spectrum of the authentic dithiophosphinate compound. The first band can be assigned to a P–O stretching mode[30] and the second to a displaced P–S stretching mode[31,32] resulting from a sulfur atom replacement by oxygen. Fractional sublimation of the crude products left a residue of the metal oxide with $M[S_2P(CH_3)_2]_2$ and $[SP(CH_3)_2]_2O$ as the only volatile components. Thus oxygen for sulfur substitution in these systems appears to be a general phenomenon; however, reproducible and stoichiometric substitution of one oxygen for a sulfur was found only in the case of $CoS_3OP_2(CH_3)_4$ prepared from hydrated Co(II) and dimethyldithiophosphinate salts in absolute ethanol. In other reactions the degree of sulfur replacement varied with the amount of water in the organic solvent. Curiously, however, mixing *aqueous* 0.1 *M* Co(II) solutions with 0.2 *M* *aqueous* solutions of the ligand salt yielded only the green dithiophosphinate complex with no substitution of S by O. Mechanical mixing of the hydrated salts in a mortar yielded the same product.

The structure of $CoS_3OP_2(CH_3)_4$ which appears to be identical with that of $Co[S_2P(CH_3)_2]_2$[22] with one sulfur atom replaced by an oxygen in each CoS_4 unit contrasts with those of the zinc(II) and cadmium(II) monothiophosphinates which consist of alternate triply bridged, dinuclear units ("beads") joined by single bridging ligands as depicted in III.[24] The two metal atoms in a "bead" are not equivalent: one is coordinated by one oxygen atom and three sulfur atoms and the other by three oxygen atoms and one sulfur atom.[24]



III

All of the oxygen-containing complexes of cobalt(II) are blue, even $Co[S_2P(OC_2H_5)_2]_2$. It seems that oxygen atoms impart a blue color to the complexes of Co(II) even in the third coordination sphere. In cases where the substituents do not contain oxygen, however, the appearance of a blue complex in cobalt dithiophosphinate systems is an indication that oxygen substitution has occurred.

Differential thermal analysis of $CoS_3OP_2(CH_3)_4$ shows that the decomposition of the complex obeys the equation

$$2CoOS_3P_2(CH_3)_4 \xrightarrow[\Delta(182°)]{} Co[S_2P(CH_3)_2]_2 + [SP(CH_3)_2]_2O + CoO \quad (3)$$

---

[27] S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, **8**, 2410 (1969).

[28] T. Ito, T. Igarashi, and H. Hagihara, *Acta Crystallogr., Sect. B*, **25**, 2303 (1969).

[29] S. L. Lawton, *Inorg. Chem.*, **10**, 328 (1971).

[30] G. E. Coates and D. S. Golightly, *J. Chem. Soc.*, 2523 (1962).

[31] J. R. Durig, D. W. Wertz, B. R. Mitchell, F. Block, and J. M. Greene, *J. Phys. Chem.*, **71**, 3815 (1967).

[32] D. M. Adams and J. B. Cornell, *J. Chem. Soc. A*, 1299 (1968).

TABLE II

MASS SPECTRAL DATA FOR THE TRIS COMPLEXES $M[S_2PX_2]_3$[a]

	m/e							
	X = CH_3		X = C_6H_5		X = OC_2H_5	X = F	X = CF_3	
Assignment	Fe[b]	Co	Fe	Co	Co	Co	Fe	Co
$MS_6P_3X_6$					614 (0)	458 (26)	755 (12)	758 (1)
$MS_5P_3X_6$						426 (19)		
$MS_4P_2X_4$	306 (100)	309 (100)	554 (100)	557 (100)	429 (100)	325 (100)	522 (100)	525 (100)
$MS_4P_2X_3$	291 (19)	294 (16)	477 (0)	480 (0)	384 (5)	306 (10)	453 (2)	456 (2)
MS_4P_2		249 (11)		249 (1)	249 (4)	249 (7)	246 (1)	249 (10)
MS_4PX_2			369 (0)	372 (0)	308 (5)	256 (352)	353 (6)	356 (22)
MS_4						187 (11)	184 (1)	187 (1)
MS_3PX_2			337 (1)	340 (1)	276 (4)	224 (26)	321 (1)	
MS_3P			183 (8)		186 (14)	186 (4)	183 (4)	186 (6)
MS_3		155 (16)				155 (22)	152 (3)	155 (2)
$MS_2P_2X_4$	242 (5)	245 (16)	490 (1)	493 (1)				461 (0)
$MS_2P_2X_3$	227 (4)	230 (13)		416 (0)				
MS_2P_2X				262 (13)			251 (0)	
MS_2P_2		185 (79)		185 (15)	185 (7)		182 (0)	185 (1)
MS_2PX_2			305 (17)	308 (18)	224 (14)	192 (303)	289 (18)	292 (45)
MS_2PX	166 (5)	169 (20)	228 (2)			173 (2)	220 (1)	223 (1)
MS_2P	151 (11)	154 (11)	151 (3)	154 (3)	154 (6)	154 (3)	151 (10)	154 (11)
MS_2						123 (78)	120 (7)	123 (8)
$MSPX_3$			350 (1)	353 (18)				329 (0)
$MSPX_2$			273 (1)			160 (29)		
MSP	119 (28)	122 (13)	119 (1)	122 (3)			119 (14)	122 (8)
MS			88 (0)			91 (57)	88 (5)	91 (3)
MPX_2	117 (21)		241 (1)	244 (3)		128 (10)		
MX			133 (2)	136 (2)		78 (16)	125 (1)	128 (1)
M		59 (149)	56 (1)	59 (2)	59 (2)	59 (47)	56 (6)	59 (3)
$S_4P_2X_4$	250 (207)	250 (450)			370 (12)	266 (41)	466 (6)	466 (21)
$S_3P_2X_4$	218 (33)	218 (285)	466 (1)	466 (0)			434 (0)	
Source temp, °C	150	125	245	310	150	60	80	100

[a] The data are presented as an array of *m/e* values for unipositive metal-containing ions followed by the relative intensities of the corresponding peaks scaled such that the intensity of the ion $MS_4P_2X_4^+$ is set at 100. Only peaks for which there is no fragmentation of the X groups are included (the omitted peaks are a significant fraction of the total metal atom containing ionization only where X = OC_2H_5, where the stepwise loss of C_2H_4 units dominates the spectrum[34]). Only peaks for which the relative intensity of at least one entry in a row is greater than 10 are included. [b] Data obtained from the residue of a green dichloromethane solution after removal of the solvent.

Extraction of the $CoS_3OP_2(CH_3)_4$ complex into polar solvents gave the expected blue solutions whereas extraction into nonpolar solvents gave green solutions. The spectrum of the green CH_2Cl_2 solution obtained by extraction of $CoS_3OP_2(CH_3)_4$ (Figure 5(B)) is not however identical with that of $Co[S_2P(CH_3)_2]_2$ which is also green in CH_2Cl_2 (see Figure 5) nor is it the same as that of the blue extract (Figure 5(A)). The nature of the solution species obtained in these extractions is not yet clear; however it seems reasonable to attribute the blue solutions to the dissolved form of $CoS_3OP_2(CH_3)_4$. The green extract may be a structural isomer of the blue complex, but it is more likely a mixture of the blue complex and $Co[S_2P(CH_3)_2]_2$ probably formed by a decomposition similar to eq 3, with the green color the result of a preferential, but not exclusive, dissolution of the more soluble dithiophosphinate. On reaction with water, the green $Co[S_2PF_2]_2$ complex was reported[9] to give a blue sublimable solid which dissociated during attempted isolation. Both the blue F-[9] and the blue polymeric CF_3-substituted complexes obtained from Co metal and a mixture of $(CF_3)_2PS_2H$ and $(CF_3)_2PSOH$ undoubtedly contain oxygen coordinated to Co, but the extent of substitution is unknown.

With the exception of the acetamide adduct $Fe[S_2P(CF_3)_2]_2 \cdot CH_3NHCHO$ and $Fe[S_2P(CH_3)_2]_2$, the yellow Fe(II) complexes were all exceedingly susceptible to attack by molecular oxygen. The identity of the air oxidation products have not been established in all cases; however, the likely products are the Fe(III) complexes since both the iron(III) bis(trifluoromethyl)-dithiophosphinate and difluorodithiophosphinate[9] complexes have been partially characterized in the products. In agreement with earlier work[9] these Fe(III) complexes are difficult to obtain in the pure state and we have given only selected properties (ir and mass spectra) of the trifluoromethyl-substituted Fe(III) complex.

Thermal and Mass Spectral Behavior.—The green organic solvent solutions of $Fe[S_2P(CH_3)_2]_3$ formed by extraction of aqueous solutions of the metal and ligand salts decompose quickly at room temperatures and deposit a light tan material. The mass spectrum of this material is dominated by the parent molecular ions $Fe[S_2P(CH_3)_2]_2$ and $[S_2P(CH_3)_2]_2$ and elemental sulfur. Similarly, $Fe[S_2P(C_2H_5)_2]_3$ undergoes spontaneous decomposition over a period of days at ordinary temperatures, even under vacuum.[13] Hot ligroin (bp 30–60°) solutions of this complex exposed to air precipitated pale yellow $Fe[O_2P(C_2H_5)_2]_3$ and elemental sulfur.[13] Thermogravimetric analysis demonstrated that the complexes $Co[S_2P(CH_3)_2]_3$, $Co[S_2P(C_6H_5)_2]_3$, and $Fe[S_2P(C_6H_5)_2]_3$ decompose according to the equation

$$2M[S_2PX_2]_3 \xrightarrow[\Delta]{} 2M[S_2PX_2]_2 + [S_2PX_2]_2 \qquad (4)$$

In contrast $Co[S_2P(OC_2H_5)_2]_3$, $Co[S_2PF_2]_3$, and $Co[S_2P(CF_3)_2]_3$ sublimed under vacuum without significant decomposition. The inductive effects of the substituents are demonstrated very clearly by the reductions of the trivalent X = CH_3, C_6H_5 complexes (eq 4)

TABLE III: MASS SPECTRAL DATA FOR THE BIS COMPLEXES $M[S_2PX_2]_2$[a]

		Source	Assignments																	
X	M	temp, °C	$MS_4P_2X_4$	$MS_4P_2X_3$	MS_4PX_2	MS_4P	$MS_3P_2X_3$	MS_3PX_3	MS_3PX_2	MS_3P	MS_2PX_2	MS_2PX	MS_2P	MS_2	MSPX	MSP	MS	MX	M	$S_4P_2X_4$
CH_3	Mn	200	305 (100)	290 (19)	244 (1)		258 (1)	227 (0)	212 (2)		180 (100)	165 (6)	150 (12)	119 (3)		118 (2)	87 (3)	70 (7)	55 (11)	
	Fe	260	306 (100)	291 (20)	245 (4)		259 (2)		213 (2)		181 (71)	166 (5)	151 (12)			119 (6)			56 (7)	
	Co	110	309 (100)	294 (15)	248 (2)		262 (2)	231 (2)	216 (2)		184 (53)	169 (5)	154 (8)	123 (3)	137 (3)	122 (11)	91 (1)	74 (0)	59 (3)	
	Zn	195	314 (100)	299 (42)	253 (3)		267 (3)		221 (6)		189 (77)		159 (6)	128 (7)						
	Cd	220	364 (100)	349 (37)					271 (3)		239 (53)		209 (1)				146 (1)		114 (4)	
	Hg	200	452 (100)	437 (1)		361 (25)													202 (292)	250 (678)
C_6H_5	Mn	250	553 (100)	476 (0)				413 (8)	336 (1)		304 (63)		150 (5)	119 (0)	195 (2)	118 (0)	87 (0)	132 (7)	55 (23)	
	Fe	225	554 (100)	477 (0)			445 (1)	414 (9)		183 (20)	305 (27)	228 (3)	151 (5)		196 (10)	119 (1)	88 (0)	133 (2)	56 (1)	
	Co	290	557 (100)	480 (0)	372 (0)		448 (1)	417 (5)	340 (5)	186 (9)	308 (22)	231 (14)	154 (14)		199 (24)	122 (16)		136 (13)	59 (14)	
	Zn	225	562 (100)	485 (1)			453 (57)	422 (79)	345 (3)		313 (71)									
	Cd	250	612 (100)	535 (1)			503 (38)	472 (53)	395 (1)		363 (20)									
	Hg	250	700 (100)															279 (20)	202 (870)	498 (1326)
OC_2H_5	Co	200	429 (100)	384 (4)	308 (6)	218 (5)			276 (4)	186 (15)	244 (17)		154 (9)	123 (9)		122 (15)	91 (2)	104 (3)	59 (13)	
	Zn	240	434 (100)		313 (3)		357 (82)		281 (8)	191 (5)	249 (21)			128 (8)		127 (9)			64 (6)	
F	Mn	40	321 (100)	302 (1)	252 (7)			239 (0)	220 (1)		188 (62)			119 (5)			87 (14)	74 (1)	55 (18)	
	Fe	50	322 (100)	303 (1)	253 (21)			240 (2)	221 (1)		189 (22)	170 (1)		120 (12)			88 (8)	75 (4)	56 (8)	
	Co	40	325 (100)	306 (1)	256 (33)				224 (2)	186 (0)	192 (29)	173 (0)	154 (0)	123 (8)	141 (0)		91 (6)		59 (5)	
	Zn	90	330 (100)	311 (1)	261 (1)		279 (0)	248 (0)	229 (5)		197 (37)	178 (0)	159 (6)	128 (6)	146 (0)					
	Hg	150	468 (100)	449 (1)					367 (6)	329 (17)	335 (4)	316 (1)			284 (1)		234 (50)		202 (118)	266 (1385)
CF_3	Mn	60	521 (100)	452 (4)	352 (3)	214 (0)	420 (6)	389 (3)	320 (1)	182 (2)	288 (38)		150 (7)	119 (4)		118 (5)	87 (3)	124 (0)	55 (6)	
	Fe	50	522 (100)		353 (2)	215 (1)	421 (7)		321 (1)	183 (1)	289 (1)	220 (5)	151 (6)	120 (2)	188 (5)	119 (13)	88 (2)	125 (0)	56 (2)	
	Co	70	525 (100)	456 (4)	356 (18)	218 (4)	424 (8)	393 (1)	324 (6)	186 (8)	292 (41)		154 (14)	123 (11)	191 (1)	122 (13)	91 (6)		59 (6)	
	Zn	135	530 (100)	461 (37)			429 (3)			191 (16)	297 (54)		159 (13)							
	Cd	60	580 (100)		411 (0)		479 (3)		379 (3)	241 (1)	347 (15)	278 (0)	209 (2)	178 (1)		177 (1)	146 (1)		114 (3)	
	Hg	100	668 (100)	599 (15)			567 (3)		467 (15)		435 (9)			266 (15)			234 (45)		202 (427)	466 (98)

[a] See footnote *a* of Table II, reading "columns" for "rows." The relative intensities were obtained considering only component peaks of major isotopic species, *i.e.*, ^{64}Zn, ^{114}Cd, and ^{202}Hg.

in contrast with the relative ease of the oxidative reactions

$$2Co[S_2PX_2]_2 + [S_2PX_2]_2 \longrightarrow 2Co[S_2PX_2]_3 \quad (X = F,^{9} CF_3) \quad (5)$$

The similar substituent effects of the F and OC_2H_5 groups (*vide infra*)[5,6] suggest that the complex $Co[S_2P(OC_2H_5)_2]_2$ would be readily oxidized in a similar fashion.

The Co(III), X = CH_3, C_6H_5 compounds may be kept indefinitely under nitrogen or vacuum. This is in contrast with $Co[S_2P(C_2H_5)_2]_3$ which is reported[13] to decompose spontaneously under the same conditions. Such instability has been attributed to the effect of the length of the alkyl chain.[33] It is also reported[13] that exposure of $Co[S_2P(C_2H_5)_2]_3$ to air for several weeks gave a mixture containing the Co(II) complex and the trisulfane $(C_2H_5)_2P(S)–S_3–P(S)(C_2H_5)_2$.

In contrast to the thermal behavior of the trivalent metal complexes (above), the divalent metal compounds all sublime, with the exception of the Co(II) and Zn(II), X = OC_2H_5 complexes. The thermal decomposition of $Zn[S_2P(OR)_2]_2$ compounds has been extensively studied.[34]

The mass spectra reflect the thermal behavior of these complexes. The thermally unstable compounds of Co(III) (X = CH_3, C_6H_5) and Fe(III) (X = C_6H_5) gave no parent ion in the mass spectrum whereas the more thermally stable complexes of both metals with X = F, CF_3, and OC_2H_5 substituents gave weak parent ions. The mass spectra for the trivalent metal complexes for which a lower valent metal complex is isolable (*e.g.*, Co^{III} and Fe^{III}) gave also a prominent peak for the diligand species $S_4P_2X_4$ which in the case of X = CH_3 complexes was the strongest ion in the spectra. All of the trivalent complexes show a very strong ion for $MS_4P_2X_4$. The mass spectra of the trivalent complexes are summarized in Table II.

The mass spectral behavior of the divalent metal complexes is given in Table III. The parent ion is the strongest ion in all spectra except those of the Hg complexes. In these cases the diligand ion $S_4P_2X_4^+$ appears as a strong ion and this ion is actually the strongest ion in the mass spectra of the Hg (X = CH_3, C_6H_5) complexes. Only the Hg complexes showed any significant diligand ion in all of the divalent metal complexes, a behavior which is reminiscent of the reducible M(III) complexes considered above and suggests that Hg(I) complexes may be stable. The $HgS_2PX_2^+$ ion was not unusually prominent relative to the other M(II) complex spectra. The mass spectrum of $CoS_3OP_2(CH_3)_4$ is a composite of the spectra of $Co[S_2P(CH_3)_2]_2$ and $[SP(CH_3)_2]_2O$ reflecting the thermal instability of the complex (eq 3).

Metastable ion patterns are similar for all divalent metal complexes, except those of Hg, according to the nature of X. The X = CH_3 complexes are characterized by loss of a CH_3 group while the X = C_6H_5 complexes show loss of SC_6H_5 and S fragments. The X = F complexes similarly lose F and S. The X = OC_2H_5 complexes show a successive loss of C_2H_4 from each OC_2H_5 substituent yielding X = OH substituted complex ions.[34] The X = CF_3 complexes also suffer substituent fragmentation showing the characteristic[35] loss of

---

(33) A. H. Ewald and E. Sinn, *Aust. J. Chem.*, **21**, 927 (1967).
(34) J. J. Dickert and C. N. Rowe, *J. Org. Chem.*, **32**, 647 (1967).
(35) R. G. Cavell and R. C. Dobbie, *Inorg. Chem.*, **7**, 101 (1968).

TABLE IV

MAGNETIC DATA FOR $M[S_2PX_2]_n$ COMPLEXES[a]

Metal	X	μ_{eff}, BM	Θ, °K	A	B	TIP × 10^6, cgsu	
						Data fitting	Spectral analysis
Mn(II)	CH_3	5.86 (6.06)	−8 (−14)	0.2332 (0.2175)	1.82 (3.14)	737	
	C_6H_5	5.92 (5.89)	−21 (−20)	0.2281 (0.2302)	4.73 (4.57)	−95[e]	
	F	6.03 (5.93)	−38 (−35)	0.2200 (0.2274)	8.36 (7.85)	−317[e]	
	CF_3	5.86 (5.88)	−5 (−6)	0.2332 (0.2314)	1.17 (1.32)	88	
Fe(III)	C_6H_5	5.91 (5.98)	0 (−2)	0.2288 (0.2236)	0.09 (0.55)	252	
Fe(II)	CH_3	5.01 (5.11)	−8 (−12)	0.3181 (0.3063)	2.66 (3.62)	294	~174[b]
	C_6H_5	5.40 (5.51)	−31 (−35)	0.2744 (0.2634)	8.50 (9.28)	334	~174[b]
	F	5.74 (5.52)	−45 (−37)	0.2428 (0.2628)	11.0 (9.78)	−678[e]	130[b]
	CF_3	5.17 (5.44)	−10 (−20)	0.2997 (0.2698)	3.04 (5.36)	874	>174[b]
Co(II)	CH_3	4.38	−11	0.4177	4.68	527	443[c]
	C_6H_5	4.21	−9	0.4511	4.22	380	443[b]
	OC_2H_5	5.49	−224	0.2651	59.3	−367[e]	422[c]
	F	4.43	−17	0.4068	7.10	874	415[c]
	CF_3	4.35	−22	0.4218	9.41	734	438[c]
$CoOS_3P_2(CH_3)_4$		4.11	−8	0.4743	3.64	1140	513[c]
$HgCo(SCN)_4$		4.21	1	0.4515	−0.38	501	428[d]

[a] Magnetic susceptibilities fitted to the Curie–Weiss equation $\chi_M = (N\beta^2/3k)[\mu_{eff}^2/(T-\Theta)] + \chi_M^{diamag} + TIP$ in the form $1/\chi_M^{cor} = AT + B$ where $\chi_M^{cor} = \chi_M - \chi_M^{diamag} + TIP$ and $N\beta^2\mu_{eff}^2/3k$ is the Curie constant. Values in parentheses were derived without a temperature-independent paramagnetic (TIP) correction. [b] TIP = $4N\beta^2/10Dq$. [c] TIP = $8N\beta^2/10Dq$. [d] B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966. [e] These negative TIP corrections arise from a slight reverse curvature of the $1/\chi$ *vs.* T plot and are probably an artifact of the data reduction procedure. The physical significance of the negative numbers is not clear and the values should not be regarded as true TIP contributions.

CF_2 to form F-substituted complex ions. The Hg(II) complexes show metastable peaks corresponding to the loss of the diligand species ($S_4P_2X_4$) and the formation of Hg^+ ions. Hg^{2+} ions are also observed in the spectra of Hg complexes. Many of the trivalent complexes show metastable ions due to the decomposition of the divalent derivatives.

Magnetic Results.—All the Co(III) complexes prepared were diamagnetic as were the Zn(II), Cd(II), and Hg(II) compounds. The magnetic susceptibilities of the remaining paramagnetic species were expressed by the Curie–Weiss equation (TIP = temperature-independent paramagnetism)

$$\chi_M = \frac{C}{T - \Theta} + \chi_M^{diamag} + TIP$$

Application of the "empirical" TIP correction[36] derived by the fitting process improves the straightness of plots of $1/\chi_M^{cor}$ *vs.* T to standard deviations of $1/\chi_M^{cor}$ to less than 0.3% from the least-squares line. However, the significance of this parameter is not well understood. Allowing for a TIP correction also compensates for possible errors in diamagnetic terms. The diamagnetic corrections for the ligand groups were made as previously described.[5] The paramagnetic susceptibility parameters are collected in Table IV.

Manganese Complexes.—$Mn[S_2PF_2]_2$[9] is the only dithio acid complex of Mn(II) for which magnetic data have been published, since the data on $Mn[S_2CN(C_2H_5)_2]_2$ have not yet been reported.[37] Our solid-state powder results agree well with the solution moment of 5.9 BM (at 30°) found for $Mn[S_2PF_2]_2$[9] and compare favorably with the values reported[38,39] for tetrahedral Mn(II) complex salts at 20°. In the solid state the complexes are probably polymeric and the high Weiss constants can be rationalized on the basis of this structural difference which provides a ready mechanism for the interaction of the magnetic centers.

Iron Complexes.—The complex $Fe[S_2P(C_6H_5)_2]_3$, like the Mn(II) compounds, is a d^5 spin-free system within the temperature range studied. The magnetic susceptibility of $Fe[S_2P(OC_2H_5)_2]_3$[10] yields a magnetic moment of 5.91 BM. However, the value of 6.23 BM ($\Theta = -11°$) reported[13] for $Fe[S_2P(C_2H_5)_2]_3$ is unexpectedly large. The high-spin behavior of the iron(III) dithiophosphinates is in marked contrast with the low-spin behavior of Fe(III) complexes of nearly all other dithio acids[2-4] and clearly places these compounds on the high-spin side of the ground state "crossover" possible in this system.[2,3]

In the powdered solid state, the $Fe[S_2PX_2]_2$ complexes have magnetic moments slightly higher than the value of 5.2 BM at 30° found[9] for $Fe[S_2PF_2]_2$ in solution (the only magnetic data previously reported for an iron(II) 1,1-dithio acid complex). All values are within the range of values reported[32,39,40] for tetrahedral complexes of Fe(II). Since the Fe(II) complexes are expected to be isostructural with the Mn(II) and Co(II) analogs, rationalization of the large Weiss constants found should be the same for each system. The explanation for the observed magnetic moments being higher than the spin-only value is still unsettled.[36] TIP values estimated from the expression $4N\beta^2/10Dq$[41] are included in Table IV.

Cobalt Complexes.—A variable-temperature magnetic investigation[13] of solid $Co[S_2P(C_2H_5)_2]_2$ gave a moment of 4.83 ± 0.05 BM ($\Theta = -49°$) (4.46 BM at 295°K calculated from the simple Curie equation). Since there is no mention[13] of a TIP correction, it can be inferred that none was made and that the large Θ value is probably the result of attempting to fit points forming a curved line to the Curie–Weiss equation. High magnetic moments were found[9] for $Co[S_2PF_2]_2$ in heptane, 1,2-dichloroethane and similar solutions both

---

(36) R. J. H. Clark, R. S. Nyholm, and F. B. Taylor, *J. Chem. Soc. A*, 1802 (1967).

(37) J. P. Fackler, Jr., and D. G. Holah, *Inorg. Nucl. Chem. Lett.*, **2**, 251 (1966).

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

(39) (a) D. Forster and D. M. L. Goodgame, *ibid.*, 268 (1965); (b) D. Forster and D. M. L. Goodgame, *ibid.*, 454 (1965).

(40) C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc. A*, 1074 (1968).

TABLE V

ELECTRONIC SPECTRA OF COBALT(II) AND COBALT(III) DITHIOPHOSPHINATES[a]

$Co[S_2PX_2]_2$ Complexes

	$10^3\nu$, cm^{-1}					
	X					
Assignments	CH_3	C_6H_5	OC_2H_5[e]	F	CF_3	$CoOS_3P_2(CH_3)_4$
$^4T_1(F) \leftarrow {}^4A_2$, ν_2	5.9 ($\sim$2) sh	5.8 ($\sim$2) sh	6.2 (2.4)[f] sh	6.0 (3)	5.8 (3) sh	5.84 (5.3) sh
	6.8 ($\sim$0.4) sh	6.8 ($\sim$0.4) sh	$\sim$7 ($\sim$0.1) ?	$\sim$7 ($\sim$0.1) sh	6.7 (0.1) ?	6.81 (1.2) sh
	7.93 (5.2)	7.93 (6.3)	8.27 (3.2)	8.41 (2.7)	8.01 (4.0)	7.74 (9.8)
			9.3 ($\sim$0.1) sh	9.3 ($\sim$0.1) sh		
$^4T_1(P) \leftarrow {}^4A_2$, ν_3	13.8 (3) sh	13.8 (3) sh	13.6 ($\sim$0.1) sh	14.9 ($\sim$1.5) ?	14.2 (1.2) i	12.74 (1.3) sh
	14.87 (8.85)	14.85 (9.7)	15.11 ($\sim$9)	15.31 (5.5)	14.99 (9.5)	13.67 (12) sh
	16.0 ($\sim$3) sh	15.6 ($\sim$2) sh	$\sim$16.0 ($\sim$0.2) sh	16.0 (6) sh	15.8 (8) sh	14.80 (6.4) sh
	17.1 (9) sh	16.9 ($\sim$5) sh	17.0 (3.7) sh	17.2 (3) sh	16.9 (3) sh	16.07 (37)
				$\sim$18.6 ($\sim$1) ?	18.0 (2) sh	17.8 (13) sh
	21.7 (5) sh	21.7 (10) sh	20.7 ($\sim$0.1) sh	20.8 ($\sim$0.1) sh	?	22.0 ($\sim$2) ?
	?	?		?		
	27.5 (130)	26.6 (190)	26.2 (160)	26.15 (150)	27.5 (81)	27.5 (110)
	28.9 ($\sim$10) sh	28.9 (160) ?	27.7 (40) sh	27.7 ($\sim$80) sh	29.5 (40) sh	29.0 (40) sh
	30.2 (130) i	?	29.5 ($\sim$50) ?	$\sim$29.0 ($\sim$50) ?	30.5 ($\sim$10) sh	30.8 (40) i
	34.01 (1210)	33.85 (2430)	31.85 (480)	32.15 (730)	$\sim$32.8 ($\sim$40) sh	34.3 (1530)
		36.1 (?)[b] sh	36.3 (730)	38.7 (700)	34.7 (800)	
		36.3 (?)[b] sh			38.1 (150) sh	
			Ligand Field Parameters[c]			
$10Dq$, cm^{-1}	4715	4716	4944	5032	4765	4076[d]
B', cm^{-1}	577	575	570	575	580	706[d]
β_{35}	0.59	0.59	0.59	0.59	0.60	0.73[d]

$Co[S_2PX_2]_3$ Complexes

	$10^3\nu$, cm^{-1}				
	X				
Assignments	CH_3	C_6H_5	OC_2H_5[e]	F	CF_3
$^1T_{1g} \leftarrow {}^1A_{1g}$, ν_1	12.76 (53.7)	12.68 (35.8)[g]	13.56 (45.3)	13.58 (30.7)	12.59 (32.8)
$^1T_{2g} \leftarrow {}^1A_{1g}$, ν_2	17.66 ($\sim$20) i	17.56 (?)[g] i	18.47 (20) sh	18.49 (120) sh	17.45 ($\sim$30) i
	21.8 (1120) sh	21.6 (884) sh	24.2 (958) sh	24.6 (790)	22.0 (820) sh
					24.8 (30) i
	27.9 (3800)	27.2 (3530) sh	29.77 (3930)	30.69 (3750)	27.7 (3110)
					$\sim$30 (?) i
					33.8 (?) i
				41.0	36.8 (?) sh
			Ligand Field Parameters[c]		
$10Dq$, cm^{-1}	13,370	13,280	14,220	14,240	13,190
B', cm^{-1}	356	355	353	353	353
β_{35}	0.33	0.33	0.33	0.33	0.33

[a] Spectra obtained from CH_2Cl_2 solutions. Positions of band maxima (in units of 10^3 cm^{-1}) are followed by the oscillator strengths $f \times 10^4$ (where $f = 4.60 \times 10^{-9}\epsilon_{max}\Delta\nu_{1/2}$) in parentheses. Resolution was achieved by bi-Gaussian analysis (*i.e.*, allowing for asymmetric band shapes). Abbreviation code: sh, peak observed as a shoulder; i, peak detected by an inflection point; ?, neither shoulder nor inflection observed but peak required to account for total observed intensity. [b] Phenyl group transitions. [c] Calculated using equations in ref 43. [d] Calculated using the centers of gravity of the ν_2 and ν_3 multiplets. [e] In agreement with ref 11. [f] The energy position quoted for this band in ref 11 does not agree with our value; however, the wavelength quoted is in reasonable agreement with our value. [g] In reasonable agreement with ref 16.

by the Gouy method (5.1 BM) and by the Evans nmr method (5.9–6.2 BM); however, our solid-state measurements give a magnetic moment in the expected range for tetrahedral Co(II) complexes leaving the anomaly unexplained. It is interesting however that the solution results[9] are more typical of octahedral than tetrahedral cobalt[41,42] suggesting that the complexes have achieved increased coordination in solution, perhaps through association or solvent coordination.

The apparently anomalous values presented here for $Co[S_2P(OC_2H_5)_2]_2$ may be somewhat suspect in view of the unreliable analytical results obtained for this compound although the electronic spectrum in solution is in good agreement with published data.[39] With this exception (which does appear to be genuine) the magnetic susceptibility results are in reasonable agreement with those found for other tetrahedral Co(II) complexes.[42] As in the Fe(II) d^6 cases, all magnetic moments are higher than expected for a spin-only system but no completely satisfactory explanation is yet available.[36] The magnitudes of the Weiss constants can be accounted for by arguments similar to those presented for the Mn(II) system. The empirical TIP values are to be compared with those derived from the solution spectra as $8N\beta^2/10Dq$[41] in Table IV.

It is noted here that our analysis of the temperature-dependent magnetic behavior of $HgCo(NCS)_4$ yielded values slightly different (Table IV) from the 4.32 BM ($\Theta = -4°$, TIP $= 428 \times 10^{-6}$ cgsu) reported previously,[42] although the agreement is good in the neighborhood of room temperature if no TIP correction is made.

Electronic Spectra. Manganese(II) Complexes.—Limited solubility of the X = CH_3, C_6H_5 complexes in noncoordinating solvents and the general instability of these complexes in solution precluded the obtaining of

---

(41) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966.

(42) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Amer. Chem. Soc.*, **83**, 4157 (1961), and references therein.

TABLE VI

INFRARED SPECTRA OF PSEUDOOCTAHEDRAL $M[S_2PX_2]_3$ COMPLEXES[a]

X = CH_3	X = C_6H_5		X = OC_2H_5	X = F	X = CF_3		Assignments
M = Co	M		M = Co	M = Co	M		
	Fe	Co			Fe	Co	
1423 w, sh	1434 s	1434 s					
1414 w							
1405 w, sh							
1397 m							δ_{CH_3}
1392 w, sh	1304 w	1304 w					
1285 w, sh			1276 w		1295 w	1291 w	
1275 w							
					1210 m, sh	1208 s	ν_{C-F}
					1200 s	1186 s, sh	
					1164 s	1163 s	
					1135 m, sh	1150 s, sh	
	1184 w	1181 w	1162 w, sh				
	1156 w	1156 w	1158 w				
		1128 w					
	1105 s	1100 s, sh	1101 w				
	1097 s	1097 s					
	1066 w	1066 w	1058 m, sh				
		1036 w	1032 m, sh				
			1007 s				ν_{P-O}
	1025 w	1025 w					
	997 w	997 w					
954 s, sh			960 s				
950 s							
940 s							
900 s							
897 s, sh							
				880 s, br			ν_{P-F}
855 m							
848 w, sh	844 w						
			812 s	821 m, br			
			795 s, sh	806 m			
	750 m, sh	745 m, sh				753 w	
742 m	741 m	742 m					
719 s	711 m, sh			712 s	720 m	720 w	ν_{P-S}
	704 s	707 s					
	685 s	691 m, sh			695 m, sh		
	670 w, sh	687 m	646 w, sh	684 m		661 m	
	639 m	640 w	629 m				
	609 m	607 w	618 s				
592 w, sh		602 w					
580 s	569 s	573 s	555 w, sh	564 m			
		560 m, sh	541 m		534 m	533 m	
	488 m	489 m					
	480 m, sh	480 m, sh					
	476 w, sh				470 m	472 m	
	450 w		396 w	403 m			
	357 w	348 w	347 w			372 m	
						320 w	
280 m		302 w	307 m	309 w		297 w	ν_{M-S}
267 w, sh	264 m	242 w					

[a] Spectra in the range 1450–250 cm^{-1} were obtained from Nujol mulls. Positions of band maxima in cm^{-1}. Abbreviations: ν, stretching mode; δ, deformation mode; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

reliable solution spectra. The reflectance spectra were also characteristically weak and poorly resolved. Consequently no discussion of the spectra is undertaken here at this time.

Iron Complexes.—The spectrum of $Fe[S_2P(C_6H_5)_2]_3$ (Figure 2) consists of an ascending sequence of shoulders. Some resolution was achieved by Gaussian analysis resulting in broad bands ($\Delta\nu_{1/2} \approx$ 1100–3500 cm^{-1}) but not the series of narrow bands expected for a d^5 system. Due to inherent difficulties in the treatment of Fe(III) spectra[43] no analysis is attempted here.

The extreme sensitivity of the Fe(II) complexes to oxidation in solution allowed us to obtain only the reflectance spectra (Figure 3). Unfortunately, the spectral range accessible with the present equipment was not quite sufficient to observe the 3000–6000-cm^{-1} region expected to contain the $^5T_2 \leftarrow {}^5E$ transition of tetra-

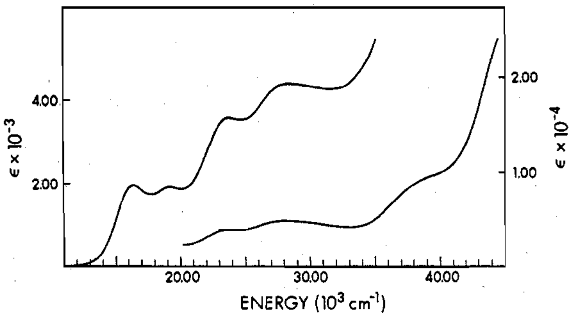


Figure 2.—The visible (left) and ultraviolet (right) spectra of $Fe[S_2P(C_6H_5)_2]_3$ in CH_2Cl_2 solution.

---

[43] A. P. B. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968.

TABLE VII

INFRARED SPECTRA OF PSEUDOTETRAHEDRAL $M[S_2PX_2]_2$ COMPLEXES[a]

$X = CH_3$						$X = C_6H_5$						Assignments
Mn	Fe	Co	Zn	Cd	Hg	Mn	Fe	Co	Zn	Cd	Hg	
1420 w	1422 w	1422 w, sh	1421 w			1431 s	1431 s	1430 s	1432 s	1431 s	1430 s	
1415 w	1415 w	1416 w	1417 w	1415 w	1414 w							
1404 w, sh	1405 w	1405 w, sh	1405 w		1403 w, sh							
	1400 w	1400 w	1399 w									
1395 m	1394 w	1394 w, sh	1394 w	1395 w	1395 w							
1295 m	1295 w	1295 m	1296 w	1297 w	1295 m	1303 w	1304 w	1304 w	1304 w	1303 w	1301 w	
1282 s	1283 m	1282 m	1283 m	1283 m	1282 m							δ_{CH_3}
						1184 w	1181 w	1180 w	1183 w	1181 w	1180 w	
						1155 w	1151 w	1151 w	1153 w	1153 w	1153 w	
						1100 s, sh	1100 s, sh	1099 s, sh	1100 s	1098 s, sh	1097 s, sh	
						1097 s	1095 s	1094 s	1096 s, sh	1093 s	1093 s	
						1024 w	1022 w	1020 w	1023 w	1023 w	1021 w	
946 s	946 m	948 m	947 m, sh	947 m	945 s	997 w	996 w	995 w	996 w	994 w	994 w	
	942 m	943 m	943 m									
912 s, sh	903 s, sh	905 s, sh	908 s, sh	910 s, sh								
904 s	901 s	901 s	900 s	904 s								
855 s	853 m	855 m	855 m	855 m	857 m							
849 s	847 m	847 m	847 m	849 m	848 m	841 w	841 w	841 w	843 w	840 w	841 w	
741 m	744 m	742 m	742 m	742 m	743 m	742 s	745 s	744 s	745 s	745 s	744 s	
719 s	717 s	718 s	719 s	719 s	716 s	717 m, sh	712 m	719 m	717 m, sh	718 m, sh	716 m, sh	ν_{P-S}
						712 m, sh	715 m	715 m	715 m	715 m	713 m	
						703 s	706 s	704 s	705 s	704 s		
						685 s	689 s	689 s	682 s, sh	689 s	687 s	
						668 w, sh	686 s, sh	685 s, sh	679 s			
						634 s	636 m	634 s	640 s	636 s	633 s	
						625 m, sh	628 m, sh	625 m, sh	628 m, sh	626 m, sh	625 w, sh	
							610 m	609 m	617 w	617 w	615 w	
						608 m	607 m, sh	604 m, sh	611 s	610 s	608 s	
590 s	578 s	578 s	583 s	585 s	583 s	564 s	565 s	564 s	563 s	568 s	566 s	ν_{P-S}
						554 s	553 s	554 s	552 s	550 s	545 s	
495 s	488 s	490 m	495 m	496 m	493 s	491 s	492 m	493 s	494 s	491 s	489 s	
						475 w	475 w	473 w	476 m	474 m	471 w	
						449 m	448 w	447 m	448 m	450 m	446 m	
	333 w	326 m	325 m	311 m	311 w	359 w	360 w	360 m	366 m	362 m	361 m	
315 s	314 m	314 m	299 w	303 w, sh	314 w	317 w	323 w	326 m	337 w	337 w	314 w	ν_{M-S}
299 m, sh	306 m, sh	287 w	287 w, sh	285 w, sh	286 w, sh		298 w	302 m, sh	302 m	283 m	302 m	
280 w, sh	285 w	280 w, sh	276 w, sh	275 w	270 w	285 m	276 w	298 m	274 m	260 m	286 w, sh	
				265 w, sh		264 m		282 m	254 m	254 m	260 w	

$X = OC_2H_5$		$X = F$				$X = CF_3$						Assignments
Co	Zn	Mn	Fe	Co	Zn	Mn	Fe	Co	Zn	Cd	Hg	
1263 w	1263 w					1291 w	1290 w	1291 w	1292 w	1290 w	1289 w	
						1211 s, sh		1218 s, sh				
								1209 s	1200 s			
						1186 s	1186 s, sh	1193 s, sh		1191 s	1184 s, sh	ν_{C-F}
						1170 s, sh		1179 s, sh				
1154 w	1153 w					1158 s	1161 s	1162 s	1160 s	1160 s, sh	1162 s	
						1138 s	1144 s	1144 s, sh	1140 s	1146 s	1150 s	

1036 s, sh	1036 s, sh											ν_{P-O}
1016 s	1017 s											
966 s, sh	968 s, sh											
955 s	956 s											
		917 s	885 vs	889 w	887 vs							ν_{P-F}
		887 vs	868 vs	819 vs	840 s							
			835 vs	806 s								
787 m, sh	788 m, sh											
774 m	775 m					751 w	750 w	751 w	754 w	745 w	750 w	
734 w, sh	735 w, sh	720 s	718 s, sh	715 vs		721 m, sh	712 w, sh		712 w, sh			
		699 s	702 vs		704 vs	696 s	691 s		691 s	680 s, sh	675 s	ν_{P-S}
		685 s			697 s, sh	686 m, sh	679 m, sh	665 w		673 s	664 s, sh	
661 s	668 s				675 s							
640 m, sh	649 m, sh											
			610 w			610 s	611 s	607 s	611 s	597 s		
						603 s, sh	602 s, sh	595 s	600 s	589 s	589 s	
539 m	541 m	550 m	559 m	559 m	558 m	541 m	541 m	538 m	541 s	533 m	536 m	ν_{P-S}
495 m	486 m		474 w			480 m	480 m	477 m	480 s	472 m	480 m	
377 w	380 w	401 m	399 m	390 m	398 m	381 m	383 m	384 m	381 m, sh		377 w	
			367 m, sh	369 m	368 s							
		357 m	355 m	358 m, sh					337 w			
313 m	310 m	320 w	311 w	314 w	368 w, sh	325 w	305 w	311 w	325 w		335 w	ν_{M-S}
									306 w			
		285 w				285 w	286 w	288 m	289 w		297 m	
								277 w	260 w		262 w	

[a] Spectra in the range 1450–250 cm^{-1} were obtained from Nujol mulls. Positions of band maxima in cm^{-1}. Abbreviations: ν, stretching mode; δ, deformation mode; s, strong; m, medium; sh, shoulder; v, very.

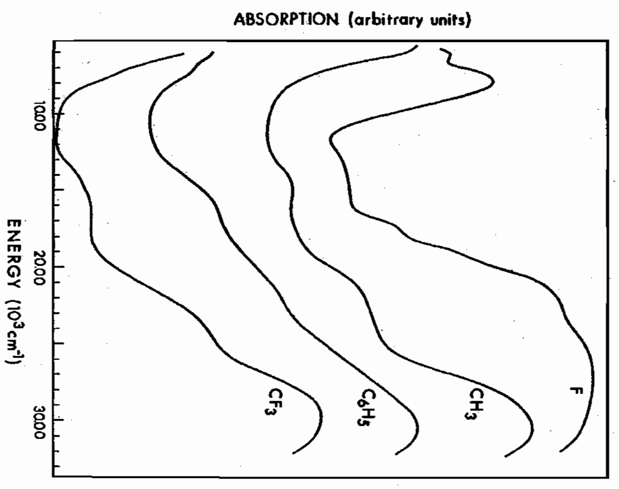


Figure 3.—Diffuse-reflectance spectra of Fe[S$_2$PX$_2$]$_2$ complexes.

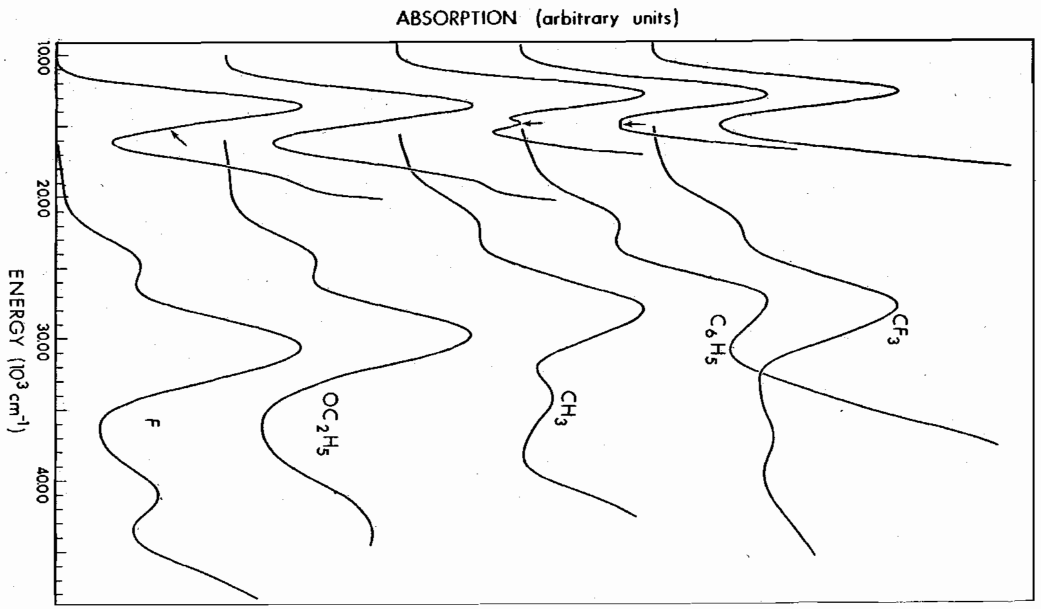


Figure 4.—Visible and ultraviolet spectra of Co[S$_2$PX$_2$]$_3$ complexes in CH$_2$Cl$_2$ solution. Arrows mark the absorption positions of Co(II) species present as impurities in the Co(III) complexes (see text). The relative absorption scale factors (uv/vis) according to X are (CH$_3$) 33.6, (C$_6$H$_5$) 37.5, (OC$_2$H$_5$) 101.4, (F) 51.3, and (CF$_3$) 62.3.

hedral Fe(II) complexes. However, reduction of the point group symmetry from T_d (the maximum symmetry is D_{2d}) should increase the energies of all electronic transitions[39b] possibly by as much as 1000–2000 cm^{-1}. This effect was observed (*vide infra*) for the cobalt(II) dithiophosphinates with respect to the tetrahedral halo complexes. Since there are no Fe(III) bands below 12,000 cm^{-1}, oxidation can be ruled out and the maximum observed at 8050 cm^{-1} in the spectrum of $Fe[S_2PF_2]_2$ can be assigned to the $^5T_2 \leftarrow {}^5E$ transition with the splitting due to the reduced symmetry of the complex. In the remainder of the series, this band is sufficiently resolved to suggest maxima near 6000 cm^{-1} which yields a tentative spectrochemical series: F > CH_3 ~ C_6H_5 ~ CF_3 for the substituents X. The band assignment results in the highest values for 10*Dq* observed for tetrahedral or pseudotetrahedral Fe(II) compounds.

Cobalt Complexes.—It proved exceedingly difficult to produce Co(III), X = CH_3, C_6H_5, and F compounds completely free of the Co(II) species. The spectra illustrated in Figure 4 thus include arrows marking contributions from these impurities. The $\nu_2(^1T_{2g} \leftarrow {}^1A_{1g})$ band, which is an easily discernible shoulder where X = F or OC_2H_5, is extracted with large uncertainty where X = CH_3, C_6H_5, or CF_3. Ligand field parameters were derived using Jørgensen's equations[43] for a d^6 octahedral system (including configurational interaction with the assumption that $C = 4B$). It is believed that neither the reduction from O_h to D_3 point group symmetry nor the failure of the assumed relationship between the Racah *B* and *C* parameters should affect the self-consistency of the results. The band maxima and derived parameters are collected in Table V. The spectrochemical ordering of ligands according to X is thus F ~ OC_2H_5 > CH_3 ~ C_6H_5 ~ CF_3 for these pseudooctahedral Co(III) compounds.

The reflectance spectra of the solid Co(II) complexes are in general agreement with their solution spectra with regard to the distribution of the ν_2 and ν_3 multiplets, although these are somewhat spread apart in the solid state. The solution spectra (Figure 5), obtained in CH_2Cl_2 are in agreement with those reported for the OC_2H_5-[11] and C_2H_5-substituted[13] compounds (in CCl_4 solutions). The most prominent features of the visible and near-ir spectra of these compounds are the "spike" at ~15,000 cm^{-1} and multiplet component at ~8000 cm^{-1} which is generally more intense than its neighbors. In determining a "self-consistent" set of ligand field parameters for comparison purposes within the set of Co(II) complexes reported herein, it was decided to use these distinctive spectral features, disregarding the remaining components in calculations. This procedure is considered to be possibly less arbitrary than using the centers of gravity of the respective multiplets as done[39] for other tetrahedral Co(II) compounds, especially in view of the recent criticism[44] of that method. The resolved band maxima and derived ligand field parameters are given in Table V. The spectrochemical ordering of the ligands according to X in this Co(II) system is F ~ OC_2H_5 > CF_3 ~ CH_3 ~ C_6H_5.

The spectra of blue-green solutions of $Co[S_2P(CH_3)_2]_2$ in methanol (Figure 6) and ethanol are nearly superimposable (even into the uv region). They are very

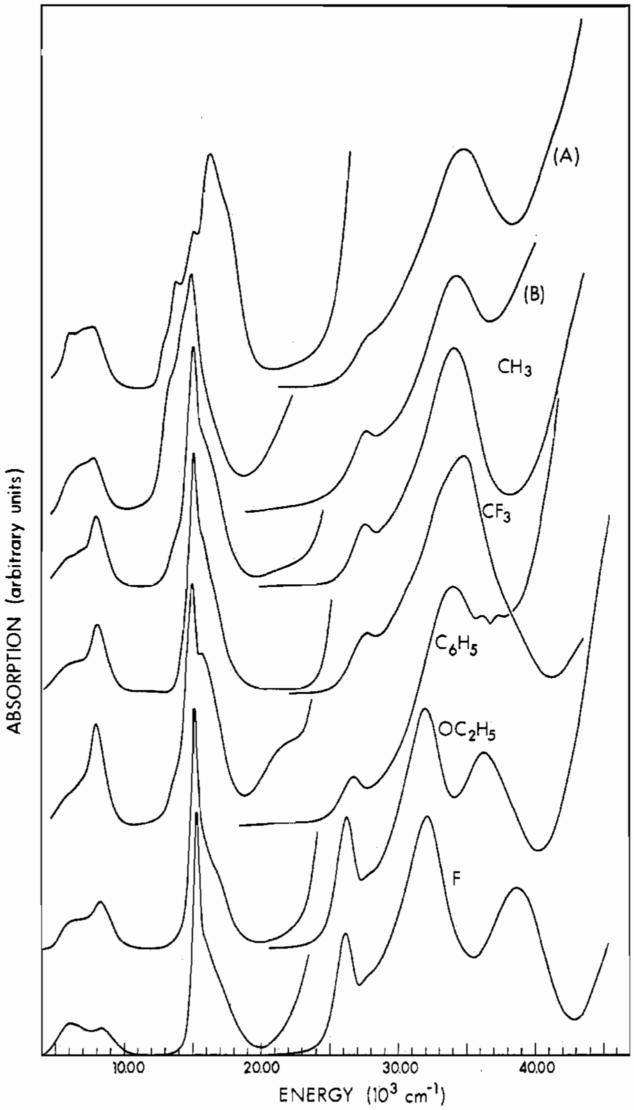


Figure 5.—Visible and ultraviolet spectra of $Co[S_2PX_2]_2$ complexes in CH_2Cl_2 solutions. In addition $CoS_3OP_2(CH_3)_4$ in CH_2Cl_2 gave spectrum (A) but in CCl_4 gave spectrum (B). The relative absorption scale factors (uv/vis) according to X are (A) 11.6, (B) 13.8, (CH_3) 19.7, (C_6H_5) 42.6, (OC_2H_5) 16.8, (F) 17.0, and (CF_3) 13.7.

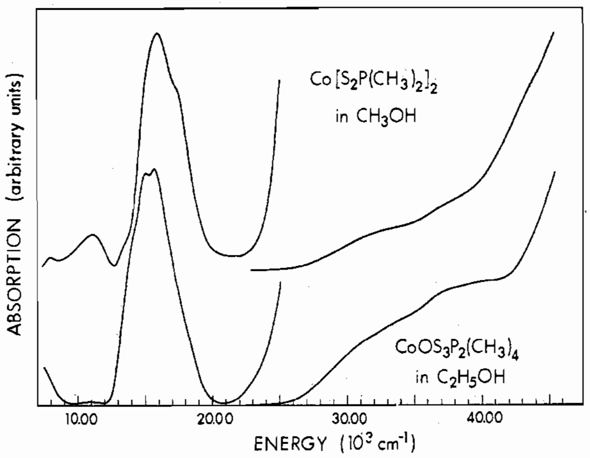


Figure 6.—Visible and ultraviolet spectra of the $Co[S_2P(CH_3)_2]_2$ and $CoS_3OP_2(CH_3)_4$ complexes in alcohol solutions. Relative absorption scale factors (uv/vis) are 60 and 237, respectively.

---

(44) J. Ferguson, *J. Chem. Phys.*, **39**, 116 (1968).

TABLE VIII

ν_{M-S}–10*Dq* CORRELATION FOR OCTAHEDRAL [M(III)] AND TETRAHEDRAL [M(II)] DITHIOPHOSPHINATES, $M[S_2PX_2]_n$[a]

	X									
	CH_3		C_6H_5		OC_2H_5		F		CF_3	
M	ν_{M-S}, cm^{-1}	10*Dq*, 10^3 cm^{-1}	ν_{M-S}, cm^{-1}	10*Dq*, 10^3 cm^{-1}	ν_{M-S}, cm^{-1}	10*Dq*, 10^3 cm^{-1}	ν_{M-S}, cm^{-1}	10*Dq*, 10^3 cm^{-1}	ν_{M-S}, cm^{-1}	10*Dq*, 10^3 cm^{-1}
V(III)	359 m 296 s	12.97	358 m 280 s	12.83	363 m 295 s	13.58	360 m 294 s	13.38	326 m 285 s	12.81
Cr(III)	313 s	13.70	305 s	13.65	315 vs	14.40	316 s	14.40	307 s	13.70
Mn(II)[b]	315 s		314 w				315 m		325 w	
Fe(II)	314 m	~6	317 w	~6			311 w	8.05	305 w	≤6
Co(III)	305 m	13.37	302 w	13.28	307 m	14.22	309 w	14.24	297 w	13.19
Co(II)	314 m	4.72	323 w 298 m	4.72	313 m	4.94	311 w	5.03	311 w	4.76

[a] Infrared spectra obtained from Nujol mulls which were close to true solutions in the cases of X = F and CF_3. 10*Dq* values were calculated from spectra of CH_2Cl_2 solutions of the complexes. [b] 10*Dq* values not obtained.

similar to the spectrum of $Co[S_2P(OC_2H_5)_2]_2$ in ethanol,[11] thought to be of the six-coordinate solvated complex. The spectra where X = CH_3 were obtained on supersaturated alcohol solutions obtained by Soxhlet extraction of the green solid. The solutions remained metastable for ~30 min after which time nearly quantitative precipitation of the green unsolvated complex occurred (suffering no significant O for S substitution).

Even in the absence of comprehensive solution molecular weight data there is some justification for presuming that the solution spectra obtained in CH_2Cl_2 were of monomeric species. The methyl- and phenyl-substituted complexes were too insoluble in common noncoordinating organic solvents to determine the solution molecular weight. However, the X = C_2H_5 and C_3H_7 compounds have been found to be monomeric in benzene over a wide range of concentrations.[13] The complex $Mn[S_2PF_2]_2$ was reported to be monomeric in a 3.4×10^{-2} *M* solution in 1,2-dichloroethane although the reactivity of the complex with air and moisture was the cause for considering this result with reservation.[9] The complex $Zn[S_2P(OC_2H_5)_2]_2$ is polymeric in the solid state, but monomeric in chloroform solution.[28] The cobalt analog, $Co[S_2P(OC_2H_5)_2]_2$, may behave similarly, although the different mass spectra of the two complexes suggests that the crystal structures may be different. The ready solubility of $Co[S_2P(CF_3)_2]_2$ suggests a low degree of association in solution. Where association is known to occur, a solvent dependence for the degree of association has been found:[1] $CCl_4 > C_6H_6 > CHCl_3$, and CH_2Cl_2 would be expected to occupy a position in the series to the right of $CHCl_3$. Finally, spectra of all the Co(II) complexes were obtained from $\sim 5 \times 10^{-3}$ *M* solutions and spectra of $Co[S_2P(CH_3)_2]_2$ in CCl_4, $CHCl_3$, and CH_2Cl_2 were not significantly different. The general similarity of the solution spectra (Figure 5) for all X indicates that even if association does occur in some cases it does not significantly affect the spectrum.

Solutions of $CoS_3OP_2(CH_3)_4$ in CH_2Cl_2 and $CHCl_3$ were deep blue and gave superimposable spectra. The spectrum in CH_2Cl_2 as illustrated in Figure 5 significantly lacks the sharp spike characteristic of the "tetrathio" complexes. Extraction of $CoS_3OP_2(CH_3)_4$ into CCl_4, C_6H_6, or CS_2 resulted in the formation of deep green solutions the spectra of which were intermediate between those of CH_2Cl_2 or $CHCl_3$ solution extracts and the spectrum of $Co[S_2P(CH_3)_2]_2$. The spectrum of the oxy–thio complex in CCl_4 is also shown in Figure 5. The total width of the ν_3 multiplet of the blue oxy–thio complex in CH_2Cl_2 (~5000 cm^{-1}) is greater than the ν_3 multiplet (~4000 cm^{-1}) of the green tetrathio compound. For lack of alternatives, the centers of gravity of the ν_2 and ν_3 multiplets were used to estimate the ligand field parameters; thus comparison with the spectra of the tetrathio analog (Table V) is not wholly reliable.

Infrared Spectra.—The infrared spectra of the six-coordinate trivalent metal ion complexes are presented in Table VI and may be compared with those of Cr(III)[5] and V(III).[6] The infrared spectra of the four-coordinate divalent metal ion complexes are presented in Table VII. Since the spectra (above 400 cm^{-1}) are largely due to ligand vibrational modes, the general similarity of the spectra for a given X substituent is to be expected. Moreover, the general similarity of the spectra for a given X group but different metal ion is taken as evidence for similarity in structure.

Ligand Field—Metal–Sulfur Stretching Frequency Correlations.—Since a monotonic relationship exists between the ligand field strength and the metal–sulfur stretching frequency of the planar nickel(II) dithiophosphinates,[8] an examination of the other geometries was indicated. Infrared bands assigned to the M–S stretching mode[32] and the corresponding 10*Dq* values for the respective complexes are collected in Table VIII. For the six-coordinate (D_3) complexes a reasonable correlation is again observed in spite of the different substituent mass effects. As expected from the wide variation of molecular structure and ligand function, no such unequivocal correlation is found for the pseudotetrahedral divalent metal complexes. A comparison of the solution infrared spectra would be preferable, but due to the limited solubility of the M(II), X = CH_3 and C_6H_5 compounds, this is not possible. Also, at concentrations sufficient to obtain reasonable infrared spectra, the degree of association becomes cause for concern.

Conclusions

In spite of their polymeric nature, the pseudo-tetrahedral $M(S_2PX_2)_2$ complexes have magnetic and spectral properties surprisingly similar to those of authentic tetrahedrally coordinated metal ion complexes and in marked contrast with other dithio acid complexes. As the dithiophosphinate ligands are also capable of acting as bridging groups it is notable that cupric and chromous acetate type structures have not yet been observed. Unfortunately the Cu(II) and Cr(II) species are most probably inaccessible (except in solution for short periods of time in the former case).

The spectrochemical order of the ligands according to X is generally found to be F $\sim$ OC_2H_5 > CH_3 $\sim$ C_6H_5 $\sim$ CF_3. The π interaction between the substituent lone pair with the phosphorus–sulfur dπ system apparently dominates the inductive effect of the substituent (*e.g.*, F *vs.* CF_3). This would be expected to produce a synergic effect in the reverse sense to that postulated for transition metal carbonyl compounds, although not so readily discernible in the P–S stretching frequencies. The nephelauxetic series of the ligands ordered according to X in order of B' is F $\sim$ OC_2H_5 < CH_3 $\sim$ C_6H_5 $\sim$ CF_3, indicating greater electronic delocalization with those substituents found to produce the largest phosphorus coupling constants in the epr spectra of the vanadyl complexes.[7]

Acknowledgments.—We thank Dr. R. M. Tuggle for his X-ray investigation of $CoOS_3P_2(CH_3)_4$ and Dr. M. J. Bennett and Mr. R. H. Sumner for permission to use Figure 1 prior to publication. We are indebted to Miss J. K. Schneider and Dr. A. R. Sanger for their preparation of the $HS_2P(CF_3)_2$ acid and to Drs. A. R. Sanger and A. J. Tomlinson for helpful discussions. We thank the National Research Council of Canada and the University of Alberta for the financial support of this work.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE-MELLON UNIVERSITY,
PITTSBURGH, PENNSYLVANIA 15213

Stereochemistry of β-Diketone Complexes of Cobalt(III). X. Synthesis and Spectroscopy of Some Azide Complexes of Bis(acetylacetonato)cobalt(III)[1]

BY L. J. BOUCHER* AND D. R. HERRINGTON

Received December 9, 1971

K{*trans*-$[Co(acac)_2(N_3)_2]$}, $[PPh_4]${*cis*- and *trans*-$[Co(acac)_2(N_3)_2]$}, *cis*- and *trans*-$[Co(acac)_2N_3py]$, and *cis*-$[Co(acac)_2N_3NH_3]$ have been synthesized and characterized. The stereochemistry of the complexes was assigned with the aid of their proton magnetic resonance spectra. In addition, infrared and ultraviolet–visible spectra of the materials were determined and the absorption bands assigned. The complexes undergo a facile trans ⇄ cis isomerization reaction in solution at 34°.

Previous work with bis(acetylacetonato)cobalt(III) complexes has centered around nitro compounds of the type *cis*- and *trans*-$[Co(acac)_2NO_2L]^{n-}$, where L is NO_2^-,[2] an amine,[3] or water.[2] In contrast to the inert diamine complexes[4,5] *cis*- and *trans*-$[Co(acac)_2L_2]^+$, the nitro derivatives are stereochemically labile.[6] This observation has promoted the study of complexes of other anions. Comparisons of the reactivities for a series of anion complexes of the type *cis*- and *trans*-$[Co(acac)_2XL]^{n-}$ will contribute toward understanding the mode of reaction of low ligand field complexes of cobalt(III).[7] We wish to report here the synthesis, characterization, and reactivity of the new azide complexes *cis*- and *trans*-$[Co(acac)_2N_3L]^{n-}$ where L is N_3^-, pyridine, or ammonia and $n = 1$ or 0. A structural representation of the complexes is given in Figure 1.

Experimental Section

Materials.—The starting material $[Co(acac)_2]$ was prepared by the method of Ellern and Ragsdale.[8] All other materials were reagent grade and used without further purification.

Syntheses. **K{*trans*-$[Co(acac)_2(N_3)_2]$}.**—Two grams of $[Co(acac)_2]$ (0.0078 mol) was dissolved in 125 ml of methanol. After the addition of 2.5 g of potassium azide (0.0308 mol) and 2 ml of glacial acetic acid (0.0348 mol), 2 ml of 30% hydrogen peroxide solution (0.0176 mol) was added dropwise. The reaction mixture was stirred at 25° for 2 hr, at which point the precipitated crude product was filtered and air-dried. The green-brown product was dissolved in $\sim$20 ml of water and 0.5 g of sodium azide and 2.0 g of potassium chloride ($\sim$0.4 *M* in N_3^- and $\sim$1.6 *M* in K^+) were added. The solution was filtered and kept at 0° for 2–3 days. The crystalline product was filtered and air-dried. A typical yield was 1.05 g, 35% based on the original cobalt(II) complex. *Anal.*[9] Calcd for $C_{10}H_{14}O_4N_6CoK$, $K[Co(acac)_2(N_3)_2]$: C, 31.58; H, 3.71; N, 22.10. Found: C, 31.47; H, 3.83; N, 21.47.

$[PPh_4]${*trans*-$[Co(acac)_2(N_3)_2]$}.—The addition of 1.2 g of $[P(Ph)_4]Br$ (0.0029 mol) to a solution of 1.0 g of K{*trans*-$[Co(acac)_2(N_3)_2]$} (0.0026 mol) in a minimum of water ($\sim$20 ml) resulted in the immediate formation of a finely divided precipitate of the tetraphenylphosphonium salt of the complex. This was washed several times with water and air-dried. A typical yield was 1.25 g, 60% based on the initial weight of the potassium salt. *Anal.* Calcd for $C_{34}H_{34}O_4N_6PCo$, $[PPh_4][Co(acac)_2(N_3)_2]$: C, 59.99; H, 5.04; N, 12.35. Found: C, 59.86; H, 5.05; N, 12.56; mp 152°.

$[PPh_4]${*cis*-$[Co(acac)_2(N_3)_2]$}.—One gram of $[PPh_4]${*trans*-$[Co(acac)_2(N_3)_2]$} was dissolved in a minimum of acetone ($\sim$30 ml) and kept at 25° for 15 min. The emerald green crystals of the cis isomer which formed were filtered, washed quickly with a small portion of acetone, and air-dried. The yield was 0.50 g, 50% based on the original trans isomer. *Anal.* Calcd for $C_{34}H_{34}O_4N_6PCo$, $[PPh_4][Co(acac)_2(N_3)_2]$: C, 59.99; H, 5.04; N, 12.35. Found: C, 59.84; H, 5.01; N, 12.28; mp 161°.

***trans*-$[Co(acac)_2N_3py]$.**—Two grams of $[Co(acac)_2]$ (0.0078 mol) was dissolved in 200 ml of water. One gram of sodium azide (0.0156 mol) and 2 ml of pyridine (0.0248 mol) were added, followed by the dropwise addition of 2 ml of 30% hydrogen peroxide solution (0.0176 mol). The reaction mixture was stirred at 25° for 2 hr, and the precipitate which formed was filtered and air-dried. The crude product was purified by dissolving in a

---

[1] Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

[2] B. P. Cotsoradis and R. D. Archer, *Inorg. Chem.*, **6**, 800 (1967).

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

[4] R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1589 (1965).

[5] L. J. Boucher, *ibid.*, **9**, 1202 (1970).

[6] L. J. Boucher and N. G. Paez, *ibid.*, **10**, 1680 (1971).

[7] R. D. Archer, *Coord. Chem. Rev.*, **4**, 243 (1969).

[8] J. B. Ellern and R. O. Ragsdale, *Inorg. Syn.*, **11**, 82 (1968).

[9] Elemental analyses performed by Meade Microanalytical Laboratory, Amherst, Mass.