

the MCD spectrum of $\text{Cr}(\text{dtp})_3$ at 20.38 kK which he associates with the 2A_1 level. (No hint of a band at this energy is seen in the absorption spectrum.) Within the limits of the calculation we have made it does not seem possible either to move the 2A_1 level near 20.38 kK (without destroying the more certain parts of the fit, *i.e.*, the ${}^4T_{2g}$ and ${}^4T_{1g}$ manifolds) or to move the ${}^2A_{1g}$ and ${}^4T_{1g}$ levels closer than *ca.* 5 kK to each other. Introduction of a large and (apparently) unlikely second-

order trigonal term (v') may suggest new assignments not yet envisioned. More work is in progress on the resolution of this ambiguity. We offer the assignments and parameters of Table V as those which best fit the data at this time.⁴⁵

(45) NOTE ADDED IN PROOF.—Tomlinson has recently published ambient temperature crystal spectra of $\text{Co}(\text{dtp})_3$ and $\text{Cr}(\text{dtp})_3$ which are in essential agreement with the ambient temperature results reported in this paper [A. A. G. Tomlinson, *J. Chem. Soc. A.*, 1409 (1971)].

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Metal Complexes of Substituted Dithiophosphinic Acids.

I. Complexes of Trivalent Chromium

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The preparation and characterization of substituted dithiophosphinate [S_2PX_2^- ($\text{X} = \text{CF}_3, \text{F}, \text{CH}_3, \text{C}_6\text{H}_5, \text{and } \text{OC}_2\text{H}_5$)] complexes of chromium(III) are described. The magnetic susceptibilities of the Cr(III) complexes over the range 90–303°K follow the Curie–Weiss law with very small Weiss constants. The susceptibilities of the diamagnetic zinc complexes were used to determine diamagnetic corrections for the ligands which for the most part agree with values calculated from Pascal's constants. Other properties of the Cr(III) complexes such as solubility, molecular weights, and mass spectral behavior are consistent with their formulation as six-coordinated, monomeric chelates. The electronic spectra are analyzed in terms of octahedral symmetry. The resultant Dq parameters of the ligands decrease in the order $\text{F} \sim \text{OC}_2\text{H}_5 > \text{CH}_3 \sim \text{CF}_3 \sim \text{C}_6\text{H}_5$ with a distinct difference observed between the complexes with F or O bonded to phosphorus as compared to those with P–C bonds and this difference is attributed to π -bonding effects. The complexes show relatively intense spectral bands which can be attributed to the distortion from octahedral symmetry or the presence of substantial covalence in the M–S bonding ($\beta_{35} \cong 0.45$) or more likely both. The infrared spectra of all of the complexes show a strong M–S stretch at 310–320 cm^{-1} .

Introduction

Following the preparation and characterization of the trifluoromethyl^{1,2} and fluorodithiophosphinic^{3–5} acids $\text{X}_2\text{P}(\text{S})\text{SH}$ it was of interest to investigate the properties of metal dithiophosphinate complexes which are obtained from the above acids and their salts. For comparison purposes related complexes of dimethyldithiophosphinic, diphenyldithiophosphinic, and bis(*O,O'*-diethyl)dithiophosphoric acids have been prepared. We wish to report herein studies of a variety of substituted trivalent chromium complexes⁶ of these dithiophosphinic acids. The *O,O'*-dialkyl dithiophosphate complexes $\text{Cr}[(\text{RO})_2\text{PS}_2]_3$ (particularly the ethoxy derivative) have been known for some time^{7,8} and now an extensive series of alkoxy homologs has been investigated.⁸ While this paper was in preparation, the synthesis of the $\text{Cr}(\text{S}_2\text{PF}_2)_3$ complex from $\text{F}_2\text{P}(\text{S})\text{SH}$ and chromium

metal was also reported;⁹ however, spectral^{9,10} and magnetic properties^{9,10} were only reported in summary. The synthesis of the complex $\text{Cr}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3$ from chromium trichloride and the phenyl acid $(\text{C}_6\text{H}_5)_2\text{PS}_2\text{H}$ ^{11,12} and the synthesis and a dipole moment study of $\text{Cr}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$ ¹³ have been reported. The complexes of the $(\text{C}_2\text{H}_5)_2\text{PS}_2^-$ ligand have been recently reviewed.¹⁴ A brief report of the synthesis of $\text{Cr}[\text{S}_2\text{PF}(\text{C}_2\text{H}_5)]_3$ along with a listing of the visible absorption bands of this complex has also appeared.¹⁵

Experimental Part

Volatile air-sensitive compounds, particularly derivatives of the fluoro and trifluoromethyl acids, were handled in a conventional vacuum system, greased with Apiezon N stopcock grease. Other systems could be handled in air or in dryboxes with typical bench-top techniques. Syntheses of $(\text{CF}_3)_2\text{PS}_2\text{H}$ ^{1,2} and $\text{F}_2\text{P}-\text{S}_2\text{H}^{3–5}$ have been described elsewhere.¹⁶

Infrared spectra were obtained on Perkin-Elmer 421 and Beckman IR-11 instruments. Ultraviolet and visible spectra were measured with a Cary 14 spectrometer; diffuse reflectance

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TABLE I
ANALYTICAL DATA

	% C		% H		% N		% S		Mol wt		
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found (soln) ^a	Found (mass spec)
Na ₂ S ₂ P(CH ₃) ₂ ·2H ₂ O	13.04	12.76	5.43	5.48
Na ₂ S ₂ P(CH ₃) ₂	16.21	16.03	4.05	4.48	43.20	42.40
NH ₄ S ₂ P(C ₆ H ₅) ₂	53.91	53.99	5.28	5.29	5.25	5.12
Na ₂ S ₂ P(OC ₂ H ₅) ₂	23.07	22.76	4.84	4.50
Cr[S ₂ P(CH ₃) ₂] ₃	16.86	16.76	4.24	4.44	428	415	428
Cr[S ₂ P(C ₆ H ₅) ₂] ₃	54.05	53.56	3.78	3.89	24.05	25.15	799	729	799
Cr[S ₂ P(OC ₂ H ₅) ₂] ₃	23.72	23.64	4.98	5.35	607	584	607
Cr[S ₂ P(CF ₃) ₂] ₃	25.61	26.85	751	...	751
Cr[S ₂ PF ₂] ₃	451	...	451
Zn[(C ₆ H ₅) ₂ PS ₂] ₂	51.11	50.99	3.58	3.71
Zn[(CH ₃) ₂ PS ₂] ₂	15.22	15.47	3.83	3.91

^a Determined in CH₂Br₂ by osmometry.

spectra were obtained with the Cary 1411 diffuse reflectance attachment operating in type II mode. Magnetic susceptibilities were measured by the Faraday technique over a range of temperatures using a cryostat of our own construction. The magnetic field was calibrated with HgCo(SCN)₄ prepared as described.¹⁷ Mass spectra were obtained by means of the direct-probe sample insertion system of the AEI MS9 mass spectrometer operating at 70 eV.

Preparation and Dehydration of Na₂S₂P(CH₃)₂·2H₂O.—The method employed is a variation of the synthesis of ethyl- and propyl-substituted acid salts reported elsewhere.¹³ Approximately equimolar quantities of tetramethyldiphosphine disulfide,¹⁹ sodium sulfide (Na₂S·9H₂O), and sulfur were mixed in a three-neck flask equipped with an N₂ inlet, a stirrer, and a reflux condenser. Dioxane was added (plus 1 ml of water per 100 ml of dioxane) and the mixture was refluxed for 18–24 hr. The resultant solution and slurry were filtered hot. Cooling the clear filtrate yielded crude crystals and recrystallization from wet dioxane (or, better, acetonitrile) gave crystals of Na₂S₂P(CH₃)₂·2H₂O with a melting range of 150–159°. Dehydration in vacuum gave the anhydrous salt Na₂S₂P(CH₃)₂ (mp 210–220°). The weight loss was 0.266 g (9.22 mmol) from 0.830 g of hydrated salt (4.48 mmol) thus confirming the formula Na₂S₂P(CH₃)₂·2H₂O. Yields were generally good (>90%) in all steps unless water is omitted. Analytical results are given in Table I. The anhydrous salt product showed infrared absorptions (Nujol mull) at 1295 (sh), 1290 (s), 1175 (w), 1085 (m), 1070 (m), 955 (sh), 950 (s), 940 (sh), 920 (s), 860 (m), 740 (m, sh), 726 (m), 680 (br), 627 (w, sh), 600 (s), 545 (w, br), 520 (w, br), 497 (m), 385 (sh), 370 (s), 281 (s), 238 (m), and 215 (w) cm⁻¹. No OH bands in the 3600-cm⁻¹ region were observed in the anhydrous salt.

Preparation of (C₆H₅)₂PS₂·NH₄⁺.—Crude commercial²⁰ diphenyldithiophosphinic acid was dissolved in benzene and filtered to remove insoluble materials. Anhydrous gaseous ammonia was then bubbled into the solution whereupon immediate precipitation of the ammonium salt occurred. The product was filtered and used without further recrystallization since the crude product gave good analyses. The salt showed infrared absorptions (Nujol mull) at 3200 (s, br), 1390 (s), 1280 (m), 1179 (w), 1100 (s), 1070 (w), 1028 (m), 1000 (m), 925 (w), 705 (s), 693 (s), 645 (s, br), 614 (s), 562 (s), 525 (w), 493 (m), 483 (m), 448 (m), 245 (w), and 220 (vw) cm⁻¹.

Preparation of (C₂H₅O)₂PS₂Na.—Anhydrous Na₂CO₃ was added to a hot ethanolic solution of commercial²⁰ bis(ethoxy)-dithiophosphinic acid as described elsewhere.^{7b} After evolution of CO₂ had ceased, the solution was filtered, concentrated, and cooled to precipitate the desired salt which was recovered by filtration and washed with ether. The infrared spectrum from 1200 to 400 cm⁻¹ (Nujol mull) shows bands at 1165 (w), 1100 (m), 1030 (s), 950 (m), 910 (s), 780 (m), 725 (s), 680 (s), and 560 (w) cm⁻¹.

Synthesis of Chromium Complexes. (A) In Solution.—Approximately 2 g of CrCl₃·6H₂O in ethanol was added to a solution of 3 g of M⁺S₂PR₂⁻ (R = CH₃, C₆H₅) also in ethanol

(mixed hot). On cooling, deep blue crystals of Cr(S₂PR₂)₃ precipitated. The product was recrystallized from a 2:1 mixture of chloroform-ethanol or 3:1 benzene-ethanol. The Cr[S₂P(OC₂H₅)₂]₃ complex was prepared as described elsewhere.^{7b}

(B) From Anhydrous Acids.—The complexes Cr(S₂PX₂)₃ (X = F, CF₃) were prepared by adding excess acid to anhydrous chromium trichloride or to chromium metal under vacuum. The acid was allowed to react in a sealed container until visual observation indicated extensive reaction had occurred. Removal of the volatile acid and HCl under vacuum left volatile Cr(S₂PX₂)₃ (X = CF₃, F⁹) complexes which were purified by sublimation. The CF₃ complex sublimed at 55° and melted at 137–138°. The Cr[S₂P(CF₃)₂]₃ complex was analyzed by alkaline hydrolysis in 10% NaOH solution which liberates one CF₃ group (as CF₃H) from each (CF₃)₂PS₂⁻ ligand.^{1,2} Anal. Calcd for Cr[S₂P(CF₃)₂]₃: CF₃, 27.6. Found: CF₃ (as CF₃H), 27.2, 27.0.

Synthesis of Zinc Complexes.—Zinc complexes were prepared as above either from zinc chloride and the salt of the ligand in aqueous solution or from the reaction of zinc metal with the F₂PS₂H⁹ or (CF₃)₂PS₂H acids. Alkaline hydrolysis of the Zn-[S₂P(CF₃)₂]₂ complex yielded 26.45% CF₃ (as CF₃H) (calcd 26.45%), assuming, as above, that one CF₃ is liberated (as CF₃H) from each S₂P(CF₃)₂⁻ ligand. The mass spectrum showed a molecular ion at *m/e* 530 (calcd for ZnS₂P₂C₄F₁₂: *m/e* 530).

Results and Discussion

General and Magnetic Properties.—All five Cr(III) complexes are dark blue solids. Both the fluoro and trifluoromethyl derivatives readily sublime under vacuum at moderate to low temperatures. All of the complexes are readily soluble in nonpolar solvents suggesting, with the volatility, that the complexes have monomeric structures which are confirmed by the solution molecular weights (Table I) and the X-ray structural determination²¹ discussed below. All of the complexes show a parent ion in the mass spectrometer corresponding to the monomeric Cr(S₂PX₂)₃ formula. No ions of mass greater than that of the parent were observed. The molar paramagnetic susceptibilities of the complexes and derived parameters are given in Table II (corrected only for the diamagnetic contribution (Table III)). It should be noted that the ligand diamagnetic susceptibilities agree quite well with the values derived solely from Pascal's constants,²² with the exceptions of complexes with X = OC₂H₅ and CH₃. The reasons for this disparity are unknown. The magnetically dilute character of these Cr(III) complexes is not surprising in view of their monomeric structures. It was found that a small negative curvature in the plots of 1/χ_M vs. *T* could be removed by a temperature-

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TABLE II
 MAGNETIC SUSCEPTIBILITIES OF Cr[S₂PX₂]₃ COMPLEXES

CH ₃		C ₂ H ₅		OC ₂ H ₅		F		CF ₃	
Temp, °K	10 ³ χ _M ^{cor} , cgsu	Temp, °K	10 ³ χ _M ^{cor} , cgsu	Temp, °K	10 ³ χ _M ^{cor} , cgsu	Temp, °K	10 ³ χ _M ^{cor} , cgsu	Temp, °K	10 ³ χ _M ^{cor} , cgsu
303.2	6.29	303.2	6.34	303.3	6.16 ^a	303.3	6.35	303.3	6.28
293.3	6.50 ^a	293.3	6.53 ^a	293.3	6.36	293.3	6.56	293.3	6.50
283.2	6.73	283.3	6.77 ^a	283.3	6.59	283.3	6.78	283.3	6.66
273.3	6.96	273.3	6.99	273.3	6.82	273.3	7.02	263.3	7.19 ^a
263.3	7.22	263.2	7.24	263.2	7.09	263.2	7.28	253.1	7.44
253.0	7.50	253.0	7.53	253.0	7.37	253.0	7.57	243.2	7.75
243.1	7.79	242.0	7.87	243.1	7.67	243.1	7.86	233.1	8.07
233.0	8.12 ^a	233.0	8.17	233.0	7.99	233.0	8.20	223.2	8.43 ^a
223.2	8.46	223.2	8.53 ^a	223.2	8.36	223.2	8.65	213.3	8.83
213.4	8.85	213.4	8.92	213.3	8.75	213.3	8.94	203.4	9.22
203.5	9.27	203.4	9.36	203.4	9.18	203.4	9.37	193.2	9.67
193.2	9.74 ^a	193.2	9.85	193.2	9.67	193.1	9.85	183.2	10.17
183.3	10.27	183.2	10.35	183.2	10.20	183.2	10.38	173.2	10.78
173.2	10.85 ^a	173.2	10.95	173.2	10.78	173.2	10.95	163.1	11.42
162.8	11.53	163.1	11.62	163.1	11.45	163.1	11.61	153.4	12.14
153.5	12.24 ^a	153.4	12.36	153.4	12.18	143.2	13.20	143.2	12.95
143.2	13.09	143.2	13.19	143.1	13.06 ^a	133.3	14.18	133.3	13.90
133.4	14.03	133.4	14.18	133.3	14.03	123.3	15.32	123.4	15.06
123.4	15.17	123.3	15.31	123.3	15.19	113.8	16.58	113.6	16.31
113.7	16.40	113.6	16.60	113.6	16.48	103.4	18.22	104.7	17.52
103.3	18.01	103.3	18.22	103.3	18.13	87.7	21.45	92.9	19.64
95.9	19.35	92.9	20.23 ^a	96.0	19.49				

TIP^b × 10⁶, cgsu

Empirical

Calcd^eA^{c,d}B^{c,d}

θ, °K

μ_{eff}, BM

211

153

0.518 (0.542)

2.34 (0.18)

-5 (0)

3.93 (3.84)

158

153

0.517 (0.535)

1.60 (0.09)

-3 (0)

3.93 (3.87)

33

145

0.537 (0.541)

-0.29 (-0.63)

0.5 (1)

3.86 (3.85)

227

145

0.515 (0.539)

1.90 (-0.16)

-4 (0)

3.94 (3.85)

223

153

0.519 (0.543)

2.99 (0.80)

-6 (-1)

3.93 (3.84)

^a These values represent averages of several measurements at the same temperature. ^b Temperature-independent paramagnetic contribution (TIP). ^c The parameters A and B define the straight line 1/χ_M^{cor} = AT + B. The Curie-Weiss law is used in the form χ_M^{cor} = C/(T - θ). ^d Parameters of linear equation after application of the TIP correction are given in parentheses. The empirical TIP correction is used. ^e See text.

TABLE III

DIAMAGNETIC SUSCEPTIBILITY OF ZINC COMPLEXES AND LIGANDS^a

Ligand (L ⁻)	ZnL ₂ complex	Ligand (L ⁻) ^b	Ligand (L ⁻)	ZnL ₂ complex	Ligand (L ⁻) ^b
S ₂ P(CH ₃) ₂ ⁻	127	57	S ₂ PF ₂ ⁻	145	66
S ₂ P(C ₂ H ₅) ₂ ⁻	316	151	S ₂ P(CF ₃) ₂ ⁻	222	104
S ₂ P(OC ₂ H ₅) ₂ ⁻	154	70			

^a At 25°. ^b Ligand susceptibilities were calculated using χ_A[Zn²⁺] = -13.5 × 10⁻⁶ cgsu¹⁸ for the zinc ion.

independent paramagnetic (TIP) correction to the susceptibility. These empirical TIP values can be compared with the values calculated from the expression²³ 8Nβ²/10Dq which are also presented at the bottom of Table II along with the least-squares line parameters derived from the TIP-uncorrected and TIP-corrected (in parentheses) data. Reasons for the difference between calculated and empirically evaluated TIP contributions in the case of Cr[S₂P(OC₂H₅)₂]₃ are unknown. It is interesting to note that the spin-only formula μ_{eff} = g[S(S + 1)]^{1/2}, where g_{av} = 1.9905,²⁴⁻²⁶ gives a value for the magnetic moment in excellent agreement with the TIP-corrected values for all the complexes.

Infrared Spectra.—The infrared spectra, listed in Table IV, show in all cases a strong band near 315 cm⁻¹ which can be assigned to the M-S stretching vi-

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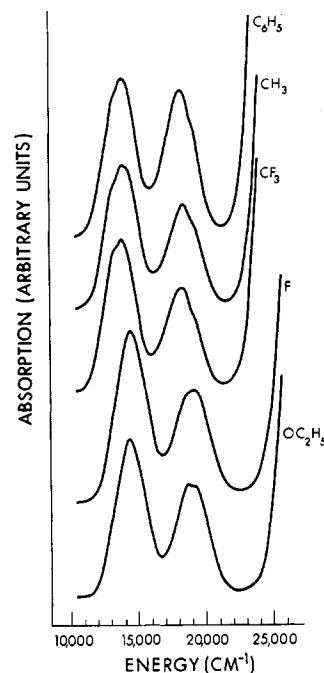


Figure 1.—Visible absorption spectra of Cr(S₂PX₂)₃ complexes in CH₂Cl₂ solution. Absorption scales are similar for all systems but not identical.

bration²⁷ plus other bands appropriate to the ligand structure for which assignments are indicated in Table IV. Attempts to obtain Raman spectra of the complexes from either the crystals or CH₂Cl₂ solutions were

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TABLE IV
 INFRARED SPECTRA OF Cr(S₂PX₂)₃ COMPLEXES^{a, b}

X					Assignment
CH ₃	C ₆ H ₅	OC ₂ H ₅	CF ₃	F	
280 m				194 m	
288 m			240 w		
308 sh	287 sh		286 sh		
313 s	305 s	315 vs	307 s	316 s	ν (M-S)
	317 sh		325 m		
	352 m	358 w		352 } s, d	
		400 w	380 s	358 } s, d	
				405 s	
	448 w		475 s		
505 s	488 s				
585 sh	525 w				
590 s	570 vs	536 m	539 s	559 s	ν (P-S)?
	590 w	550 w			
	610 s				
	638 sh				
	640 s	642 } s, d	618 s		
		658 }	628 sh		
	688 s		683 s		
	708 s			700 s, br	
730 s				720 sh	
740 sh	745 s				
		785 sh			
840 m	850 vw	800 sh			
850 w		812 s			
				855 sh } ν (P-F)	
				895 s }	
				925 sh }	
855 m					
900 s					
905 s	920 vw				
947 s					
950 s		970 s			
	1000 m				
	1030 w				
	1070 w				
	1105 s	1015 s			
	1130 w	1040 sh			
	1160 w	1060 sh			
	1185 w	1105 w			
	1313 m	1160 w			
			1130 sh		
			1150 }		
			1160 } s		ν (CF ₃)
			1175 }		
			1185 sh		
1222 s			1205 s		
1235 w			1295 w		

^a As Nujol mulls between 400 and 1300 cm⁻¹. All values are in cm⁻¹. ^b Abbreviations: ν , stretching; δ , deformation; s, strong; m, medium; w, weak; v, very; d, doublet; sh, shoulder.

unsuccessful due to strong internal absorption in all cases. This result is to be expected in view of the lack of luminescence observed in X = C₆H₅, OC₂H₅ complexes.¹¹ Exciting lines in the near-ir region might be more useful in these systems.

Electronic Spectra.—The spectra for the five complexes of the form Cr(S₂PX₂)₃ (where X = CF₃, F, CH₃, C₆H₅, OC₂H₅) are very similar to one another indicating that the range of ligand substitution encountered here has only a small effect on the MS₆ chromophore. Solution spectra (in CH₂Cl₂) illustrated in Figures 1 and 2 are essentially identical with the diffuse reflectance spectra of the solids for all of the complexes indicating the absence of dramatic structural changes upon dissolution and confirming the monomeric chelate structures suggested by gross physical properties. The electronic spectral band positions obtained on CH₂Cl₂ solutions are given in Table V. The most noticeable feature is that the bands are considerably

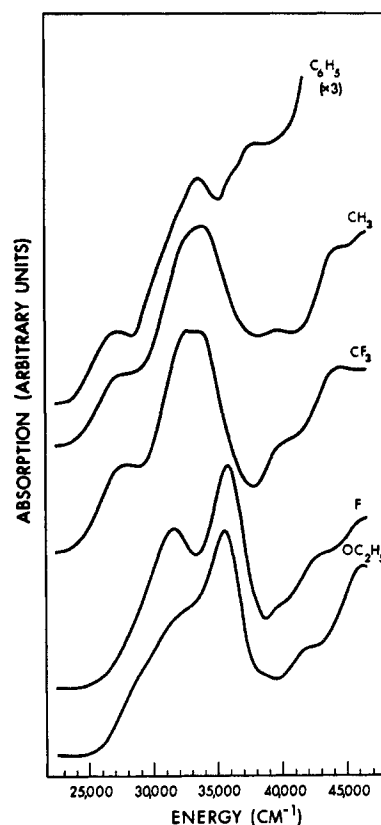


Figure 2.—Ultraviolet absorption spectra of Cr(S₂PX₂)₃ complex in CH₂Cl₂ solution. The absorption scale pertaining to the C₆H₅ derivative has been multiplied by a factor of 3 to improve clarity of presentation. The others are displayed with similar (but not identical) absorption scales.

more intense than is usual for octahedral Cr(III) complexes, and although this and other work^{7a, 8, 28, 29} suggest a high degree of covalency in the bonding of the bidentate chelate PS₂ unit, the enhancement of the electronic spectral intensity of the d-d transitions must also in part be due to the lack of a center of symmetry in the complex.⁷ A complete crystal and molecular structural determination²¹ of the complex Cr[S₂P(CH₂)₂]₃ shows that the molecule has D₃ symmetry with all metal-sulfur bonds essentially equivalent at approximately 2.43 Å and all sulfur-phosphorus distances are likewise equivalent at ~2.00 Å. In addition the S₆ coordination environment is not a regular octahedron but representative of the D₃ symmetry. This structure is very similar to that of V[S₂P(OC₂H₅)₂]₃ reported^{30, 31} while this work was in progress. The complex is therefore more properly regarded as a trigonally distorted octahedron as has been assumed elsewhere.³² A notable feature of the structure²¹ is that the MS₂P ring is not planar but rather is folded about the S-S axis by about 3-10° suggesting that the ligand may be rather flexible. It is appropriate to mention here that although the crystals are dichroic^{7b} and the single crystals which are obtained appear to be composed of only one optical enantiomorph,²¹ attempts to determine the optical activity in solution or to mea-

(28) R. G. Cavell, W. Byers, E. D. Day, and P. M. Watkins, unpublished observations.

(29) J. R. Wasson, personal communication.

(30) C. Furlani, P. Porta, A. Sgamellotti, and A. A. G. Tomlinson, *Chem. Commun.*, 1046 (1969).

(31) C. Furlani, A. A. G. Tomlinson, P. Porta, and A. Sgamellotti, *J. Chem. Soc. A*, 2929 (1970).

(32) C. K. Jørgensen, *Mol. Phys.*, **5**, 485 (1962).

TABLE V
 ELECTRONIC SPECTRA OF $\text{Cr}[\text{S}_2\text{PX}_2]_3$ COMPLEXES^a

	$10^{-3}\nu$ (10 ³), cm^{-1}				
	C_6H_5	CH_3	CF_3	F	OC_2H_5
I	{ 12.5 (34) ^c 13.65 (333) 16.4 (46) ^b	{ 12.61 (48) 13.70 (263) 14.8 (81) ^b	{ 12.6 (15) 13.7 (265) 15.5 (15) ^b	{ 13.0 (17) ^c 14.4 (367)	{ 12.95 (33) ^c 14.38 (404)
II	{ 18.10 (279) 19.24 (32) ^c	{ 18.3 (241) 19.5 (36)	{ 18.1 (229) 19.1 sh ^c	18.95 (293)	18.95 (340)
III	{ 27.04 (10,950) 31.90 (34,100) 33.75 (8169) 37.03 (46,000)	{ 27.4 (9354) 31.2 (8488) ^c 34.1 (32,120)	{ 27.4 (9407) 32.4 (28,280) 34.6 (9559) ^d	{ 31.5 (20,780) 35.8 (20,430)	{ 28.70 (6879) ^c 31.91 (16,310) 35.63 (26,030)
CT and intraligand	{ 40.82 (30,560) ^c 46.7 (255,800) ^b	{ 39.2 (9202) 43.5 (1846) 46.6 (63,160) ^b	{ 39.6 (3102) 44.5 (69,840)	{ 39.7 (7900) 42.5 (1397) 46.6 (37,800) ^c	{ 38.93 (14,610) ^c 41.85 (4620) 46.43 (3250)

^a Oscillator strength (f) given by $f = 4.60 \times 10^{-9} \epsilon_{\text{max}} \nu^{1/2} / \nu_{\text{max}}$. The components which are resolved by gaussian analysis are clearly indicated in the spectrum by a shoulder or pronounced inflection of the curve unless otherwise noted. ^b Component resolved by gaussian analysis only. No inflections are observed. ^c Inflection noted but component not readily resolved. ^d Component extracted is broad and exact position is uncertain.

sure the circular dichroism were unsuccessful probably because the ligand is sufficiently flexible to permit rapid racemization upon dissolution.

On an octahedral model three spin-allowed d-d transitions are expected (Figure 3) but the ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{A}_{2g}$

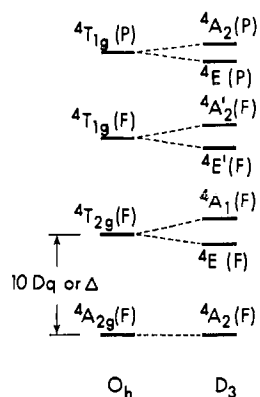


Figure 3.—Sketch of symmetries of one-electron energy levels in O_h and D_3 $\text{Cr}(\text{III})$ systems. The O_h levels are given in the correct order for the dithiophosphate systems but the D_3 levels are uncertain. The primes denote levels of the same symmetry in D_3 which correspond to different levels in O_h .

transition is generally submerged under charge-transfer and intraligand transitions in the near-uv spectra,³³ and this appears to be the case here also although there are indications that ν_3 can be detected in some cases. We can assign with relative certainty bands I and II to the ${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$ octahedral transitions, respectively. The asymmetric appearance of the bands is in keeping with the D_3 symmetry of the complexes which will split the T states into A and E components (Figure 3) so that, instead of three, six transitions are expected. If the actual deviation from O_h symmetry is not large however (as is suggested by the crystal structure determination) the "octahedral" bands may simply be broadened by the distortion and not actually separated. In fact only in a few cases do bands I and II show any sign of splitting which could be ascribed to the reduction in the microsymmetry of the complex although these bands are relatively broad. Other possible sources of asymmetry and/or splitting in these bands such as first-order spin-

(33) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968.

orbit coupling or the appearance of spin-forbidden bands is less likely because of the small spin-orbit coupling constant in $\text{Cr}(\text{III})$ complexes ($\sim 40 \text{ cm}^{-1}$)⁸ and because the spin-forbidden bands are expected to be sharp in $\text{Cr}(\text{III})$ complexes. Gaussian analysis of the spectral bands³⁴ shows that the asymmetric bands can generally be satisfactorily broken down into two components, one of which is usually much more intense than the other.

The smaller component of the ν_1 band could be due to the ${}^2\text{E}_g$, ${}^2\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ spin-forbidden transitions frequently observed in octahedral $\text{Cr}(\text{III})$ spectra,^{11,33,35} however, this does not explain the components which can be similarly extracted from ν_2 . Also, these spin-forbidden transitions are expected to be weak and sharp in contrast to the broad components which are obtained by this procedure. A more likely alternative is to assign the components of ν_1 (${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ in O_h) to the ${}^4\text{A}_1 \leftarrow {}^4\text{A}_2$ and ${}^4\text{E} \leftarrow {}^4\text{A}_2$ transitions in D_3 . Both of these transitions are orbitally allowed and should exhibit polarizations in the z and xy directions, respectively. In the same fashion the components of ν_2 (${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$ in O_h) could be assigned to the ${}^4\text{A}_2(\text{F}) \leftarrow {}^4\text{A}_2$ orbitally forbidden transition (which should be weak if it can be observed at all) and the ${}^4\text{E}(\text{F}) \leftarrow {}^4\text{A}_2$ allowed transition (with xy polarization) in D_3 . The structure of ν_3 should be similar to that of ν_2 since the symmetry of ν_2 and ν_3 (${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{A}_{2g}$ in O_h) transitions is the same. More detailed understanding of the spectra will however require single-crystal polarization and low-temperature spectral studies.^{35a}

Since the distortions from the octahedral structure are relatively small and because there is a lack of supporting detailed spectral data, the spectra have been analyzed in terms of the octahedral model and the octahedral parameters Dq and B' have been extracted in or-

(34) A program BIGAUSS has been developed to analyze spectra obtained on a wavelength base into gaussian or bigaussian components on a linear energy scale. Our FORTRAN program was developed from an ALGOL program supplied by J. P. Fackler, Case Western Reserve University. We thank Dr. Fackler for supplying this program.

(35) L. S. Forster, *Transition Metal Chem.*, **5**, 1 (1969).

(35a) NOTE ADDED IN PROOF.—A recent single-crystal spectral study of $\text{Cr}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_3$ in a matrix of $\text{In}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_3$ [A. A. G. Tomlinson, *J. Chem. Soc. A.*, 1409 (1971)] also suggests that the splitting in ν_1 is due to the presence of two orbitally allowed components in D_3 . The splitting in ν_2 is however attributed, on the basis of point charge calculations, to the near coincidence of the orbitally allowed ${}^4\text{E} \leftarrow {}^4\text{A}_2$ and the spin-forbidden ${}^2\text{E}$, ${}^2\text{A}_1 \leftarrow {}^4\text{A}_2$ transitions, with the high intensity of the latter being attributed to the proximity of these two bands.

der that they may be compared with those obtained elsewhere for similar complexes.⁷⁻¹¹ In general the errors arising from this procedure will be small because it appears that small structural distortions have their greatest effect on the intensities of the electronic transitions rather than upon the energies of the transitions. Using the listed Dq and B' values given in Table VI, the

TABLE VI

OCTAHEDRAL LIGAND FIELD PARAMETERS OF CHROMIUM(III) DITHIOPHOSPHINATE COMPLEXES $\text{Cr}[\text{S}_2\text{PX}_2]_3$

Ligand substituent (X)	Dq , cm^{-1}	B' , cm^{-1}	β_{35}	Ligand substituent (X)	Dq , cm^{-1}	B' , cm^{-1}	β_{35}
C_6H_5	1365	422	0.46	F	1440	432	0.47
CH_3	1370	439	0.48	OC_2H_5	1440	432	0.47
CF_3	1370	416	0.45				

band center of $\nu_3(^4\text{T}_{1g}(\text{P}) \leftarrow ^4\text{A}_{2g})$ is to be expected near $29,000 \text{ cm}^{-1}$ for the $\text{X} = \text{CF}_3$, CH_3 , and C_6H_5 complexes and distinctly higher (near $32,000 \text{ cm}^{-1}$) for $\text{X} = \text{F}$ and OC_2H_5 complexes. All of the complexes except the fluoro and ethoxy complexes exhibit pronounced shoulders near $27,000 \text{ cm}^{-1}$ which can be readily resolved from the underlying intense absorption and it is tempting to assign this band (III) to ν_3 in the $\text{X} = \text{CF}_3$, CH_3 , and C_6H_5 complexes. The intensities quoted are derived from an arbitrary gaussian analysis and are undoubtedly unrealistically large; although ν_3 might be expected to be somewhat more intense than ν_1 or ν_2 because of intensity borrowing.³³ In the spectra of the complexes with $\text{X} = \text{F}$ and OC_2H_5 no pronounced feature is present in the $25,000\text{--}30,000\text{-cm}^{-1}$ portion of the spectrum although in the latter case an inflection on the side of the strong absorption can be transformed into a gaussian component. The arbitrary nature of this procedure however makes it more desirable to assume that ν_3 is not observed in these two complexes but is hidden under the intense charge-transfer absorptions in this region.

The remaining uv bands are almost certainly charge transfer and intraligand in origin particularly in view of the relative simplicity of the spectra of the $\text{X} = \text{F}$ and OC_2H_5 complexes in this region and the complexity of the spectrum of the $\text{X} = \text{C}_6\text{H}_5$ complex. The low-energy absorptions observed for the corresponding ferric complexes³⁶ and the reducing nature of the ligands strongly indicate the direction of charge transfer to be from the ligand to the metal. The general similarity of the major bands occurring in this region further confirms the interpretation that this region of the spectrum of these and similar complexes originates in the MS_6 chromophore.³² Only a qualitative interpretation of this region of the spectrum can be advanced at present.

The Dq values obtained from the visible spectrum, taking the weighted band maximum of band I as $10 \cdot Dq$,^{33,35} can be classified into two groups; the compounds in which carbon is directly bound to phosphorus ($\text{X} = \text{CF}_3$, CH_3 , and C_6H_5) have $Dq \approx 1370 \text{ cm}^{-1}$ while those in which O or F is directly bonded to phosphorus ($\text{X} = \text{F}$, OC_2H_5) have Dq some 70 cm^{-1} higher (1440 cm^{-1}).

(36) E. D. Day, W. Byers, P. M. Watkins, and R. G. Cavell, unpublished results.

While this trend is not large, it does appear to be real as a similar effect is observed³⁷ in the spectra of the vanadium(III) complexes (d^2). The trend in Dq cannot be attributed to inductive effects of the X group since the $(\text{CF}_3)_2\text{PS}_2^-$ complexes should then differ from the $(\text{CH}_3)_2\text{PS}_2^-$ complexes. Rather it is more reasonable to propose that lone pairs on the O or F substituents when directly bound to phosphorus are involved in π back-donation to the "d" orbitals of phosphorus which increases the electron density on sulfur since the sulfur lone pairs will then be less strongly pulled into the PS_2 π system. This increase of electron density on sulfur would be expected to raise both the $\sigma^*(e_g)$ and the $\pi^*(t_{2g})$ levels with respect to the sulfur lone-pair electrons. The shifts of charge-transfer bands to higher energies in F and OC_2H_5 complexes support this interpretation. Also further support is derived from the observation that these two ligands appear to be less reducing than the other three suggesting an increased gap between sulfur and metal orbitals.

The Racah parameter, B' , was obtained by analytical solution of the equation for the d^3 system which relates B' to ν_1 , ν_2 , and $10Dq$ given elsewhere.³³ Weighted band maxima obtained from the values given in Table V were used for the calculation. The nephelauxetic parameter, β_{35} , was obtained by comparing the calculated B' value with the free-ion B value³⁸ of 918 cm^{-1} . The value of B' varies with the substituent X ($\text{CH}_3 > \text{F} \cong \text{OC}_2\text{H}_5 > \text{C}_6\text{H}_5 > \text{CF}_3$) but since the range of values is small ($439\text{--}416 \text{ cm}^{-1}$) and B' may be regarded as essentially equal within experimental error, no significance should be ascribed to the apparent order. The reduction of B' from the free-ion value is however substantial ($\beta_{35} = 0.45\text{--}0.48$) and this has been taken to indicate substantial covalency in the metal-sulfur bonding^{7a,8} which is not unexpected. Other factors can, however, create similar effects³³ and this conclusion is only qualitative.

The "soft" character of the dithiophosphinate ligands and the availability of the sulfur electrons leads to their ability to act as reducing ligands. It is notable however that no evidence for Cr(II) complexes has yet been obtained in this system even in the reaction of chromium metal with $(\text{CF}_3)_2\text{PS}_2\text{H}$ which provides the most favorable case. Preliminary polarographic studies of the $\text{Cr}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_3$ complex show no evidence for any reduction processes at the dropping mercury electrode; however, an oxidation step is observed. Further studies on the chemical behavior of these complexes is warranted as is a study of electronic spectral and magnetic effects of single crystals and diluted crystals in order that the behavior of these interesting dithiophosphinate chelates can be more clearly understood.

Acknowledgment.—We are grateful to the National Research Council of Canada for financial support of this work. We are also indebted to Mr. A. A. Pinkerton for the initial preparation of the $\text{Cr}[\text{S}_2\text{P}(\text{CF}_3)_2]_3$ complex and to Dr. P. M. Watkins for the preparation of $\text{Zn}[\text{S}_2\text{P}(\text{CF}_3)_2]_2$ and analysis of both CF_3 ligand complexes.

(37) R. G. Cavell, E. D. Day, W. Byers, and P. M. Watkins, *Inorg. Chem.*, **10**, 2716 (1971).