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Metal Complexes of Substituted Dithiophosphinic Acids.
II. Complexes of Trivalent Vanadium

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The complexes $V[S_2PX_2]_3$ ($X = CH_3, C_6H_5, OC_2H_5, F, CF_3$) have been prepared as deep brown to orange-red air-sensitive crystals. The decomposition of $V[S_2P(CH_3)_2]_3$ in air is discussed. The magnetic behavior over the range 90–300°K, the solution electronic spectra, and the infrared spectra are described. The solution spectra show the two-electron transition ${}^3A_{2g}(F) \leftarrow {}^2T_{1g}(F)$ suggesting that nonoctahedral symmetry is preserved in solution.

Introduction

As part of a continuing study[1] on the complexes formed from the dithiophosphinic acids F_2PS_2H[2] and $(CF_3)_2PS_2H$[3] we have investigated the complexes of trivalent vanadium with these ligands and with the related substituted dithiophosphinates $X_2PS_2^-$ ($X = C_6H_5, CH_3$, and OC_2H_5). During the course of our studies two reports appeared on $V[S_2PX_2]_3$ complexes in which the substituents were $X = OC_2H_5$[4] and $X = C_6H_5$[5] which are now substantiated and extended by the present work.

Experimental Part

Air- and moisture-sensitive compounds were handled in conventional vacuum apparatus greased with Apiezon N stopcock grease or in a drybox. Mass spectra were measured on an AEI MS9 mass spectrometer operating at 70 eV. Solid samples were introduced by means of the direct-probe sampling device. Infrared spectra were obtained as Nujol mulls using Perkin-Elmer 421 and Beckman IR-11 spectrophotometers. Magnetic measurements were obtained by the Faraday method over the range 90–300°K with $HgCo(SCN)_4$ as a field calibrant[6] using a cryostat of our own construction.[1] Visible and uv spectra were obtained as solution or diffuse reflectance spectra with a Cary 14 spectrophotometer.[1] The electronic spectra obtained were manually digitized and then rescaled and resolved into component gaussian bands as described elsewhere.[1] Thermogravimetric analyses were carried out under rotary oil pump vacuum using the Du Pont Model 950 thermogravimetric analyzer as a module attachment to the Du Pont 900 differential thermal analyzer. All chemicals not specifically prepared were reagent grade. Chlorocarbon solvents were dried by vacuum distillation from P_4O_{10}. The acids HS_2PF_2[2] and $HS_2P(CF_3)_2$[3,7] were prepared by literature methods. The salts $NH_4S_2P(C_6H_5)_2$, $NaS_2P(CH_3)_2 \cdot 2H_2O$, and $NaS_2P(OC_2H_5)_2$ were prepared as described elsewhere.[1]

Preparation of Complexes. $\mathbf{V[S_2P(CH_3)_2]_3}$.—Solvent (~50 ml of absolute ethanol or acetonitrile) was vacuum distilled onto stoichiometric amounts (5:15 mmol) of VCl_3 and $NaS_2P(CH_3)_2$ (anhydrous). After stirring (12 hr in the case of CH_3CN) until all the VCl_3 had dissolved and little $NaS_2P(CH_3)_2$ remained undissolved, the solvent was stripped off and the residual solid extracted with ~50 ml of CCl_4 in a Soxhlet extractor under an atmosphere of dry nitrogen. The resultant deep red-brown CCl_4 solution which contained some flat needle-like crystals of $V[S_2P(CH_3)_2]_3$ was then evaporated to dryness under vacuum to yield impure $V[S_2P(CH_3)_2]_3$ (contaminated with $VO[S_2P(CH_3)_2]_2$). Final purification of $V[S_2P(CH_3)_2]_3$, obtained as deep brown crystals, was achieved by fractional sublimation in a long glass tube mounted vertically with a thermal gradient provided by a copper jacket heated at the bottom in an oil bath. The lack of observable V=O infrared absorption (which is very intense[8]) was a good indication of purity of the product. *Anal.* Calcd for $C_6H_{18}P_3S_6V$: C, 16.9; H, 4.25; S, 45.11; P, 21.79; V, 11.95. Found: C, 16.5; H, 4.05; S, 45.61; P, 21.69; V, 12.13.

$\mathbf{V[S_2P(C_6H_5)_2]_3}$.—$VCl_3$ (1 mmol) was added to a concentrated, filtered aqueous solution of $NH_4S_2P(C_6H_5)_2$ (>3 mmol in 5 ml). The greenish yellow precipitate was washed with freshly boiled water (at room temperature) and dried *in vacuo*. Recrystallization from halocarbon solvents yielded larger crystals which have a dark brown color. The product was characterized by analysis. *Anal.* Calcd for $C_{36}H_{30}S_6P_3V$: C, 54.1; H, 3.8; S, 24.0; P, 11.7. Found: C, 54.0; H, 4.2; S, 20.4; P, 11.7.

$\mathbf{V[S_2P(OC_2H_5)_2]_3}$ was prepared as described above from VCl_3 and $NaS_2P(OC_2H_5)_2$ or as described elsewhere.[4] It was also obtained as a residue in the vacuum distillation of $VO[S_2P(OC_2H_5)_2]_2$.[8] *Anal.* Calcd for $C_{12}H_{30}O_6S_6P_3V$: C, 23.76; H, 4.99. Found: C, 23.68; H, 5.17.

$\mathbf{V[S_2PF_2]_3}$.—Vanadium trichloride and an excess of HS_2PF_2 were refluxed for ~4 hr in a sublimer after which the resultant HCl and excess F_2PS_2H were removed by vacuum distillation. The deep red-brown crystalline product was purified by two successive sublimations at 40° to a cold finger maintained at 10°. The desired complex $V[S_2PF_2]_3$ melted at 45–48° (sealed capillary) and showed a strong parent ion in the mass spectrum which was characterized by mass measurement (*m/e:* calcd for $F_6P_3{}^{32}S_6V$, 499.6884; found, 499.6886). The reaction of V_2O_5 or $VOCl_3$ with HS_2PF_2 under very similar conditions also gave yields of $V[S_2PF_2]_3$ with some $VO[S_2PF_2]_2$ impurity. The two complexes could be separated by careful sublimation.

$\mathbf{V[S_2P(CF_3)_2]_3}$ was prepared from VCl_3 and $HS_2P(CF_3)_2$ in a manner similar to the preparation of $V[S_2PF_2]_3$ described above. The complex melted at 116° (sealed capillary) and showed a strong parent ion in the mass spectrum characterized by mass measurement (*m/e:* calcd for $C_6F_{18}P_3{}^{32}S_6V$, 749.6689; found, 749.6692). *Anal.* Calcd for $C_6F_{18}P_3S_6V$: S, 25.6. Found: S, 25.3.

Results and Discussion

These vanadium(III) complexes are crystalline solids ranging from deep brown ($X = CH_3, C_6H_5$) to orange-red ($X = OC_2H_5$). They were readily obtained from V(III) salts and the appropriate acid or ligand salt under anhydrous conditions. Synthesis of the methyl complex was unaccountably difficult; however, good yields could be obtained from VCl_3 and the sodium salt of $(CH_3)_2PS_2^-$ in alcohol. The methyl complex, even when pure, showed a marked tendency to oxidize to the vanadyl complex which may account in part for our dif-

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(1) Part I: R. G. Cavell, W. Byers, and E. D. Day, *Inorg. Chem.*, **10**, 2710 (1971).

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

(3) (a) R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Amer. Chem. Soc.*, **90**, 2015 (1968); (b) K. Gosling and A. B. Burg, *ibid.*, **90**, 2011 (1968).

(4) (a) C. Furlani, A. A. G. Tomlinson, P. Porta, and A. Sgamellotti, *J. Chem. Soc. A*, 2929 (1970); (b) C. Furlani, P. Porta, A. Sgamellotti, and A. A. G. Tomlinson, *Chem. Commun.*, 1046 (1969).

(5) A. Müller, V. V. K. Rao, and E. Diemann, *Chem. Ber.*, **104**, 461 (1971).

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

(7) The improved method now used for the synthesis of $(CF_3)_2PS_2H$ was described by A. A. Pinkerton and R. G. Cavell, *J. Amer. Chem. Soc.*, **93**, 2384 (1971).

(8) R. G. Cavell, E. D. Day, and P. M. Watkins, in preparation

TABLE I

MAGNETIC SUSCEPTIBILITIES OF VANADIUM(III) COMPLEXES

	$V[S_2P(CH_3)_2]_3$		$V[S_2P(C_6H_5)_2]_3$		$V[S_2P(OC_2H_5)_2]_3$		$V[S_2PF_2]_3$		$V[S_2P(CF_3)_2]_3$	
	Temp, °K	$10^3\chi_M^{cor}$, cgsu	Temp, °K	$10^3\chi_M^{cor}$, cgsu	Temp, °K	$10^3\chi_M^{cor}$, cgsu	Temp, °K	$10^3\chi_M^{cor}$, cgsu	Temp, °K	$10^3\chi_M^{cor}$, cgsu
	312.6	3.190	303.3	3.007	303.3	3.236[a]	303.3	3.186	313.3	3.181
	283.3	3.478	293.3	3.089	293.3	3.328	293.3	3.284	293.3	3.367
	253.0	3.840	283.3	3.169	283.3	3.425	283.3	3.383	273.3	3.581
	203.5	4.659	273.3	3.269	273.3	3.540	273.3	3.486	253.0	3.831
	153.4	6.012	263.2	3.368	263.2	3.657	263.2	3.606	233.0	4.119
	123.3	7.351	253.0	3.502	253.0	3.786	253.0	3.729	213.3	4.457
	89.0	9.950	243.1	3.608	243.2	3.919	243.1	3.873	193.2	4.873
			233.0	3.748	233.0	4.067	233.0	4.016[a]	173.2	5.374
			223.1	3.882	223.2	4.288	223.1	4.185[a]	153.4	6.010
			213.3	4.018	213.4	4.401	213.3	4.336	133.3	6.848
			203.4	4.189	203.4	4.597	203.4	4.526	113.7	7.946
			193.1	4.401	193.2	4.808	193.1	4.729	89.2	9.982
			183.2	4.613	183.2	5.047	183.2	4.960		
			173.1	4.853	173.2	5.315	173.2	5.208		
			163.1	5.102	163.1	5.607	163.0	5.504		
			153.3	5.392	153.4	5.329	153.3	5.810		
			143.2	5.731	143.2	6.234	143.2	6.182		
			133.3	6.092	133.3	6.758	132.1	6.648		
			123.2	6.560	123.2	7.273	123.2	7.079[a]		
			114.3	7.038	107.7	8.266	114.4	7.535		
			103.4	7.713	85.9	10.14	103.7	8.230		
			86.2	9.112			86.0	9.776		
Empirical TIP[b] × 10^6, cgsu	416		535		448		373		454	
A[c]	0.950 (1.142)[c]		1.024 (1.333)		0.962 (1.181)		0.972 (1.142)		0.954 (1.168)	
B[c]	18.82 (3.42)		27.05 (1.27)		20.061 (1.34)		21.708 (8.65)		18.825 (0.78)	
Θ, °K	−20 (−3)		−26 (−1)		−21 (−1)		−22 (−7)		−20 (−1)	
μ_{eff}, BM	2.90 (2.65)		2.79 (2.45)		2.88 (2.60)		2.87 (2.65)		2.90 (2.65)	

[a] These values represent averages of several measurements at the same temperature. [b] Temperature-independent paramagnetism. [c] The parameters A and B define the straight line $1/\chi_M^{cor} = AT + B$. The values in parentheses are the corresponding parameters obtained following the application of TIP corrections shown. The Curie–Weiss law is used in the form $\chi_M = C/(T - \Theta)$.

ficulties in preparation. It was also possible to prepare the $V[S_2PF_2]_3$ and $V[S_2P(CF_3)_2]_3$ complexes along with the analogous vanadyl complexes[8] from the reaction of the acids X_2PS_2H ($X = F, CF_3$) with V_2O_5 or $VOCl_3$ as well as the methods described above. It is now quite apparent that both V(III) and VO^{2+} complexes of the dithiophosphinates can be obtained[4,8] in spite of earlier assertions[4b] to the contrary. In fact many syntheses yield both the V(III) and VO^{2+} complexes, the relative proportions depending on the nature of the ligand substituent X and the reaction conditions employed. By suitable choice of preparative methods and by utilizing fractional sublimation techniques for separating the V(III) and VO^{2+} complexes we have been able to prepare pure samples of both the V(III) and the VO^{2+} complexes. Further details of the vanadyl system will be reported elsewhere.[8]

The stability of the complexes to air oxidation is also dependent upon the particular substituent X. Only the $X = C_6H_5$ complex can be kept intact in air for longer than a few minutes. Exposure of $V[S_2P(CH_3)_2]_3$ to air resulted in the formation of a pale blue solid which was obviously a mixture of compounds. The thermogram of this mixture taken after a sample of the compound had been in contact with the air for 48 hr indicated that the mixture contained $VO[S_2P(CH_3)_2]_2$, $[S_2P(CH_3)_2]_2$, and $[(CH_3)_2PS]_2O$ in the molar ratio 4:1:1, respectively. All of the species were identified in the mass spectrum of the mixture by mass measurement of the parent ions in the mass spectrometer. The weight losses observed in the thermogram were in good agreement with the loss of the metal-free species listed above and the residual weight of solid was in agreement with the vanadyl complex as formulated. The overall reaction stoichiometry can be expressed by the equation

$$4V[S_2P(CH_3)_2]_3 + {}^5/_2O_2 \longrightarrow 4VO[S_2P(CH_3)_2]_2 + [S_2P(CH_3)_2]_2 + [(CH_3)_2PS]_2O + 2S$$

Sulfur loss from the V(III) complex is required to balance the equation. Unfortunately the deficiency of sulfur which amounts to 1/25 or 4% of the original weight of the vanadium complex could not be accounted for in either the mass spectrum or the thermogram. We suggest that elemental sulfur is present in the product because the blue mixture yielded a milky suspension when extracted with chloroform and all of the listed species with the exception of sulfur are soluble in that solvent. It is also possible that air oxidation of the sulfur to SO_2 or hydrolysis to H_2S has occurred during the exposure to the air which would also account for the loss of sulfur but we think this unlikely. The formation of the thiophosphoryl disulfide $[S_2P(CH_3)_2]_2$ is readily explained on the basis of the well-known oxidation of dithiophosphinates $S_2PX_2^-$ to the $[S_2PX_2]_2$ dimers by bromine and other oxidizing agents.[9]

The vanadium(III) dithiophosphinate complexes are readily soluble in chlorocarbon solvents and the solutions are stable for extended periods provided that air (O_2) and moisture are rigorously excluded. Exposure to air resulted in the formation of blue solutions presumably as a result of oxidation to vanadyl species in a fashion similar to that discussed above.

The molar susceptibilities of the complexes (corrected only for ligand diamagnetism[1]) and the derived parameters expressing the temperature behavior of the magnetic susceptibilities are given in Table I. The

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[9] F. Feher and F. Vial, *Z. Anorg. Allg. Chem.*, **335**, 113 (1965); see also D. E. Rogers and G. Nickless, "Inorganic Sulfur Chemistry," G. Nickless, Ed., Elsevier, Amsterdam, 1968.

TABLE II

ELECTRONIC SPECTRAL PARAMETERS (cm^{-1}) OF VANADIUM(III) DITHIOPHOSPHINATES $V[S_2PX_2]_3$[a]

X	ν_1	ν_2	Ligand band	ν_3	Ligand and charge-transfer bands			ν_3(calcd)	*Dq*	*B'*
CH_3	12,180 (4.0)[b]	17,450 (9.4)	22,390 (230)	~27,100 (45)[c]	~33,000			25,290	1297	404
C_6H_5	12,060 (3)	17,210 (10)	22,230 (120)	~25,000 (30)	*d*			24,890	1283	394
CF_3	12,030 (5)	17,270 (10)	22,600 (280)	~26,400 (160)[c]	~33,000			24,840	1281	401
OC_2H_5	12,820 (7)	18,080 (12)	22,700 (260)	~26,400 (260)[c]	33,100 (1000)[c]	36,200 (140)[c]	39,400 (3900)[c]	26,380	1358	404
F	12,900 (8)	17,950 (5)	22,450 (180)	~26,100 (300)[c]	32,300 (450)[c]	35,800 (1000)[c]	40,500 (3400)[c]	26,100	1338	411

[a] d–d transitions are denoted $\nu_1(^3T_{2g}(F) \leftarrow {}^3T_{1g}(F))$, $\nu_2(^3T_{1g}(P) \leftarrow {}^3T_{1g}(F))$, and $\nu_3(^3A_{2g} \leftarrow {}^3T_{1g}(F))$ on the basis of the d^2 octahedral model discussed in the text. [b] Values shown in parentheses are oscillator strengths ($10^5 f$) where $f = 4.6 \times 10^{-9}\epsilon_{\max}\nu_{1/2,\max}$. [c] Oscillator strengths calculated from computer-resolved components hence are not to be considered absolutely reliable. [d] No structure observed on strong charge-transfer tail to 40,000 cm^{-1}.

small regular negative curvature in the $1/\chi_M^{\text{cor}}$ *vs.* T plots could be completely accounted for (with standard deviations of less than 0.1%) by application of a sufficiently large temperature-independent paramagnetic (TIP) contribution to χ_M. The resultant empirical TIP corrections are shown in Table I and the revised equation coefficients and magnetic parameters are also shown enclosed in parentheses. As before,[1] μ_{eff} can be calculated from the equation $\mu_{\text{eff}} = g[S(S+1)]^{1/2}$, and the value of 2.64 calculated for $S = 1$ (d^2) and $g_{\text{av}} = 1.87$ obtained from esr results on V(III)[10] is in good agreement with the value of μ_{eff} derived from the corrected molar susceptibility values (including empirical TIP corrections).

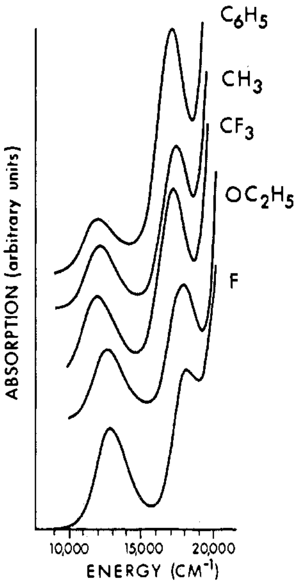

Figure 1.—Visible absorption spectra of $V(S_2PX_2)_3$ complexes in CH_2Cl_2 solution.

Electronic Spectra.—The electronic absorption energies and the derived values of 10*Dq* and *B'* which best fit the spectrum are given in Table II. The ligand field parameters were derived by analytic solution of the equations[11] which relate band maxima to 10*Dq* and *B'* for the octahedral d^2 system. Oscillator strengths, calculated from computer-resolved peaks, are also given in Table II. Oscillator strengths of clearly separated bands are probably quite reliable; however, values derived by computer analysis of the band shapes are suggested values only. The spectra are illustrated in Figures 1–3.

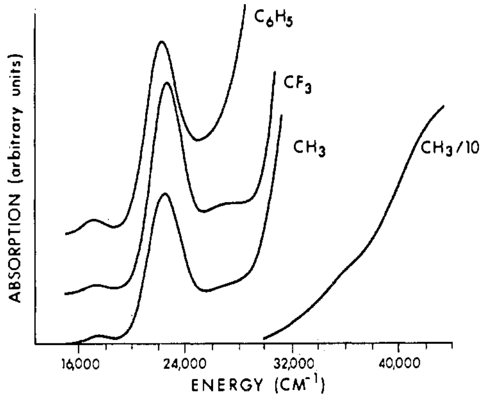

Figure 2.—Ultraviolet (and part of the visible) spectrum of carbon-substituted (X = CH_3, CF_3, and C_6H_5) vanadium(III) dithiophosphinates, $V[S_2PX_2]_3$, in methylene chloride solution.

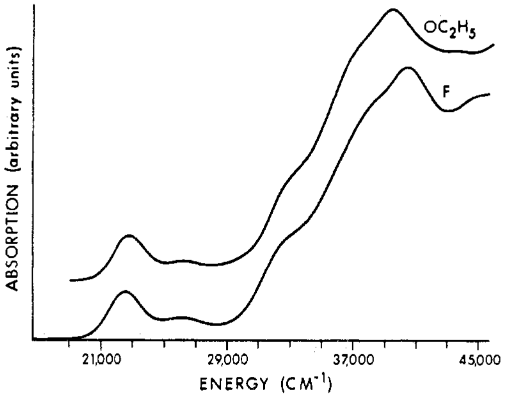

Figure 3.—Ultraviolet (and part of the visible) spectrum of $V[S_2P(OC_2H_5)_2]_3$ and $V[S_2PF_2]_3$ in CH_2Cl_2 solution.

As in the case of Cr(III) complexes[1] the spectra of the V(III) complexes do not show large deviations from octahedral symmetry although crystallographic determinations indicate that true D_3 symmetry prevails.[4] Interpretation is based on the octahedral model in order that comparisons can be made with other systems.

The electronic spectra of these compounds in methylene chloride show the two expected transitions $^3T_{2g}(F) \leftarrow {}^3T_{1g}(F)$ and $^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$ and the uncommonly observed two-electron transition $^3A_{2g}(F) \leftarrow {}^3T_{1g}(F)$ also reported elsewhere[4] for the $V[S_2P(OC_2H_5)_2]_3$ system. The observation of this two-electron transition which is forbidden[11] in O_h symmetry and is generally not observed in solution spectra but has on occasion been observed in solid-state spectra[12] of V(III) complexes appears to be a reliable indication of the

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(10) G. M. Zverev and A. M. Prokhorov, *Sov. Phys.—JETP*, **7**, 707 (1958), and references therein.

(11) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1969.

(12) (a) D. S. McClure, *J. Chem. Phys.*, **36**, 2757 (1962); (b) W. D. Low, *Z. Phys. Chem.* (*Frankfurt am Main*), **11**, 205 (1957); (c) R. Dingle, P. J. McCarthy, and C. J. Ballhausen, *J. Chem. Phys.*, **50**, 1957 (1969).

presence of a nonoctahedral crystalline field.[13] The fact that this two-electron transition is observed in the *solution* spectra of all of these vanadium(III) dithiophosphinate complexes strongly suggests that the nonoctahedral (D_3) symmetry observed in the crystal[4] is preserved in the solution. In the case of $V(urea)_6^{3+}$ and similar systems[12] the trigonal components provided by solid-state effects which lead to appreciable intensity for the ν_3 band were not preserved in the solutions and this band went undetected. Additional contributions to the intensity of ν_3 may arise from intensity borrowing from nearby charge-transfer bands or the high intensities may be artifacts of the gaussian analysis procedure. In the absence of more detailed information it is not possible to exclude the presence of a coincident intraligand band providing significant contributions to the observed intensity of ν_3.

It would appear in general that a small distortion which reduces the microsymmetry of the chromophore from O_h has its greatest effect on the intensities rather than the positions (energies) of the bands. Hence the analysis of the energy levels of these complexes, which presumably have D_3 symmetry in all cases similar to that shown for $V[S_2P(OC_2H_5)_2]_3$, in terms of the octahedral model does not introduce serious errors and permits the comparison of a range of simple systems. The large intensity variations observed in the spectra of these and similar complexes are probably more indicative of the reduced microsymmetry of the complex rather than the *exclusive* result of a substantial increase in the covalency of the metal–sulfur bond.[14] There is however no doubt that covalent contributions play an important role in the overall bonding picture particularly in view of the relatively large nephelauxetic effect demonstrated by the dithiophosphinate complexes (*vide infra*).[14]

The β' and Dq parameters do not exhibit parallel trends as observed before.[1] Within the series of ligands investigated a spectrochemical series with the order $S_2P(CF_3)_2^- \sim S_2P(C_6H_5)_2^- \sim S_2P(CH_3)_2^- < S_2PF_2^- < S_2P(OC_2H_5)_2^-$ can be assigned which is approximately the same as the order of Dq values obtained for the same ligands complexed[1] to Cr^{III}. A clear distinction in ligand field strength can be seen in the ligands with carbon atoms directly bound to phosphorus and those ligands in which O or F atoms are directly bound to phosphorus which, as we have suggested elsewhere,[1] probably arises from π interactions between the p lone-pair orbitals on the substituent and the phosphorus d orbitals. In contrast to the Cr(III) system[1] there appears to be a distinction in ligand field strength of $X = OC_2H_5$ and $X = F$ complexes of V(III), the former exhibiting the larger effect. The measurement errors are sufficiently large, however, to place such a small difference within the limits of uncertainty. The Racah electron repulsion parameter B' varies in the order $S_2P(C_6H_5)^- < S_2P(CF_3)_2^- < S_2P(CH_3)_2^- \sim S_2P(OC_2H_5)_2^- < S_2PF_2^-$ although the range of values (394–404 cm^{-1}) is within the limits of accuracy of determination of this parameter and the variations can hardly be accorded a great significance.

Infrared Spectra.—Ligand vibrations predominate in the infrared spectra of the complexes shown in Table III. The general appearance of the spectra is very similar to that of the Cr^{III} spectra.[1] Bands above 1000 cm^{-1} are mainly due to vibrations within the substituent X, and since we shall be concerned mainly with the MS_2P unit, bands above 1300 cm^{-1} are omitted from the tabulation. Several bands are to be found in the 200–400-cm^{-1} region in which M–S stretches are to be expected,[15] and since it has been suggested[15] that M–S stretches are mainly dependent upon the mass of the metal, the group of strong bands at 280–296 cm^{-1} in the vanadium(III) compounds are probably due to the M–S stretching vibration. Other ligand assignments are indicated in Table III.

TABLE III

INFRARED SPECTRAL BANDS OF VANADIUM(III) DITHIOPHOSPHINATES, $V[S_2PX_2]_3$[a]

X					Assignment
CH_3	C_6H_5	OC_2H_5	F	CF_3	
1286 w[b]		1288 w		1295 w	
1276 m					
				1210 m, sh	
				1194 s, sh	$\nu(CF_3)$
				1180 s	
	1186 w			1165 s	
	1159 w	1161 m		1135 m, sh	
	1131 w				
	1100 s	1106 m			
	1105 s, sh				
	1068 w	~1060 s, sh			
	1027 w	1043 s, sh			
	1000 w	1015 s			
951 s		973 s			
940 s					
			905 s		$\nu(PF)$
909 s					
901 m					
856 w					
852 w, sh					
844 m		819 s			
		803 s, sh			
738 m	745 m	789 s, sh		755 w	
726 s	708 s	727 w	714 s	724 w, sh	
	689 s	663 s	694 s, sh	689 s	
		667 s, sh			
	641 m	642 m, sh			
592 s	612 m			615 s	
585 s	567 s	549 m	558 m	540 s	
505 s	517 w	536 m			
	486 m			477 s	
	448 w	397 w	404 s	383 s	
	358 m	363 m	360 m	326 m	
			352 m		
296 s	280 s	295 s	294 s	285 s	$\nu(M–S)$
280 w, sh				273 s	
267 s					
238 w					
200 w	207 w	212 w		210 w	

[a] In the range 1300–200 cm^{-1} as Nujol mulls. [b] Abbreviations: ν, stretching; s, strong; m, medium; w, weak; sh, shoulder; v, very.

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