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Metal Complexes of Substituted Dithiophosphinic Acids. III. Vanadyl Complexes[1]

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The preparation and characterization of dithiophosphinato complexes of oxovanadium(IV), $OV(S_2PX_2)_2$ (X = CH_3, C_6H_5, CF_3, OC_2H_5, F), are described. Solution and glass epr spectra show hyperfine coupling to ^{31}P and ^{51}V; the former is isotropic at 77°K in the CH_3, C_6H_5, and OC_2H_5 cases. Difficulties were experienced in obtaining glass spectra of X = F and CF_3 complexes and these two systems also show anomalous bulk magnetic susceptibility behavior (over the temperature range 90–303°K) which is thought to arise from interactions between molecules through the formation of VOV chains. Infrared spectra of X = F and CF_3 complexes show a large reversible shift of the VO absorption between solution and solid states which substantiates this interpretation. Electronic spectra are discussed with reference to the current state of knowledge of VO^{2+} spectra.

Introduction

Although the epr spectrum of the complex $OV[S_2P(OC_2H_5)_2]_2$ has been reported several times,[2-6] isolation of the compound was apparently not achieved. The difficulty in isolation has even been taken to imply inherent instability of the complex.[4] We wish to dispel impressions of unusual instability of the complexes in this oxovanadium(IV) system by describing the ready preparation and physical properties of the series of dithiophosphinate complexes $OV[S_2PX_2]_2$, where X = CH_3, C_6H_5, OC_2H_5, F, or CF_3, as part of our continuing investigation of the transition metal complexes of this series of ligands.[1] A preliminary account of this work has been presented.[7] Epr data have also been given for the complexes with the identical ligand substituents X = X′ = C_3H_7 and C_6H_5 and for the complex containing two different substituents on phosphorus: X = C_2H_5 and X′ = OC_2H_5.[5] The preparation and characterization of the X = C_6H_5[8] and X = C_2H_5 and C_3H_7[9] complexes were also reported while this work was in preparation.

Experimental Section

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 were handled in air or nitrogen-filled glove bags with typical bench-top techniques. Syntheses of $HS_2P(CF_3)_2$[10-12] and HS_2PF_2[13-15] have been described elsewhere.

Infrared spectra were obtained on Perkin-Elmer 421 and Beckman IR-11 instruments. Ultraviolet and visible spectra were measured with a Cary 14 spectrometer, and diffuse reflectance spectra were obtained with the Cary 1411 reflectance attachment. Gaussian analyses of spectra were performed using the program BIGAUSS.[16] Epr spectra on both solutions and glasses were obtained on a Varian X-band spectrometer. Numerical data from solution spectra were derived by fitting simulated spectra to observed spectra using the computer program SIMESRLQ.[17] Mass spectra were obtained by means of the direct probe sample insertion system of the AEI MS9 mass spectrometer operating at 70 eV. Variable-temperature magnetic susceptibilities were measured by the Faraday technique using a cryostat of our own construction.[16] The magnetic field was calibrated with $HgCo(SCN)_4$ prepared as described.[18] Analyses (C, H, and S) were performed by the microanalytical service of the University of Alberta and by Schwarzkopf Laboratories, Woodside, N. Y. The CF_3 compound was analyzed by alkaline hydrolysis, each $(CF_3)_2PS_2^-$ unit yielding one unit of CF_3H.[10,16] Final purification of fluoro and CF_3 complexes was effected by fractional sublimation in a vertically mounted long glass tube.[1] Analytical data are given in Table I.

Synthesis of the Complexes. (a) $OV[S_2P(CF_3)_2]_2$. (i) **From Aqueous Solution.**—Bis(trifluoromethyl)dithiophosphinic acid, $(CF_3)_2PS_2H$ (0.402 g), was condensed into a solution of 0.09 g of Na_2CO_3 in 0.5 ml of water contained in an evacuated vessel equipped with a cooled sublimation probe and the solution was stirred for 1 hr. The vessel was opened and vanadyl sulfate, $VOSO_4 \cdot 2H_2O$ (0.172 g), was added to the solution and the entire apparatus was again evacuated. The blue, aqueous solution was stirred a further 30 min, and then the volatile materials were removed under vacuum with the probe cooled to 10°. After most of the water had been removed by this procedure, the vessel was warmed to 60° and a black sublimate was collected on the probe. The ir of a Nujol mull of the black sublimate showed the following bands (cm^{-1}): 3250 (vb), 1610 (m), 1297 (w), 1212 (sh), 1194 (s), 1178 (s), 1163 (s), 1130 (sh), 1012 (m), 973 (w), 863 (m), 771 (w), 726 (mw), 693 (m), 680 (w), 646 (w), 613 (s), 535 (m), 472 (m). This sublimate was transferred in a drybag and resublimed [subl pt 52° (10^{-2} Torr)] to yield about 0.2 g of $VO[S_2P(CF_3)_2]_2$. *Anal.* Calcd[19] for $OVS_4P_2C_4F_{12}$ (*m/e* 532.7555): S, 24.17; CF_3, 26.25. Found (*m/e* 532.7550): S, 25.32; CF_3 (as CF_3H), 26.0.

(ii) **From Vanadium Pentoxide.**—Excess $(CF_3)_2P(S)SH$ was condensed onto V_2O_5 and the acid was refluxed under vacuum for 24 hr in an evacuable vessel equipped with a sublimation probe. With the probe cooled to 10°, the volatile products were then removed under vacuum. Warming the base of the sublimer to 70° caused a brown material to collect on the cooled probe.

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[19] Accurate mass values are calculated for the ^{32}S isotope.

TABLE I

ANALYTICAL DATA FOR $VO[S_2PX_2]_2$ COMPLEXES

Compound	% C		% H		% V		% P		% S		Mol wt		
											By mass spectrometry		By osmometry[c]
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$VO[S_2P(C_6H_5)_2]_2$	50.97	50.94	3.56	3.59	8.9	9.2	10.8	10.8	22.3	23.0	565	565	620[a]
$VO[S_2P(CH_3)_2]_2$	15.14	15.30	3.81	3.68	16.1	16.04	19.56	19.78	40.3	40.67	316.8686	316.8680	335
$VO[S_2P(OC_2H_5)_2]_2$	21.97	21.91	4.61	4.61	11.67	11.30	14.2	14.67	29.3	29.96	437	437	
$VO[S_2P(CF_3)_2]_2$	*b*	*b*	...	...	...	...	...	...	24.17	25.32	532.7555	532.7550	
$VO[S_2PF_2]_2$	...	...	...	...	...	...	...	...	...	...	332.7679	332.7681	

[a] In acetone, mol wt 588. [b] CF_3 (as CF_3H) analysis: calcd for formula given, 26.25; found, 26.0. [c] In CH_2Br_2.

Mass spectra and ir analysis of this product showed it to be a mixture of $VO[S_2P(CF_3)_2]_2$ and $V[S_2P(CF_3)_2]_3$.[1]

(iii) **From $OVCl_3$.**—Vanadium oxytrichloride (0.118 g, 0.68 mmol) and $(CF_3)_2PS_2H$ (0.494 g, 2.11 mmol) were separately condensed into a sublimer at −196° and allowed to warm slowly to room temperature. Reaction occurred at low temperature to form first a red, then a purple, and finally a brown liquid mixture as the vessel warmed. The mixture was allowed to react at 25° for 30 min since an initial experiment showed that immediate removal of the volatile materials upon reaching room temperature gave only a trace of sublimate. Sublimation of the volatile solids (after removal of liquid and gaseous volatile products) to a probe maintained at 10° gave 0.084 g of a brown sublimate shown by mass spectrometry to be about 15% $V[S_2P(CF_3)_2]_3$ and 85% $VO[S_2P(CF_3)_2]_2$. Volatile fractionally distilled products were identified as $[(CF_3)_2PS_2]_2$ (a trace only, collected in a trap at −23°), $(CF_3)_2PS_2H$ (0.062 g, 1.24 mmol) which was recovered at −63°, and HCl (1.7 mmol) collected in a cold trap at −196°. A grayish brown involatile solid remained in the sublimer which showed on ir examination a broad band at 920 cm^{-1} and typical ligand absorptions. After brief aerial exposure this solid showed a typical V=O terminal stretch at approximately 1010 cm^{-1} in the infrared spectrum. Addition of excess of the acid to a sample of the original brown involatile solid which had been protected from air and moisture gave a mixture of $V[S_2P(CF_3)_2]_3$ and $VO[S_2P(CF_3)_2]_2$.

No intermediate containing both vanadium and chlorine has been isolated although such species are extremely likely since the reduction of $VOCl_3$ appears to proceed with stepwise replacement of Cl. The proportion of V^{III} to V^{IV} product increases with contact time of the reactants, and if the reaction was allowed to proceed for a long period of time (*e.g.*, overnight) before separation of the products, the major product was found to be $V[S_2P(CF_3)_2]_2$.[1] Treatment of $VOCl_3$ with excess acid resulted in the removal of all three chlorines as HCl and approximately 2 mol of ligand was consumed per mole of vanadium; however, the yield of vanadyl complex was at best 50% based on vanadium. The observed ligand dimer $[(CF_3)_2PS_2]_2$ is an expected product of dithiophosphinate oxidation;[12,20] however the yield was far less than that expected for complete reduction of all of the vanadium to tetra- and trivalent states as found suggesting that other products must be present in the system.

(b) **$OV(S_2PF_2)_2$.**—Method i above yielded a sticky brown solid, from which no sublimate could be obtained on heating. Use of alcohols as solvents was similarly unsuccessful. Method ii above gave a brown sublimate, found to be a mixture of $V(S_2PF_2)_3$[1] and $VO(S_2PF_2)_2$. Method iii above gave a black sublimate [subl pt <25° (10^{-2} Torr)] containing more than 99% $VO(S_2PF_2)_2$ (*m/e*: calcd,[19] 332.7679; found, 332.9681) and according to mass spectrometry less than 1% $V(S_2PF_2)_3$[1] provided that the reaction was terminated within 30 min of initial achievement of room temperature following mixing of the reagents. Longer reaction times gave greater quantities of V(III) complex.

(c) **$OV[S_2P(CH_3)_2]_2$.**—Powdered $OVSO_4 \cdot 2H_2O$ (5 mmol) was stirred with 10 mmol of $NaS_2P(CH_3)_2 \cdot 2H_2O$ in 25 ml of methanol. After several hours the sulfate had completely dissolved. The solvent was then removed under vacuum and the vanadyl complex was extracted into $CHCl_3$. To avoid oxygen attack on the solution, the $CHCl_3$ was then removed slowly under vacuum, leaving lustrous blue crystals which were washed quickly with cold acetone and then with diethyl ether and finally were dried under vacuum. The complex sublimed at 162° (10^{-2} Torr) without melting.

(d) **$OV[S_2P(C_6H_5)_2]_2$.**—Cold concentrated aqueous solutions of the $OVSO_4 \cdot 2H_2O$ and $NH_4S_2P(C_6H_5)_2$ salts were mixed in the molar proportions of 1:2, resulting in immediate formation of a light blue precipitate, which was well washed with water and cold ethanol. The product was recrystallized from $CHCl_3$. The complex decomposed at 250° (10^{-2} Torr) without melting.

(e) **$OV[S_2P(OC_2H_5)_2]_2$.**—Concentrated aqueous solutions of $OVSO_4 \cdot 2H_2O$ and $NaS_2P(OC_2H_5)_2$ were mixed to give a purple precipitate which was extracted into cyclohexane and recrystallized by removal of solvent *in vacuo*. The blue-purple needlelike crystals melted at 65° (1 atm) and distilled [107° (10^{-2} Torr)] onto a cold finger maintained at 15°, leaving a small residue[1] of $V[S_2P(OC_2H_5)_2]_3$. The vanadyl complex is soluble in most organic solvents, forming solutions which were stable to oxygen attack for several minutes. The solid, however, on exposure to air, rapidly became a black intractable mixture, which was insoluble in nonpolar organic solvents.

Reactions with Oxygen.—When oxygen was bubbled into solutions of the complexes with X = CH_3 and C_6H_5 in organic solvents, the solutions turned green and eventually colorless depositing dark solids (black, green, or brown depending on the solvent used) which gave very low C, H, and S analyses. The dark solids were water soluble, producing blue solutions characteristic of $OV(H_2O)_5^{2+}$ and are thought to be forms of vanadium(IV) oxide. In $CHCl_3$ solution the compound $OV[S_2P(OC_2H_5)_2]_2$ gave an intermediate deep red solution before the decolorization and deposition of the dark solid. Removal of $CHCl_3$ from the red solution before decolorization had occurred left only the starting complex.

Discussion

The vanadyl bis(ethoxydithiophosphinate) complex, $VO[S_2P(OC_2H_5)_2]_2$, can be readily prepared, in contrast to a previous claim to the contrary,[4b] from the reaction of hydrated $VOSO_4$ with $NaS_2P(OC_2H_5)_2$. The difference in results can be explained by the fact that previous workers employed long reflux times (3 hr) with *in situ* preparation of the acid which allows the complete reduction of the vanadyl complex, which we find is first formed in the reaction, to occur. Throughout this series, as discussed more fully below, we have observed that reduction of the higher valence states of the metal occurs fairly readily with these dithiophosphinate ligands. In the specific case of the (ethoxydithiophosphinato)vanadyl complex, we have found that vacuum distillation of the crude $VO[S_2P(OC_2H_5)_2]_2$ product always leaves a residue of $V[S_2P(OC_2H_5)_2]_3$ indicating either that both complexes are present in the initial product or that thermal decomposition has occurred.

All five oxovanadium compounds prepared in the present series are stable solids and can be kept indefinitely under nitrogen or vacuum. The ethoxy, fluoro, and trifluoromethyl complexes are particularly rapidly decomposed by moist air. Their solutions in organic solvents are stable for several days provided that air and moisture are rigorously excluded.

The relative reducing abilities of the trifluoromethyl- and fluorodithiophosphinic acids are demonstrated by

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their reactions with $OVCl_3$ and vanadium pentoxide. In all cases some reaction to V^{III} was observed in addition to the formation of the desired vanadyl complex. Similar behavior has been reported for reactions of maleonitriledithiolate ion with vanadyl salts.[21] In no case did reduction proceed to V^{II}. The difficulties associated with the separation of the two complexes discourage the use of these reactions for synthetic purposes; however the reaction of $OVCl_3$ with F_2PS_2H proved to be the only feasible route to the $OV[S_2PF_2]_2$ complex. Fortunately the less pronounced reducing ability of the fluoro acid combined with careful control of conditions gave this complex with $\geq 99\%$ purity. Under very similar conditions the reaction of $(CF_3)_2PS_2H$ with $OVCl_3$ gave approximately 15% $V[S_2P(CF_3)_2]_3$ impurity in the vanadyl complex, thus demonstrating that the CF_3 acid is a much stronger reducing agent than the F acid.

The reaction of vanadyl sulfate with the $(CF_3)_2PS_2^-$ salt in aqueous solution gave an initial product which appeared to be a hydrate as indicated by the presence of ir bands at 3250 and 1610 cm^{-1} and also by the fact that the product had a normal V=O stretch (1012 cm^{-1}),[22] whereas the final resublimed product shows no coordinated water according to the ir nor does it have any bands around 1000 cm^{-1}. If this final product is exposed briefly to moist air, a strong ir band near 1000 cm^{-1} appears which decreases in intensity if the exposed product is again resublimed, suggesting that a reversible reaction is occurring with water. The X = CF_3 complex is the only one of the series which was obtained in a hydrated form from water; all other complexes which could be obtained from water solutions (X = C_6H_5, CH_3, OC_2H_5) were anydrous on formation. It appears that displacement of water from the coordination sphere does not occur until the complex actually precipitates because when an aqueous solution of $(C_6H_5)_2PS_2^-NH_4^+$ was added to a vanadyl sulfate solution, which presumably contains $OV(H_2O)_5^{2+}$, only the characteristic electronic (visible) spectrum[22,23] of the aquovanadyl ion was observed. This aquovanadyl spectrum persisted in solution even during the final stages of the concentration phase during which anhydrous $OV[S_2P(C_6H_5)_2]_2$ precipitated. All of the complexes precipitated from water as anhydrous products (X = CH_3, C_6H_5, OC_2H_5) cannot readily be redissolved in water; however they are quite soluble in organic solvents. These observations suggest that $OV(H_2O)_5^{2+}$ is the only or at least the dominant species in solution and that the complex forms by the displacement of water from the first coordination sphere. Once the chelate complex is formed, it precipitates and cannot be easily redissolved because the chelate structure resists disruption by water. The X = CF_3 complex may provide an exception to this behavior since it forms initially as a hydrate although this may only provide support for the proposal of stepwise replacement of water by the chelate ligand. In this case we are however unable to distinguish unambiguously between a complex with two chelate substituents and H_2O in the sixth coordination position (which would block VOV polymer formation) and a species in which one of the chelated ligands is replaced by a monodentate $X_2PS_2^-$ ligand and a coordinated water molecule in the usual five-coordinate square-pyramidal structure of the vanadyl system. The X = F complex might provide another example of hydrate formation but the complex cannot be prepared from water.

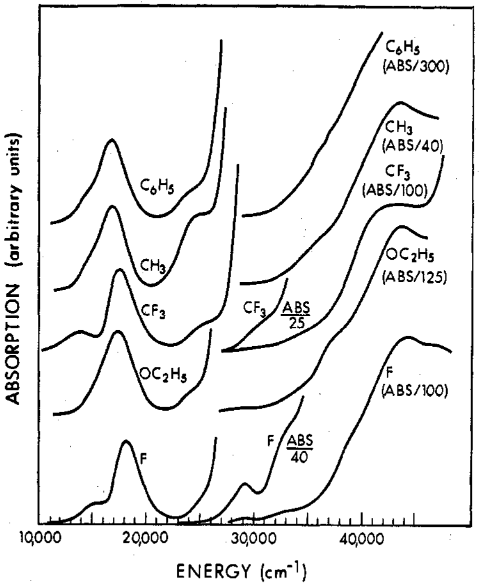

Figure 1.—Visible and ultraviolet absorption spectra of $VO[S_2PX_2]_2$ complexes in CH_2Cl_2 solution. The ultraviolet bands have been reduced by the following factors: C_6H_5 (300), CH_3 (40), CF_3 and F (100), and OC_2H_5 (125). In the intermediate region CF_3 (25) and F (40) are shown with lesser reductions to indicate the absorption present at about 30,000 cm^{-1}. The absorption scales are not identical for each complex but are similar throughout.

The complexes which are blue (X = CH_3, OC_2H_5, C_6H_5) or black (X = CF_3, F) give blue (X = CH_3, OC_2H_5, C_6H_5), mauve (X = F), or purple (X = CF_3) solutions in a variety of organic solvents and these solutions have similar electronic spectra (Figure 1). The infrared spectra of Nujol mulls of $VO(S_2PF_2)_2$ and $VO[S_2P(CF_3)_2]_2$ do not show the characteristic[22] strong ν(V=O) in the region 950–1030 cm^{-1}, which is present in the spectra of the other compounds (Table II), but rather a strong, broad absorption at 860 cm^{-1} (X = F) or 870 cm^{-1} (X = CF_3) is observed, which may be attributed to a VO stretching frequency in a V–O–V–O chain structure.[24] Gradual dilution of the mulls of the CF_3 and F complexes with additional Nujol leads to reduction in the relative intensities of the 860- and 870-cm^{-1} bands and the appearance of a weak but sharp band at 1024 cm^{-1} (in both compounds) as the mull becomes more of a solution in Nujol. Solution ir spectra of both F and CF_3 complexes in carbon disulfide give strong sharp bands at 1024 cm^{-1} and the 860- and 870-cm^{-1} bands are not observed. Diffuse reflectance spectra of the blue compounds (X = CH_3, C_6H_5, OC_2H_5) in the visible region are almost identical with the methylene chloride solution spectra, while the reflectance spectrum of the CF_3 compound (Figure 2) contains little structure and differs considerably from the solution spectrum. We suggest that the dif-

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TABLE II

VIBRATIONAL SPECTRA OF $VO(S_2PX_2)_2$ COMPLEXES[a]

	X = OC_2H_5			X = F		X = CF_3		
X = C_6H_5	Ir (Mull)	Raman	X = CH_3	Mull	CS_2 soln	Mull	CS_2 soln	Assignment
		1535 w	1412 w					
		1450 w	1400 w					
	1386 ms							
1374 ms	1371 ms		1379 s					
1361 sh	1360 m					1300 w	1300 w	
1304 w	1281 mw	1281 w	1282 ms					
1180 w	1152 m						1200 vs	
1158 w		1110 m				1200 br, s	1175 vs	
1100 sh							1140 s	
1095 ms	1095 m, sh							
1060 w								
1020 w	1000 br, s[b]	1000 vs[b]	991 s	1025 w	1024 s	1020 w, br	1023 s	V═O str
998 s	960 s							
			945 s		910 sh			
			911 s	899 vs	899 vs			
			900 mw					
			853 m					
				860 s		870 ms		V—O···V?
	810 s	820 s						
740 m			746 m					
710 ms	720 w		728 s	720 sh			753 w	
701 ms								
687 ms				712 sh	717 s	720 w		
				700 s				
	650 s	660 mw		695 sh		692 ms	698 s	
639 m						682 m		
612 m								
590 w			596 s	600 w		612 s	614 s	
568 s								
515 w	530 s	540 s		560 m	555 ms			
			503 s			538 ms		
484 m	498 w	490 w						
448 w		450 w						
	400 w			406 ms		476 ms		
				377 sh				
361 m	367 s		365 vs	370 m		382 ms		
			358 vs	355 m				
340 m	330 m	340 s	343 s	335 mw				
300 w			297 w	307 w		356 ms		
			290 w	294 w				
			276 mw	283 w		317 w		
			267 mw	260 w		286 m		
230 w			238 mw			277 m		
	200 w					277 m		
			181 w			205 w		

[a] All values refer to infrared absorption energies (in cm^{-1}) determined on Nujol mulls unless otherwise noted. The Raman spectrum was determined on a crystalline sample. Abbreviations: s, strong; m, medium; w, weak; br, broad; sh, shoulder; v, very. [b] Intense ligand absorption bands obscure VO stretch in both solid and solution.

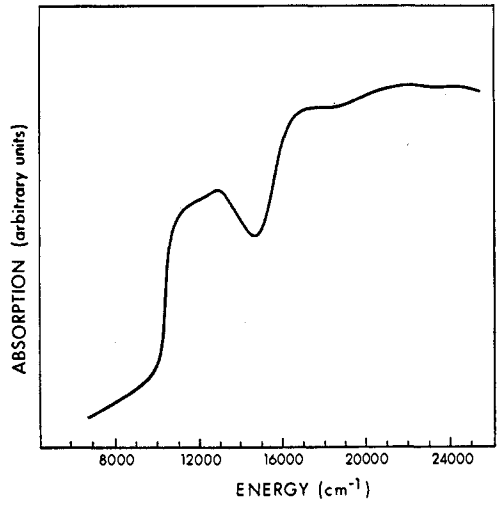

Figure 2.—Diffuse reflectance spectrum of the solid complex $OV[S_2P(CF_3)_2]_2$ obtained with the Cary 1411 reflectance attachment.

ferent properties of the blue and black solids are due to the manner in which the molecules are arranged in the crystal, and this is supported by magnetic results discussed below. The crystal and molecular structure[25] of $OV[S_2P(CH_3)_2]_2$ clearly shows the presence of a typical monomeric square-pyramidal chelate complex of the vanadyl species with no strongly interacting atom in the sixth position nor any strong interaction between the individual molecules in the solid state. The clearly different properties of the F- and CF_3-substituted complexes, especially the loss of the characteristic V═O stretch in the solid state, are strongly suggestive of an interaction between molecules which involves coordination of the V═O perhaps through the formation of V═O···V═O chains in the solid. It is interesting to note also that the $OMo(S_2PF_2)_2$ complex[26] exhibits behavior similar to that of the $OV(S_2PF_2)_2$ and $OV[S_2(CF_3)_2]_2$ complexes in the solid

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TABLE III

MAGNETIC SUSCEPTIBILITIES OF $OV[S_2PX_2]_2$ COMPLEXES

	X									
	CH_3		C_6H_5		OC_2H_5		F		CF_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
	95.0	3.828^a	94.6	3.867	90.1	3.857	113.8	6.342^a	89.9	6.885^a
	103.2	3.518^a	103.4	3.581	103.3	3.360	133.3	5.387^a	113.6	5.448
	113.9	3.204	113.8	3.271	113.6	3.046	153.4	4.654	131.9	4.637
	123.3	2.963^a	123.4	3.012	123.3	2.806	173.2	4.093	153.4	4.012
	133.3	2.740^a	133.3	2.787	133.3	2.592	193.2	3.640	173.1	3.533
	143.2	2.553	143.2	2.609	143.2	2.409	213.3	3.263	193.2	3.149
	153.4	2.387	153.4	2.435	153.4	2.245	233.0	2.959	213.3	2.831
	163.1	2.241	163.1	2.298	163.1	2.113	253.0	2.698	233.0	2.573
	173.2	2.112	173.2	2.156	173.2	1.988	273.3	2.476	253.0	2.349
	183.2	2.001	183.2	2.046	183.2	1.881	293.3	2.287	273.3	2.158
	193.2	1.900	193.2	1.928	193.3	1.783	313.2	2.125	293.3	1.998
	203.4	1.800	204.0	1.838	203.4	1.693			313.2	1.838
	213.3	1.723	213.3	1.758	213.3	1.619				
	223.2	1.643	223.2	1.678	223.2	1.545				
	233.0	1.574	233.0	1.611	233.0	1.476				
	243.1	1.508	243.2	1.556	243.1	1.416				
	253.0	1.445	253.0	1.495	253.0	1.359				
	263.2	1.395	263.2	1.434	263.2	1.311				
	273.3	1.348	273.3	1.375	273.3	1.260				
	283.3	1.301	283.3	1.344	283.3	1.216				
	293.3	1.256	293.3	1.295	293.3	1.175				
	303.3	1.210^a	303.3	1.257	303.3	1.138				
$TIP^b \times 10^6$ (empirical)	6.3		50		21		-330^d		-329^d	
A^c	2.706 (2.723)		2.592 (2.733)		2.911 (2.975)		1.581 (1.294)		1.763 (1.436)	
B^c	4.1 (2.7)		13 (1.6)		−2.1 (−7.6)		−27 (2.4)		−18 (10)	
Θ,^{c} °K	−1.5 (−0.98)		−5.1 (−0.59)		0.7 (2.6)		17 (−1.8)		10 (−7)	
μ_{eff}, BM	1.72 (1.71)		1.76 (1.71)		1.66 (1.64)		2.25 (2.49)		2.13 (2.36)	

[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 Curie–Weiss law is used in the form $\chi_M^{cor} = C/(T - \Theta)$. The parameters in parentheses are those obtained as a result of the application of indicated TIP corrections. [d] The negative TIP corrections in the F and CF_3 cases arise from the reverse curvature of the magnetic plots and are given to illustrate the anomalous magnetic behavior of these systems and the effect of an arbitrary application of the corrections to the magnetic parameters. The physical significance of the negative numbers is not clear and the values should not be regarded as true TIP contributions.

state in that the Mo=O vibration is also greatly shifted to lower wave number values. Clearly, crystal structures of any of these unusual systems would be of great interest.

Magnetic Results.—All of the complexes show nearly linear Curie–Weiss behavior (Table III) with normal magnetic moments except for the X = F and CF_3 complexes which had anomalously high moments (Table III). Without exception, all of the complexes behave normally in solution and have magnetic moments, calculated from the observed g value by the formula $\mu_{eff} = g[S(S + 1)]^{1/2}$, in agreement with the spin-only value of 1.73. The normal solution behavior of the X = F and CF_3 complexes was further confirmed by magnetic susceptibility measurements on the solutions by the Evans (nmr) method[27] yielding $\mu_{eff} = 1.75$ and 1.77 BM, respectively. Solid $VO[S_2P(C_6H_5)_2]_2$ gave a broad-line esr spectrum with $g \approx 1.9$ testifying to the normal magnetic behavior of this system while the $VO[S_2P(CF_3)_2]_2$ complex gave a broad band centered at $g = 2.3$ from which the magnetic moment of the solid is calculated to be ~2.0 BM thus confirming the anomalous value observed by Faraday method measurements. The anomalous magnetic behavior of the X = F and CF_3 complexes is most likely an effect of the interaction in the solid state which has been discussed above and cannot be attributed to decomposition or the presence of impurities for the following reasons. First, Faraday and esr measurements on different samples of the solid complexes gave similar results. Second, solution magnetic measurements performed on samples immediately following the solid-state magnetic measurements quoted in Table III showed normal, spin-only values for μ_{eff}. Third, the anomalously high magnetic moment cannot be attributed to contamination of the sample by V^{III} because the sample would necessarily contain 30–40% V(III) in order to give the observed results, and a visible spectrum of a solution of the *entire* magnetic sample recorded immediately following susceptibility measurements showed no evidence for more than 1–2% of the V(III) complex. The V(III) complex is easily detected above these concentrations by the characteristic intense band[1] at 22,450 cm^{-1} which appears in an absorption minimum of the VO^{2+} system (*vide infra*). A final feature of the magnetic behavior of these complexes which supports the proposal of solid-state magnetic interactions in the X = F and CF_3 systems is the reproducible, inverse dependence of the magnetic susceptibility on the magnetic field strength (higher fields yielded lower susceptibility and hence a lower moment), a result which is not a likely consequence of V^{III} (or V^{II}) contamination. The system is obviously not a simple magnetically dilute $3d^1$ system, but it is difficult to rationalize the observed magnetic behavior since intereacting d^1 systems usually offer low rather than high magnetic moments, as was the case for the vanadyl acetate polymer.[24]

The epr spectral data obtained in solutions at room

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[27] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

TABLE IV

EPR PARAMETERS OF $OV[S_2PX_2]_2$ SYSTEMS[a]

	X							
	C_6H_5	OC_2H_5	OC_2H_5[c]	OC_2H_5[b]	C_3H_7[b]	CH_3	F	CF_3
g_{av}	1.980	1.981	1.980	1.986	1.985	1.975	1.974	1.985
$g_\perp$	1.981	1.987	1.991	1.990	1.984	1.981		
$g_\parallel$	1.960	1.967	1.971	1.970	1.963	1.963		
A_{av}^V, G	94.7	94.5	93.8	94	95	94.8	100.0	100.9
$A_\perp^V$, G	60	57.9	66.7	67	62	56.8		
$A_\parallel^V$, G	169	167.8	161.9	162	167	167		
A_{av}^P, G	33.7	51.3	45.5	49	28	33.7	59.6	33.7
$A_\perp^P$, G	34.2	50.6	51.6	52	28	33		
$A_\parallel^P$, G	34.2	52.6	53.2	52	28	34.7		

[a] A^V refers to hyperfine splitting of vanadium; A^P, that of phosphorus. [b] Reference 3. [c] Reference 6.

temperature and in glasses at 77°K are collected in Table IV, together with published data for comparison. The parameters of all of our complexes, which have been isolated and independently characterized, compare reasonably well with parameters obtained elsewhere[3,6] and assigned to $VO[S_2PR_2]_2$ complexes (without isolation and characterization in many cases). The general features of these vanadyl epr spectra are now well known,[2,6] but certain properties resulting from this investigation are notable. The line widths for the X = CH_3 and CF_3 complexes are exceptionally narrow and ^{31}P nuclear hyperfine splittings are such as to result in good resolution without overlap of triplets as illustrated for the X = CF_3 complex in Figure 3. Line widths are broader for the OC_2H_5 and F derivatives and with the larger ^{31}P splittings result in overlapping triplets which are difficult to resolve by eye. The computer simulation of spectra gives a good fit to all observed spectra[17] and the quoted parameters have been obtained by this method. In all three cases where phosphorus is bonded to carbon the same phosphorus coupling is observed. Wasson has noted a similar consistency for the series of alkoxy derivatives.[6] The ^{31}P hyperfine couplings (A^P) increase in the order C < O < F which is the order of the inductive ability (or electronegativity) of the atoms directly bound to phosphorus. The vanadium hyperfine couplings (A^V) are not amenable to such a simple rationalization since A^V is distinctly larger for the groups X = CF_3 and F as compared to the groups X = OC_2H_5, CH_3, and C_6H_5, each group having the same coupling constant within experimental error. No evidence was obtained for ^{19}F superhyperfine splitting in the room-temperature spectra of either the X = F or CF_3 complexes in spite of careful attempts to resolve it. Anisotropic parameters have not yet been obtained for the fluoro- and trifluoromethyl-substituted complexes for reasons apparently peculiar to these systems, and investigations on these compounds are continuing. The anisotropic vanadium hyperfine couplings of the other compounds follow the trends described above for the averaged coupling constants observed at room temperature. The ^{31}P couplings are essentially isotropic in the glass phase. An interesting discussion of these has recently appeared,[5] which unfortunately makes assumptions about the structure of the complexes which may not be justified. More appropriate molecular orbital descriptions based on the observed molecular structure[25] are being developed[28] to facilitate discussion of the hyperfine couplings. The revised scheme, however, will not likely disagree with the proposal[5] that the unpaired electron resides in a metal-based $d_{x^2-y^2}$ (placing the sulfur atoms between the *xz* and *yz* planes) orbital in the ground state.

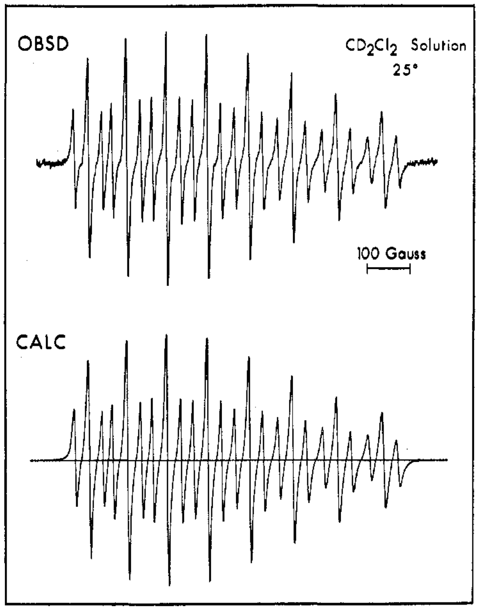

Figure 3.—Observed and calculated epr spectra of $OV(S_2P(CF_3)_2)_2$ in CD_2Cl_2 solution at 25°. The computed parameters were obtained using the program SIMESRLQ[17] and the values from which the illustrated computed spectrum was obtained are given in Table IV.

Electronic Spectra.—Solution spectra of the complexes in methylene chloride (Table V and Figure 1) show the characteristic series of visible bands common to vanadyl systems, designated bands I, II, and III by Selbin,[22] about which there has been recent discussion.[22,29] These bands are in general very clearly distinguishable as separate bands or shoulders as illustrated in Figure 1 except in the X = OC_2H_5 case where band I can only be obtained from the asymmetric peak at 17,500 cm^{-1} by gaussian analysis and for X = F where band III appears as an indistinct shoulder between 24,000 and 25,000 cm^{-1} on the shoulder of the large charge-transfer band. The reflectance spectra of solid $VO[S_2P(OC_2H_5)_2]_2$ and $VO[S_2P(C_6H_5)_2]_2$ are essentially identical with their solution spectra, while that of $VO[S_2P(CF_3)_2]_2$ (Figure 2) is significantly different, as expected, for the reasons discussed above.

On bubbling oxygen into blue solutions of the methyl and phenyl derivatives, the color changed to green and

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(28) R. E. D. McClung, University of Alberta, unpublished results.

(29) (a) G. Vigee and J. Selbin, *J. Inorg. Nucl. Chem.*, **31**, 3187 (1969); (b) B. J. McCormick, *Inorg. Chem.*, **7**, 1965 (1968).

TABLE V

ELECTRONIC SPECTRA OF $VO[S_2PX_2]_2$

	$10^{-3}\nu$, cm^{-1} ($10^4 f$)				
	X				
	CH_3	C_6H_5	OC_2H_5	F	CF_3
I	14.5 (0.4) sh	14.4 (0.7) sh	15.1 (1) sh	15.1 (1) sh	14.0 (1) sh 16.8 (0.2) sh
II	16.86 (4.55)	16.89 (5.92)	17.51 (16.0)	18.21 (5.40)	17.7 (4.60) ~18.8 (~0.2) sh
III	24.4 (3.6) sh	24.2 (2) sh	24.2 (2) sh	24.7 (0.8) sh	25.7 (~2) sh
Ligand bands	30.4 (80) sh	*b*	29.0 (31) sh	29.0 (29) sh	30.4 (20) sh
	34.7 (200) sh		34.3 (200) sh	32.5 (30) sh	35.2 (200) sh
	?		37.2 (800) sh	38.7 (500) sh	?
	43.3 (1000)		43.9 (12,000)	44.1 (3000)	41.2 (~2000) sh

[a] Spectra are recorded in CH_2Cl_2 solution. The numbers given are the positions of resolved band maxima, in units of 1000 cm^{-1}, followed by the oscillator strengths $f \times 10^4$ in parentheses, where $f = 4.60 \times 10^{-9}\epsilon_{max}\Delta\nu_{1/2}$ and sh implies band observed as a shoulder.
[b] Unresolved monotonically increasing absorption upon which are imposed the phenyl group transitions.

a band appeared at 10,000 cm^{-1} in the case of X = C_6H_5 and two bands appeared at 9600 and 11,800 cm^{-1} in the case of X = CH_3. In the light of the above behavior, however, we would concur with the uncertainty expressed concerning the identity of the band ascribed as ν_1 reported[8] for $OV[S_2P(C_6H_5)_2]_2$ since we do not observe this band except in oxygenated solutions. The reversible red coloration which appears upon bubbling oxygen into $CHCl_3$ solutions of $OV[S_2P(OC_2H_5)_2]_2$ may be due to the formation of a complex of molecular oxygen with the vanadyl complex or, perhaps more likely, a peroxovanadium complex. The system is under investigation.

The spectra obtained herein can be satisfactorily assigned in terms of the Ballhausen and Gray model;[23] however this does not, as has been pointed out by others,[2,22] confirm the validity of that scheme. The model of VanQuickenborne and McGlynn[30] seems to be more suitable for the present system since the symmetry (C_{2v}) and geometry used therein more closely approximate those which have been established by the crystal structure analysis of $OV[S_2P(CH_3)_2]_2$[25] which has C_{2v} molecular symmetry with an angle between OV and the SVS bisector of 105°. For qualitative purposes either scheme is satisfactory. Although it is likely, as Selbin has noted,[29a] that the substitution of sulfur atoms for oxygen in the ligands may drastically alter the energy levels, we note that the electronic spectra of the dithiophosphinates are remarkably similar to those of the acetylacetonate complexes[22] rather than other OVS_4 chromophores.[21,29] In view of the limited scope of the spectral data presented here and the fact that epr parameters do not distinguish between the spectral assignments[22b] we propose to defer specific assignments until more information becomes available.

It is interesting to note that if the band II maximum is assigned to 10*Dq* as indicated elsewhere,[23] then the spectrochemical series formed by these ligands arranged in order of the substituent X is $CF_3 < CH_3 \sim C_6H_5 < OC_2H_5 < F$. This is an ordering similar to that found for other complexes of these ligands[1,16,31,32] except for the unexpected difference between the CF_3- and CH_3-substituted ligands.

We note that the decomposition of $V[S_2P(OC_2H_5)_2]_3$ in toluene solution recently claimed[4] to give $OV[S_2P(OC_2H_5)_2]_2$ gives a visible spectrum[4] unlike that of the authentic compound. We have kept the V(III) compound[1] in solution in dry, oxygen-free solvents for more than 2 days without noticeable change in the electronic spectrum, although a weak epr spectrum typical of $OV[S_2P(OC_2H_5)_2]_2$ developed with time suggesting that the major reaction which occurs involves the V(III) complex and either water or oxygen in the toluene.

Electronic spectra and epr studies of the vanadyl complexes in solution which are presently in progress suggest that ligand displacement (disruption of the chelate structure) may be an important process in the interaction of O and N donors with the vanadyl complexes.[28,31] Such processes may account in part for the observed changes in the spectrum of $[(C_2H_5)_2PS_2]_2VO$ in various donor solvents.[10]

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