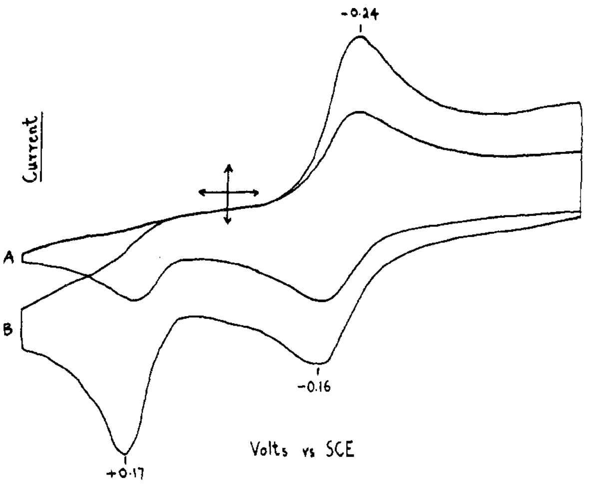

Figure 4. Cyclic voltammogram of $Mo(CO)_2(dppe)_2$ in DMF (10^{-3} *F*) at a Pt electrode with tetraethylammonium perchlorate (10^{-1} *F*) as supporting electrolyte; scan rates of 5.0 Hz (curve A) and 20.0 Hz (curve B).

THF solution of *trans*-$Mo(N_2)_2(PPh_2Me)_4$ (30 min) to produce an oil which could not be crystallized. The infrared spectrum showed four bands in the carbonyl region at 2032 (m), 1950 (s), 1903 (vs), and 1850 (m) cm^{-1} (hexane solution). In order to gain an insight into the nature of the carbonyl-containing species in the oil the previously unknown *cis*-$Mo(CO)_4(PPh_2Me)_2$ was prepared from $Mo(CO)_6$ and PPh_2Me. The infrared spectrum in hexane solution exhibited bands due to $\nu(CO)$ at 2028 (m), 1931 (m), and 1906 (vs) cm^{-1}. A mixture of *cis*-$Mo(CO)_4(PPh_2Me)_2$ and *mer*-$Mo(CO)_3(PPh_3Me)_3$ appears to constitute the carbonyl-containing part of the oil formed at ambient temperature. In a separate experiment carbon monoxide was bubbled through a THF solution of a pure sample of *mer*-$Mo(CO)_3(PPh_2Me)_3$ for 1 hr. The product was identified as *cis*-$Mo(CO)_4(PPh_2Me)_2$, by infrared spectroscopy.

Carbon monoxide did not react with *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ at −78° in THF. However, at ambient temperature *fac*-$Mo(CO)_3(PMe_2Ph)_3$ was formed slowly after several hours. This isomer was identified by infrared spectroscopy.[14] No evidence for further substitution was observed when the reaction was allowed to continue for 24 hr at ambient temperature.

In no case did dinitrogen appear to react with the carbonyl complexes of molybdenum.

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Registry No. $[Mo(N_2)_2(dppe)_2]I_3$, 38887-40-0; $[Mo(N_2)_2(arphos)_2]I_3$, 41375-70-6; *cis*-$Mo(CO)_2(arphos)_2$, 41367-49-1; *fac*-$Mo(CO)_3(PPh_2Me)_3$, 41367-50-4; *mer*-$Mo(CO)_3(PPh_2Me)_3$, 41367-51-5; *cis*-$Mo(CO)_4(PPh_2Me)_2$, 37438-49-6; $Mo(N_2)_2(dppe)_2$, 25145-64-6; $Mo(N_2)_2(arphos)_2$, 37138-36-6; *cis*-$Mo(CO)_2(dppe)_2$, 17523-42-1; $Mo(N_2)_2(PPh_2Me)_4$, 33248-03-2; $MoCl_4(PPh_2Me)_2$, 30411-57-5; phosphorus-31; 7723-14-0; iodine, 7553-56-2.

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Electron Spin Resonance Study of Coordination of Lewis Bases to Vanadyl Dithiophosphinate Complexes

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The results of an esr study of the five-coordinate vanadyl complexes, bis(dimethyldithiophosphinato)oxovanadium(IV), bis(diphenyldithiophosphinato)oxovanadium(IV), and bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV), in the noncoordinating solvents toluene and CS_2 are presented. The esr spectra correspond to the interaction of the unpaired electron with the ^{51}V nucleus and two equivalent ^{31}P nuclei. Addition of 1–5% by volume of the strongly coordinating ligands pyridine, dimethylformamide, or hexamethylphosphoramide results in esr spectra indicative of hyperfine interactions with the ^{51}V nucleus and a single ^{31}P nucleus. It is shown that, in this vanadyl species, the added ligand coordinates at an equatorial site, resulting in a five-coordinate species in which one of the dithiophosphinate groups is monodentate and a six-coordinate species in which one of the chelating dithiophosphinates is rearranged so that one sulfur atom occupies an equatorial position and the other the axial position. The equilibrium constants and heats of adduct formation for the equatorial ligand addition were determined from the esr spectra. At higher ligand concentrations, the esr spectra show no ^{31}P hyperfine interactions which indicate that both chelating dithiophosphinate groups become monodentate. Infrared and conductivity measurements indicated that the vanadyl dithiophosphinate dissociates completely in solutions with still higher ligand concentrations but that several vanadyl species containing one or two dithiophosphinate moieties coordinated to the vanadium atom are present in these solutions.

Introduction

Four- and five-coordinate compounds of vanadium(IV) are known to undergo substitution at vacant coordination sites.[1-5] The formation of adducts of vanadyl complexes with many Lewis bases in dilute solutions in noncoordinating solvents has been studied by electronic,[5-10] vibrational,[11-13] and

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electron spin resonance[8-10,14,15] (esr) spectroscopies. Adduct formation is usually accompanied by a shift in some of the electronic transitions to lower energies,[7-10] a decrease in the V-O stretching frequency in the infrared spectrum,[11-13] and a change in the ^{51}V nuclear-electronic hyperfine splitting in the esr spectrum.[8-10,14,15]

The esr studies of vanadyl complexes have been concerned mainly with acetylacetonates,[9,10,14,16] monothioacetylacetonates,[8] oxalates,[17] and dithiocarbamates.[15] In these molecules, there are no nuclei, other than the ^{51}V nucleus, which show observable hyperfine interactions with the unpaired electron which is essentially localized on the vanadium atom. The solvent dependence of the g tensor and the vanadium hyperfine interaction tensor has been studied,[9,10,14] but the results give very little direct information about coordination at the vacant site because the interpretation of the esr parameters requires an assignment of the electronic absorptions observed in the visible spectrum. This assignment of electronic transitions has been the subject of a long debate in the literature,[18,19] and no unequivocal assignment of the transitions has been given. It has also been suggested[10] that, in addition to coordination at the sixth position, solvent molecules may hydrogen bond to the vanadyl oxygen, so that interpretation of the esr data in terms of coordination at the sixth position is a difficult task. We have studied the formation of adducts of some substituted vanadyl dithiophosphinate complexes with strongly coordinating ligands. In these complexes, the presence of two ^{31}P nuclei, which can give rise to observable hyperfine interactions with the unpaired electron, gives additional information about the bonding in these complexes.

X-Ray studies[4] of the vanadyl acetylacetonate adduct with dioxane indicate that the sixth coordination site, trans to the vanadyl oxygen, is occupied by a dioxane oxygen atom. Infrared studies[13] of the V-O stretching frequency in adducts formed from vanadyl acetylacetonate with substituted pyridines suggest the existence of two geometrical isomers: a trans isomer where the pyridine nitrogen atom coordinates on the side of the vanadium atom opposite to the vanadyl oxygen and a cis isomer in which one of the pentanedione groups has rearranged so that the pyridine nitrogen occupies a position cis to the vanadyl oxygen. No esr evidence for this geometrical isomerism has been presented, although it has been reported[14] that the esr spectrum of vanadyl acetylacetonate, $VO(AcAc)_2$, in solutions containing hexamethylphosphoramide (HMP) indicates the presence of two different species.

The enthalpies of adduct formation for vanadyl acetylacetonate, $VO(AcAc)_2$, with several strongly coordinating ligands have been measured calorimetrically,[2,5] and the equilibrium constants have been determined spectrophotometrically.[5] The rates of ligand exchange in some of these vanadyl acetylacetonate adducts were rapid enough that they could be studied by esr.[14] We have found that the ligand exchange rates in the substituted vanadyl dithiophosphinate adducts with HMP, dimethylformamide (DMF), and pyridine are much slower, and we have determined the equilibrium constants and enthalpies of adduct formation from our esr measurements.

Experimental Section

The three substituted vanadyl dithiophosphinate complexes, bis(dimethyldithiophosphinato)oxovanadium(IV), bis(diphenyldithiophosphinato)oxovanadium(IV), and bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV), henceforth to be referred to as methyl, phenyl, and ethoxy complexes respectively, were prepared by treating vanadyl sulfate with the sodium salt of the corresponding dithiophosphinic or dithiophosphoric acid.[20] The methyl and phenyl complexes could be stored under nitrogen without decomposition, but the ethoxy complex was less stable and was prepared as a chloroform solution immediately prior to use. The chloroform was then removed under vacuum.

All liquids used were purified by vacuum distillation. Reagent grade toluene was distilled from a sodium mirror and stored under vacuum over molecular sieves. Analytical grade carbon disulfide was distilled from molecular sieves and stored over the same. The coordinating ligands, HMP, DMF, and pyridine, were distilled from P_2O_5 and stored over molecular sieves.

Solutions of the vanadyl complexes were prepared under vacuum by distilling a calibrated volume of solvent (toluene or CS_2) into a bulb containing a weighed amount of the vanadyl compound. Required amounts of coordinating ligand were either distilled in (DMF and pyridine) or added with a syringe in a glove bag under nitrogen (HMP). The solution was then thoroughly degassed by several freeze-pump-thaw cycles and transferred under vacuum to an attached 1-cm quartz spectrophotometer cell for optical measurements and/or a 4-mm Pyrex tube suitable for esr measurements. The samples containing the phenyl complex were stable under all conditions employed in the experiments, but solutions of the methyl and ethoxy complexes turned dark green or black, indicating decomposition, when kept above 100° for prolonged periods. The ligand concentration in the solutions was measured most conveniently as per cent composition by volume. Toluene solutions of the complexes containing pyridine consistently showed black deposits in the sample tube when prepared at room temperature. At lower temperatures, no decomposition was observed, but the esr lines were so broad at these temperatures that the hyperfine splitting details of the spectra were not resolved. In order to study the pyridine-vanadyl dithiophosphinate complexes, CS_2 was used as a solvent. The much lower viscosity of CS_2 produced spectra showing well-resolved hyperfine structures over the temperature range -45 to $+45°$. The disadvantage of using CS_2 as a solvent is that the complexes do not remain in solution as the frozen state is approached and glass spectra could not be obtained.

The esr spectra were obtained with a Varian V-4502 epr spectrometer equipped with an Alpha Model 3093 digital nmr gaussmeter for magnetic field calibration. g values were measured relative to Fremy's salt ($g = 2.00550$)[21] using a Varian V-4532 dual cavity accessory. The sample was maintained at constant temperature (±1°) with a Varian V-4557 temperature controller and the temperature was measured with a copper-constantan thermocouple. Visible and near-infrared spectra were recorded on a Cary 14 spectrophotometer, and infrared spectra were recorded with a Beckman IR 11 spectrophotometer using CsBr cells.

Results

The esr spectra of 10^{-3} M solutions of the three vanadyl complexes in toluene at 30° are shown in Figure 1 and are similar to those reported previously by other workers.[20,22-24]

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These liquid solution spectra consist of eight lines due to the interaction of the unpaired electron with the ^{51}V nuclear spin ($I = {}^7/_2$); each of these eight lines is further split into a 1:2:1 triplet of lines by the interaction of the electron with two equivalent ^{31}P nuclei ($I = {}^1/_2$). Some of the 24 possible lines are not resolved in the spectra of the ethoxy complex because the phosphorus hyperfine splitting is approximately half as large as the vanadium splitting so that there is considerable overlapping of lines. It is apparent from the variation in the intensities of the lines that the line widths of the different hyperfine components are not equal and depend on the ^{51}V nuclear spin quantum number. This line width variation indicates that the anisotropic hyperfine and Zeeman interactions are not completely averaged out by the tumbling of the moleucles in the liquid, and they contribute significantly to the line widths.[25] The large difference in the line widths in the methyl and phenyl complexes in toluene can be attributed to the difference in their molecular dimensions which directly influences the rate of tumbling in the liquid.

The esr spectra of the vanadyl dithiophosphinate complexes in liquid solutions can be described by the isotropic Zeeman and nuclear-electronic hyperfine interactions included in the spin Hamiltonian

$$\mathcal{H} = g_0\beta(BS_z + a^{V}\mathbf{I}_{V}\cdot\mathbf{S} + a^{P1}\mathbf{I}_{P1}\cdot\mathbf{S} + a^{P2}\mathbf{I}_{P2}\cdot\mathbf{S}) \qquad (1)$$

where β is the Bohr magneton, B is the magnetic flux, g_0 is the isotropic g value, and a^V, a^{P1}, and a^{P2} are the isotropic nuclear-electronic hyperfine splittings (in gauss) of the ^{51}V and the two ^{31}P nuclei, respectively. $\mathbf{S}$, $\mathbf{I}_V$, $\mathbf{I}_{P1}$, and $\mathbf{I}_{P2}$ are, respectively, the spin angular momentum operators for the electron, ^{51}V nucleus, and the two ^{31}P nuclei. The allowed transitions, when a microwave field at frequency ω_0 is applied, occur at the fields B which satisfy the resonance condition

$$\frac{\hbar\omega_0}{g_0\beta} = B + a^{V}M_{V} + \frac{(a^{V})^2[I(I+1) - M_{V}^2]}{2B} + a^{P1}M_{P1} + a^{P2}M_{P2} \qquad (2)$$

where M_V, M_{P1}, and M_{P2} are the nuclear spin quantum numbers of the ^{51}V and two ^{31}P nuclei and $\hbar$ is Planck's constant divided by 2π. In eq 2, the vanadium hyperfine interaction is treated up to second order since these effects are observed in the spectra. The contributions to the positions of the resonance lines from second-order terms in a^{P1} and a^{P2} are much smaller and are neglected.

In the solutions without added ligand, the two phosphorus nuclei give equal hyperfine splittings a^P. Since the overlapping of lines and the variation of the line widths of the hyperfine components prevent the direct determination of the hyperfine splittings a^V and a^P from the spectrum in many cases, the observed spectra were compared with those synthesized by a digital computer.[26] The hyperfine splittings and the line widths used in the computer synthesis were adjusted until the agreement between the observed and calculated spectra was satisfactory. In the computer calculations, each line in the stick spectrum was assumed to have a Lorentzian shape with a characteristic width. The relative widths of the various lines in the spectrum were estimated from the peak-to-peak intensities of the lines as Wilson and Kivelson[25] have done for VO(AcAc)$_2$. Measurement of the width of one of the outermost lines, which are not greatly affected by overlap, gave an absolute width from which estimates of the absolute widths of the various hyperfine lines were obtained. When overlap was serious, some adjustments to the line widths were made when comparison of calculated and observed spectra indicated that such adjustment was required. The calculated spectra which agreed best with the observed ones are included in Figure 1.

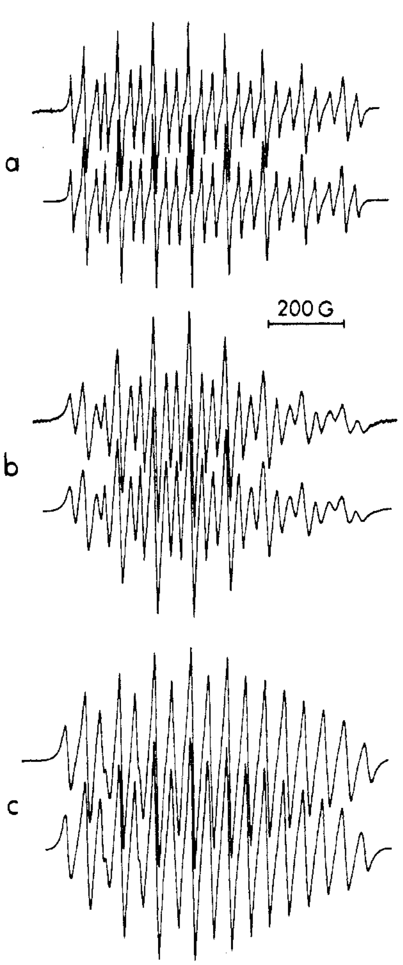

Figure 1. Esr spectra of 10^{-3} *M* liquid solutions of the vanadyl dithiophosphinate complexes in toluene at 30°: (a) bis(dimethyldithiophosphinato)oxovanadium(IV); (b) bis(diphenyldithiophosphinato)oxovanadium(IV); (c) bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV). The experimental spectra are shown above the computer simulations in each case.

The values of the magnetic parameters g_0, a^V, and a^P for the CS$_2$ and toluene solutions of the three complexes are given in Table I. The temperature dependence of these parameters is similar to that observed[25] for VO(AcAc)$_2$ and indicates that the molecular structure does not change with temperature.

The esr spectrum of the phenyl complex in toluene at −150° is shown in Figure 2a. This spectrum can be described in terms of the Zeeman and nuclear-electronic hyperfine interactions of axial symmetry included in the spin Hamiltonian

$$\mathcal{H} = g_{\parallel}\beta B\cos\theta\, S_z + g_{\perp}\beta\sin\theta\, S_x + g_{\parallel}\beta A_{\parallel}^{V}S_zI_z^{V} + g_{\perp}\beta A_{\perp}^{V}(S_xI_x^{V} + S_yI_y^{V}) + g\beta a^{P1}(\mathbf{I}^{P1}\cdot\mathbf{S}) + g\beta a^{P2}(\mathbf{I}^{P2}\cdot\mathbf{S}) \qquad (3)$$

where $g_{\parallel}$ and $g_{\perp}$ are, respectively, the g values parallel to and

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Table I. Isotropic Magnetic Parameters[a] for Vanadyl Dithiophosphinates in CS_2 and Toluene Solutions

Substituent of dithiophosphinate	CS_2 at −30°			CS_2 at 30°			Toluene at 30°			Toluene at 116°		
	g_0	a^V	a^P	g_0	a^V	a^P	g_0	a^V	a^P	g_0	a^V	a^P
Methyl	1.9777	94.8	34.0	1.9766	95.4	33.4	1.9773	94.8	32.8	1.9728	95.7	32.4
Phenyl	1.9787	95.0	34.2	1.9781	95.5	33.3	1.9784	95.5	33.0	1.9765	95.9	32.6
Ethoxy	1.9819	94.8	50.7	1.9811	95.2	50.2	1.9814	95.0	49.7	1.9798	95.6	49.2

[a] Hyperfine splittings are in gauss. Estimated errors are ±0.3 G for hyperfine splittings and ±0.0003 for g values.

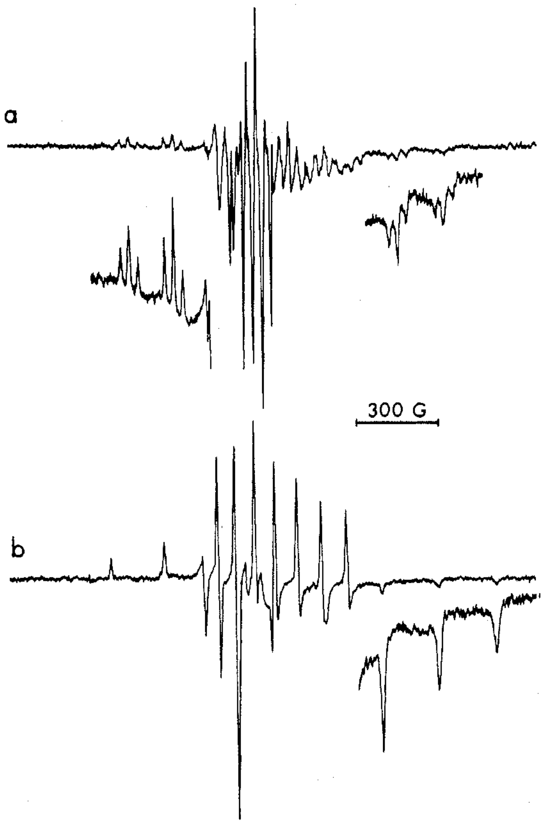

Figure 2. Esr spectra of 10^{-3} M solid solutions of bis(diphenyldithiophosphinato)oxovanadium(IV) at −150° in (a) toluene and (b) 5% HMP-toluene.

perpendicular to the axis of symmetry, θ is the angle between the symmetry axis and the laboratory z axis, and $A_\parallel^V$ and $A_\perp^V$ are the components of the ^{51}V hyperfine interaction tensor (in gauss) along the parallel and perpendicular directions. The esr spectrum is governed by the resonance condition

$$\frac{\hbar\omega_0}{g\beta} = B + A^V M_V + \frac{A_\perp^{V2}(A_\parallel^{V2} + A^{V2})[I(I+1) - M_V^2]}{4A^{V2}B} + a^{P1}M_{P1} + a^{P2}M_{P2} \qquad (4)$$

where

$$g^2 = g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta \qquad (5)$$

and

$$g^2A^{V2} = g_\parallel^2 A_\parallel^{V2} \cos^2\theta + g_\perp^2 A_\perp^{V2} \sin^2\theta \qquad (6)$$

$\theta = 0$ for the parallel resonances and $\theta = \pi/2$ for the perpendicular resonances. In eq 3 and 4, only the isotropic phosphorus hyperfine interactions have been included since the spectra showed no evidence for anisotropy in these interactions.[20,22,23] Some of the previous esr work[24] suggested that the ^{31}P hyperfine interaction was anisotropic, but the isotropic phosphorus splittings observed in liquid solution did not agree well with those predicted from the anisotropic splittings.

The axially symmetric spin Hamiltonian (eq 3) was used to interpret our spectra, rather than a spin Hamiltonian of orthorhombic symmetry, because the small differences to be expected in the two perpendicular directions were not resolved in the spectra. Since there is considerable overlapping of lines in the perpendicular part of the glass spectra of some of these vanadyl complexes in toluene, only $g_\parallel$, $A_\parallel^V$, and the parallel component of the ^{31}P hyperfine interaction could be determined directly from the spectra in some cases. See Figure 2a. In these cases, values for $g_\perp$ and $A_\perp^V$ were computed from the isotropic parameters, describing the liquid spectra, using the relations

$$g_\perp = (3g_0 - g_\parallel)/2 \qquad (7)$$

and

$$A_\perp^V = (3a^V - A_\parallel^V)/2 \qquad (8)$$

The parallel components of the phosphorus hyperfine splittings were equal, within experimental error, to the observed isotropic splittings in the liquid spectrum. The magnetic parameters determined from the glass spectra are given in Table II.

The appearance of the esr spectra of the vanadyl complexes is changed dramatically when a small amount of a strongly coordinating ligand is added to the solution in an inert solvent at room temperature. The triplet structure superimposed on the vanadium hyperfine components is replaced by a doublet pattern indicative of a species in which the unpaired electron is interacting with only one phosphorus nucleus. See Figure 3a. Furthermore, the phosphorus splitting has decreased substantially compared to the splittings observed in solutions without added ligand.

The esr spectra of 10^{-3} M solutions of the methyl complex in 5% HMP-toluene solution at various temperatures are shown in Figure 3. The doublet patterns are observed in the range 0-30°. Below 0°, the spectral lines become broad and poorly resolved. As the temperature of the solution is increased a triplet hyperfine pattern begins to appear and the doublet pattern decreases in intensity. See Figure 3b. At 120°, the doublet structure is very weak and the spectrum is predominantly triplets, indicating that the unpaired electron is interacting with two equivalent ^{31}P nuclei. Since the magnetic parameters describing this spectrum are identical with those for the vanadyl complexes in the absence of HMP, it is logical to conclude that this high temperature in 5% HMP-toluene solution arises from the vanadyl dithiophosphinate complex which is not coordinated by HMP.

The appearance of the spectra of the vanadyl complexes in 5% HMP-toluene at 0 and 120° suggests that the spectra obtained at intermediate temperatures are superpositions of doublet and triplet patterns. The doublet phosphorus splittings in the low-temperature spectra were determined by fitting the observed spectrum at 0° with computer-synthesized spectra. With these phosphorus splittings and the triplet phosphorus splittings and the line widths of the various hyperfine components from the corresponding triplet spectra in toluene, computed spectra for a mixture of the two

Table II. Anisotropic Magnetic Parameters[a] of the Vanadyl Dithiophosphinate Complexes in Different Solvents at −150°

Solvent	Methyl complex				Phenyl complex				Ethoxy complex			
	$g_\parallel$	$g_\perp$	$A_\parallel^V$	$A_\perp^V$	$g_\parallel$	$g_\perp$	$A_\parallel^V$	$A_\perp^V$	$g_\parallel$	$g_\perp$	$A_\parallel^V$	$A_\perp^V$
Toluene[b]	1.959	1.986	168	58	1.957	1.989	167	60	1.968	1.988	167	59
5% HMP–toluene	*c*	*c*	*c*	*c*	1.923	1.974	203	77	1.949[d]	1.980[d]	180[d]	62[d]
HMP	1.922	1.975	206	77	1.923	1.974	201	76	1.922	1.974	206	78
5% DMF–toluene	*c*	*c*	*c*	*c*	1.936	1.977	195	71	1.933	1.975	196	72
DMF	1.935	1.977	198	72	1.932	1.977	197	73	1.935	1.976	196	72
5% pyridine–toluene	*c*	*c*	*c*	*c*	1.956	1.982	169	58	1.959[e]	1.982[e]	168[e]	60[e]
Pyridine	1.956	1.977	174	58	1.954	1.979	171	57	1.954	1.980	173	60

[a] Hyperfine splitting constants are in gauss. Estimated errors are ±0.002 in *g* values and ±1 G in splittings. [b] The spectra in toluene show isotropic hyperfine interaction with two equivalent ^{31}P nuclei. ^{31}P splittings are 33.1, 33.5, and 51.5 G, respectively, for the methyl, phenyl, and ethoxy complexes. $g_\perp$ and $A_\perp^V$ could not be measured directly and were determined from the relations $g_\perp = (3g_0 - g_\parallel)/2$ and $A_\perp^V = (3a^V - A_\parallel^V)/2$. [c] The spectrum is a complicated mixture of several species and the parameters could not be measured accurately. [d] The spectrum of the ethoxy complex in 5% HMP–toluene is a superposition of a spectrum showing no ^{31}P interaction and a spectrum indicating hyperfine interaction with a single ^{31}P nucleus. The parameters in the table are those of the doublet spectrum with $a^{P^1} = 31.5$ G. The parameters for the singlet species are essentially the same as those for the ethoxy complex in HMP. [e] The spectrum of the ethoxy complex in 5% pyridine–toluene is predominantly a spectrum indicating hyperfine interaction with a single ^{31}P nucleus. The parameters in the table are those of the doublet spectrum with $a^{P^1} = 36.4$. The parameters for the singlet species are essentially the same as those for the ethoxy complex in pyridine.

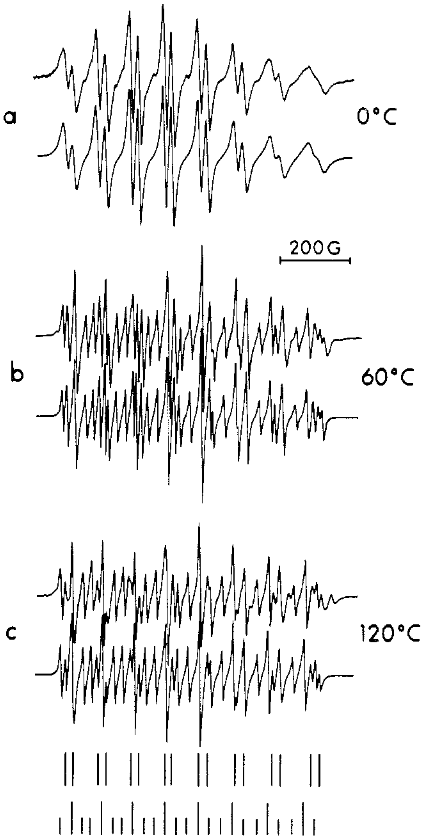

Figure 3. Esr spectra of 10^{-3} *M* liquid solutions of bis(dimethyldithiophosphinato)oxovanadium(IV) in 5% HMP–toluene at various temperatures. The experimental spectra are shown above the computer simulations in each case. Stick spectra for the two dominant vanadyl species are given at the botton of the figure.

species with one and two phosphorus splittings were generated. Since the *g* values of the doublet and triplet spectra are different (see Table III), a field shift between the centers of the two spectra to be superimposed was incorporated in the spectral computation. The relative proportions of doublet and triplet spectra were adjusted until the agreement between calculated and observed spectra was satisfactory. The line widths of the doublet species obtained in pyridine-CS_2 solutions of the methyl complex were studied from −45 to +45°. In all cases, the line widths of the doublet species were larger than the line widths of the triplet species in CS_2 solutions of the methyl complex at the same temperature.

Table III. Isotropic Magnetic Parameters[a] for Vanadyl Dithiophosphinates in 5% HMP–Toluene and 5% Pyridine–CS_2 at 30° [b]

Substituent of dithiophosphinate	5% Pyridine–CS_2			5% HMP–toluene		
	g_0	a^V	a^P	g_0	a^V	a^P
Methyl	1.974	95.0	24.9	1.970	100.1	24.0
Phenyl	1.975	95.0	25.5	1.968	100.2	24.5
Ethoxy	1.976	94.8	36.0	1.972	99.4	31.2

[a] Hyperfine splittings are in gauss. Estimated errors are ±0.5 G for splittings and ±0.001 for *g* values. [b] Only the ethoxy dithiophosphinate in 5% DMF–toluene at 30° gives a predominantly doublet spectrum with $g_0 = 1.975$, $a^V = 97.5$ G, and $a^P = 35.0$ G. Other dithiophosphinate complexes give only triplets.

Since the amounts of pyridine required for predominance of the doublet species were small (1–5%), these differences could not be attributed to solution viscosity differences. Detailed studies of the line widths of the doublet species obtained in the HMP–toluene and DMF–toluene systems were not carried out because the addition of large amounts of these ligands to the solutions would be required in order for the doublet species to predominate. The estimation of doublet line widths, in solutions containing considerably less ligand, from the line widths obtained from solutions where the doublet species predominate is difficult because the solution viscosities are often very different. Instead, we have assumed that the line widths of the doublet species in HMP–toluene and DMF–toluene solutions can be approximated by those of the triplet species in pure toluene at the same temperature. This approximation will lead to small errors in the determinations of the relative amounts of doublet and triplet species from comparison of calculated and observed spectra. The calculated spectra which agreed most closely with the observed ones are shown in Figure 3, and the magnetic parameters characterizing the doublet species are given in Table III.

The esr spectra of the methyl complex in CS_2-pyridine mixed solvents at −45° are shown in Figure 4. It is clear that the doublet spectrum observed at low concentrations of pyridine decreases in intensity as the pyridine concentration is increased and a new spectrum appears which has no ^{31}P hyperfine structure. When the vanadyl complexes are studied in pyridine, HMP, or DMF solvent at 30°, the esr spectra consist of eight singlet hyperfine lines. At higher temperatures, the esr spectra of these solutions consist of superposi-

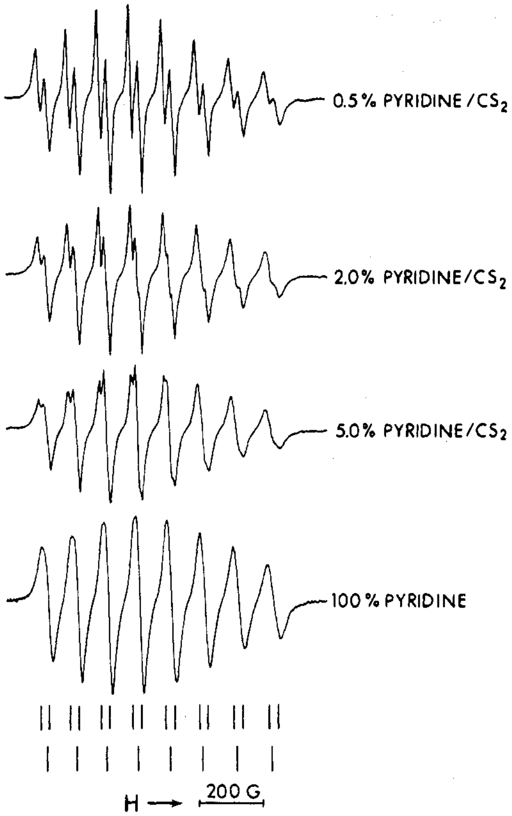

Figure 4. Esr spectra of 10^{-3} *M* liquid solutions of bis(dimethyldithiophosphinato)oxovanadium(IV) in pyridine-CS$_2$ mixtures of various compositions at $-45°$. The spectrum in 100% pyridine was taken at 30°. The stick spectra for the two dominant vanadyl species are given at the bottom of the figure.

tions of singlet and doublet hyperfine patterns. The isotropic magnetic parameters of the singlet species derived from the three vanadyl dithiophosphinate complexes and the strongly coordinating ligands are given in Table IV.

Esr spectra of the phenyl complex in 5% HMP-toluene (see Figure 2b) and in HMP at $-150°$ showed no phosphorus splittings. However, the spectrum of the methyl complex showed a mixture of several species whose individual magnetic parameters could not be measured. The spectra of the ethoxy complex in 5% HMP-toluene indicated the presence of two species, one without phosphorus hyperfine splitting and another with splitting due to one phosphorus nucleus. The relative intensities of the singlet and doublet patterns in the ethoxy spectrum were altered by changes in the HMP concentration. The spectrum of the ethoxy complex in 1% HMP-toluene at $-150°$ is predominantly doublets and the magnetic parameters given in Table II were obtained from this spectrum. The spectrum at higher HMP concentrations becomes predominantly singlets, as it is in 100% HMP solutions. The magnetic parameters for the three complexes in various solvents are given in Table II. The parameters for the singlet spectra in 5% ligand-toluene solutions are equal, within experimental uncertainty, to those for pure ligand solutions.

A close examination of the spectra of the vanadyl complexes in liquid toluene solutions with low HMP concentrations indicates the presence of peaks of low intensity which are not accounted for by the dominant doublet and triplet spectra. See Figure 3c. These weaker lines occur at positions which are very close to those found in the singlet spectra of the complexes in solutions with high HMP concentrations. It appears that, in all cases, when HMP is added to the toluene solutions of the vanadyl complexes, three species are present, each with a dramatically different esr spectrum.

Table IV. Isotropic Magnetic Parameters[a] of Vanadyl Dithiophosphinate Complexes in Coordinating Solvents

	Pyridine at 30°		DMF at 30°		HMP at 116°	
Complex	g_0	a^V	g_0	a^V	g_0	a^V
Methyl	1.9740	93.5	1.9666	111.0	1.9657	113.9
Phenyl	1.9741	95.8	1.9649	112.9	1.9605	118.8
Ethoxy	1.9738	95.6	1.9652	113.0	1.9675[b]	109.8[b]

[a] Hyperfine splittings are in gauss. Estimated errors are ±0.5 G for hyperfine splittings and ±0.0005 for *g* values. [b] Spectrum is predominantly doublets. Parameters are those of the doublet species with $a^P = 30.0$ G.

In the above description of the results of our experiments, we have concentrated on the effects of the ligands HMP, DMF, and pyridine on the esr spectra of the vanadyl dithiophosphinate complexes. We have also performed experiments with other ligands which are less strongly coordinating. In toluene solutions containing various concentrations of dimethyl sulfoxide, phosphoryl chloride, triphenylphosphine oxide, or trimethyl phosphate, the esr spectra indicated the presence of more than one species and most of the lines could be ascribed to singlet, doublet, or triplet ^{31}P hyperfine patterns. Detailed analyses of the behavior of the dithiophosphinate complexes in these solvent systems were not carried out since the HMP, DMF, and pyridine systems typify the results to be expected in other cases, and a clear separation of the different species was possible in the HMP, DMF, and pyridine solutions by variations in ligand concentration and sample temperature.

It has been reported[23] that the ethoxy complex is unstable in ethanol solutions. We have investigated the esr spectra of both phenyl and ethoxy complexes in ethanol and find that the phenyl complex gives triplet ^{31}P hyperfine splitting, while the ethoxy complex shows a mixture of doublet and triplet hyperfine patterns whose relative intensities vary with the temperature. The previous workers had reported singlet hyperfine patterns for the ethoxy complex.[23]

The visible and near-infrared spectra of the phenyl complex in different solvents are shown in Figure 5. The spectrum in toluene shows absorption bands in the region of 14,000-18,000 and above 25,000 cm^{-1} similar to those of other vanadyl complexes in noncoordinating solvents.[7,10] When 5% HMP is added, the 14,000-18,000-cm^{-1} absorption is shifted to lower frequency while the shoulder on the 25,000-cm^{-1} band disappears. In solutions of DMF and pyridine the 17,100-cm^{-1} band is shifted to 12,700 cm^{-1} while the shoulder at 14,300 cm^{-1} is shifted to slightly higher energy. The electronic spectra of the methyl and ethoxy complexes show similar changes with solvent composition.

The infrared spectra of dithiophosphinates in the region 500-700 cm^{-1} show absorptions due to the P-S stretching vibrations. The position of the symmetric P-S stretch, ν_{sym}, is sensitive to the nature of the bonding of the sulfur atoms in the dithiophosphinate moiety.[27] See Table V. ν_{sym} decreases progressively as the bonding at the sulfur atoms changes from bidentate to ionic to monodentate. We have studied the infrared absorption of the bis(diphenyldithiophosphinato)oxovanadium(IV) complex in CS$_2$ solutions with various amounts of pyridine added, and the results are shown in Figure 6. In the absence of pyridine, a single ν_{sym} absorption is observed at 570 cm^{-1}. Upon the addition of pyridine, additional absorptions at 560 and 538 cm^{-1} appear.

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(27) E. D. Day, Ph.D. Thesis, University of Alberta, 1972.

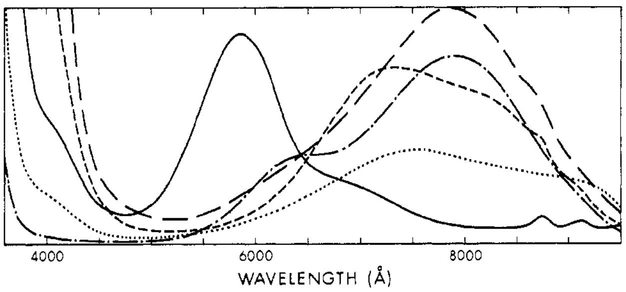


Figure 5. Electronic absorption spectra of bis(diphenyldithiophosphinato)oxovanadium(IV) in various solvents: (——), toluene; (- - - -), 5% HMP-toluene; (· · · ·), HMP; (— · —), DMF; (— — —), pyridine.

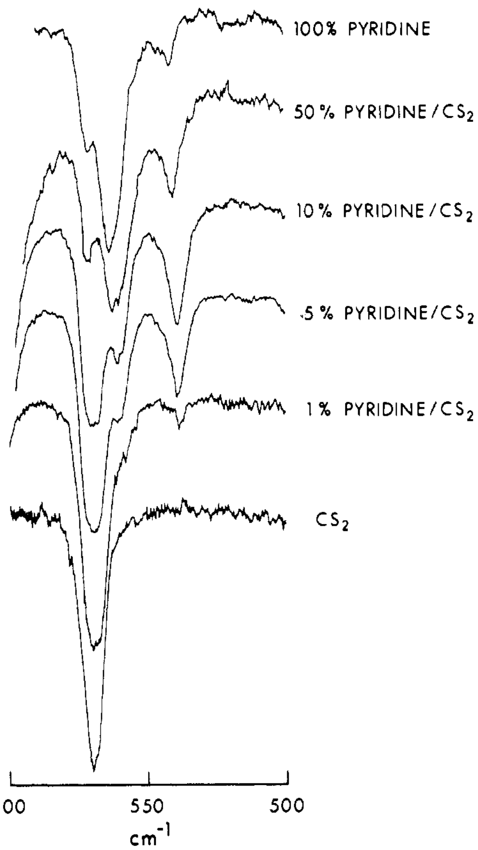
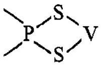
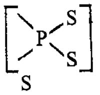
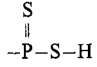


Figure 6. Infrared spectra of bis(diphenyldithiophosphinato)oxovanadium(IV) in pyridine–CS$_2$ solutions of various compositions.

Table V. Frequencies of Symmetric P–S Stretching Vibrations in Diphenyldithiophosphinate Compounds[a]

Compound	Bonding at sulfur	ν_{sym}, cm^{-1}	Medium
Bis(diphenyldithiophosphinato)oxovanadium(IV)		570	CS$_2$
Sodium diphenyldithiophosphinate		565	Nujol mull
Ammonium diphenyldithiophosphinate		561	Nujol mull
Diphenyldithiophosphinic acid	 $-\overset{\overset{S}{\|}}{P}-S-H$	530	

[a] Infrared frequencies from ref 26.

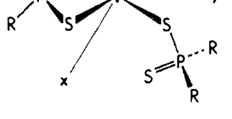
As the concentration of pyridine is increased, the intensity of the absorption at 570 cm^{-1} decreases, while the intensities of the peaks at 538 and 560 cm^{-1} increase. The absorption at 538 cm^{-1} is maximum at a pyridine concentration of 10% and decreases in intensity at higher pyridine concentrations. It is clear from Figure 6 that three distinct absorptions are present in the symmetrical P-S stretching region in 100% pyridine solutions of the phenyl complex. Spectral studies of the methyl complex were hampered by the low solubility of the complex in CS$_2$, and the air sensitivity of the ethoxy complex prevented study of its infrared spectrum.

Discussion

Equilibria between Different Vanadyl Species. The esr, infrared, and electronic spectral results presented in the previous section indicate the presence of at least three distinct vanadyl species in solutions containing a low concentration of a vanadyl dithiophosphinate complex and varying concentrations of a strongly coordinating ligand. The species which dominates at the highest temperatures with low concentrations of coordinating ligand, and gives rise to a triplet ^{31}P hyperfine pattern in the esr spectrum, indicating the presence of two equivalent phosphorus atoms, has been identified as the five-coordinate vanadyl dithiophosphinate itself and will be referred to as species T.

A second vanadyl species, to be referred to as species D, is characterized by a doublet hyperfine structure in the esr spectrum, which indicates that the unpaired electron is interacting with only one ^{31}P nucleus. This vanadyl species may contain a single phosphorus atom or it may contain two nonequivalent phosphorus atoms, only one of which gives rise to an observable hyperfine splitting. The former possibility would require dissociation of the vanadyl dithiophosphinate to form a species with a single dithiophosphinato chelating moiety. Since the only possible ligands which can replace the chelating ligand are the uncharged Lewis bases in relatively low concentration in the solution, any vanadyl species containing a single dithiophosphinate chelate would be charged, a most unlikely species in nonpolar solvents such as toluene and CS$_2$. In order to clarify this matter, the conductivities of solutions containing different concentrations of the phenyl complex in the solvents 1% HMP-toluene and 5% pyridine-CS$_2$ were determined. In both solvent systems, the conductance was unaffected by the presence of the complex at concentrations up to 7×10^{-3} *M*, the highest concentration used in the conductivity studies. The esr spectra of these solutions exhibited a predominantly doublet hyperfine pattern.

The infrared spectrum of the phenyl complex in 5% pyridine-CS$_2$ solution indicates the presence of three dithiophosphinate species in addition to species T, the five-coordinate vanadyl complex (see Figure 6). A small shoulder at 560 cm^{-1} suggests that the solution contains an ionic diphenyldithiophosphinate species (see Table V), which could be either an ion pair or a free dithiophosphinate ion at a concentration below the detection level of our conductance apparatus ($<10^{-4}$ *M*), neither of which would impart observable conductivity to the solution nor give triplet esr spectra. The infrared absorption at 538 cm^{-1} indicates the presence of a species containing a monodentate dithiophosphinate moiety,[28] for which we suggest the structure I.



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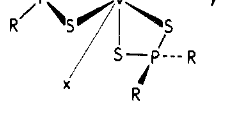

II

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[28] N. D. Yordanov and D. Shopov, *Inorg. Nucl. Chem. Lett.*, **9**, 19 (1973).

In this structure, one phosphorus nucleus is sufficiently far removed from the vanadium atom that it will not experience significant hyperfine interaction with the unpaired electron. The presence of a third species, for which we suggest a possible structure II, is indicated by a broadening of the band at 570 cm^{-1} due to overlapping with a new absorption at lower frequency (see Figure 6). This second band could arise from a structure with one of the diphenyldithiophosphinate ligands arranged so that one of its sulfur atoms occupies the axial coordination site, and a pyridine ligand is coordinated at the equatorial site (structure II). Similar arrangements are known for adducts of $VO(AcAc)_2$.[13] The axial sulfur-vanadium bonding is expected to be weaker than the equatorial sulfur-vanadium bonding, and the nonequivalence of the sulfur atoms should cause the P-S stretching frequency to shift toward that of monodentate dithiophosphinates. In structure III, the two phosphorus nuclei are nonequivalent and it is expected that the hyperfine interaction of the phosphorus nucleus in the cross-coordinated chelate would be too small to be observed in the esr spectrum.

On the basis of the intensities of the infrared absorptions, the concentration of the species which gives rise to the absorption at 560 cm^{-1} is small in solutions containing 5% pyridine or less and need not be considered further in our discussion of species D. The esr spectra of solutions where the doublet hyperfine pattern predominates provide no evidence for the existence of two distinct species, structures I and II, as suggested by the infrared spectra. The magnetic parameters, particularly the ^{31}P hyperfine interactions, of structures I and II are likely to be similar since the axial sulfur-vanadium bonding is expected to be very weak. (We know that the coordination of a pyridine molecule at the axial position either does not occur or that the effect of such coordination on the magnetic parameters of the complex is insignificant, because the esr spectra of the vanadyl species T in 1% pyridine-CS_2 and in pure CS_2 solutions are identical.) Furthermore, the rate of exchange between structures I and II is probably fast on the esr time scale so that any small differences in the esr spectra of structures I and II would be averaged out and undetectable. We therefore conclude that species D is in fact two distinct species with structures I and II, but the esr measurements can detect only the composite spectrum of these structures.

The number of ligand molecules x involved in the equilibrium

$$\text{T} + x\text{L} \rightleftarrows \text{D}$$

was determined by studying the esr spectra of solutions containing different ligand and bis(diphenyldithiophosphinato)-oxovanadium(IV) concentrations. The fractions of the vanadyl species T and D were determined from computer-synthesized esr spectra which resembled the observed esr spectra. These relative concentrations and the initial ligand and vanadyl concentrations were used to calculate values for the equilibrium constant

$$K_{\text{T-D}} = [\text{D}]/[\text{T}][\text{L}]^x \tag{9}$$

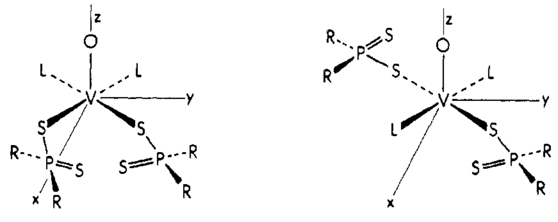
for integral values of x. Consistent values of $K_{\text{T-D}}$ were obtained only for the case $x = 1$, which is compatible with structures I and II for species D. The equilibrium constant $K_{\text{T-D}}$ was determined at several temperatures for the three complexes in various solvent systems, and the values of $K_{\text{T-D}}$ at 298 K and the enthalpies of reaction $\Delta H°_{\text{T-D}}$ calculated from the temperature dependence of $K_{\text{T-D}}$ are given in Table VI. The heats of adduct formation are similar in magnitude to those for the vanadyl acetylacetonate adducts with HMP, DMF, and various amines.[2,5] The room temperature equilibrium constants obtained from spectrophotometric measurements of the vanadyl dithiophosphinate complexes in toluene solutions containing different amounts of HMP and DMF were also calculated. The equilibrium constants obtained from the spectrophotometric measurements were consistently higher than expected from an extrapolation of the equilibrium constants obtained from the esr studies. This discrepancy can be attributed to the presence of a third vanadyl species (which gives the singlet hyperfine structure in the esr) in low concentrations. In the esr measurements, the ratio [D]/[T] is determined from the observed spectra, but this ratio cannot be measured spectrophotometrically since a solution containing only D cannot be prepared and the extinction coefficients of this adduct cannot be determined. Instead, the concentration of T is measured spectrophotometrically and the concentration of species D is obtained by difference from the known total vanadyl concentration in the solution. The spectrophotometric equilibrium data are, therefore, less reliable than the esr data but do substantiate the conclusions based on the analysis of our esr data. Furthermore, the ratio [D]/[T] calculated from the best-fit esr spectra for the HMP-toluene and DMF-toluene systems will be lower than the true value because the D and T line widths were assumed to be equal. The pyridine results suggest that the doublet pattern has slightly larger line widths than the triplet pattern. If one broadens the doublet spectrum in the computer synthesis of the spectra, a larger [D]/[T] ratio would be required to produce a spectrum with relative intensities similar to those obtained if triplets and doublets are assumed to have the same widths. Thus, the $K_{\text{T-D}}$ values calculated from esr spectra in the HMP-toluene and DMF-toluene systems are lower limits for the equilibrium constants. This accounts for some of the discrepancy between $K_{\text{T-D}}$ values determined from spectrophotometric and esr measurements.

Table VI. Equilibrium Constants at 298 K and Enthalpies of Adduct Formation[a]

Complex	Ligand	$K_{\text{T-D}}$, l./mol	$-\Delta H°_{\text{T-D}}$, kcal/mol
Methyl	HMP	42	5.7 ± 0.9
	Pyridine	23	9.3 ± 0.2
Phenyl	HMP	63	7.7 ± 1.2
	Pyridine	31	7.7 ± 0.4
Ethoxy	HMP	160	7.5 ± 1.1
	DMF	1	7.2 ± 1.1

[a] Experimental $K_{\text{T-D}}$ values were least squares fitted to $K_{\text{T-D}} = A \exp(-\Delta H°_{\text{T-D}}/RT)$ and errors given are the standard errors from the least-squares routine. $K_{\text{T-D}}$ at 298 K is calculated using the least-squares parameters.

A third vanadyl species, henceforth referred to as species S, gives rise to an esr spectrum which shows no hyperfine interactions between the unpaired electron and the phosphorus nuclei. The absence of ^{31}P hyperfine interactions indicates that species S has no chelating dithiophosphinate moieties. This species predominates under conditions of low temperature and high ligand concentration. The conductivities of solutions of the phenyl complex in 10% HMP-toluene, HMP, pyridine, and DMF vary linearly with the concentration of the vanadyl complex. This implies that the vanadyl dithiophosphinate complex dissociates under these conditions. The infrared spectrum of the phenyl complex in 10% pyridine-CS_2 solution (Figure 6) indicates that dithiophosphinate species with bidentate and monodentate coordination are present in addition to the ionic species. The structures III are suggested as possible molecular arrangements which are consistent with the esr spectrum and with monodentate dithiophosphinate coordination. The cis and trans isomers of III are possible and could give rise to different esr spectra if the magnetic parameters of the two isomers were sufficiently different and the isomers were not being interconverted rapidly by chemical exchange.



III

The relative concentrations of the D and S species involved in the equilibrium

$$D + x'L \rightleftarrows S$$

in 1-5% pyridine-CS_2 solutions were determined by comparing the observed esr spectra with computed spectra. The equilibrium constant

$$K_{D\text{-}S} = [S]/[D][L]^{x'} \qquad (10)$$

was calculated for integral values of x', and the values obtained were consistent with $x' = 1$ only. At −45°, $K_{D\text{-}S}$ has the value 3.1 l./mol for the methyl complex. This result indicates that the formation of species S from species D involves displacement of one of the sulfur atoms from vanadyl coordination by a ligand molecule. The species S involved in this equilibrium is assumed to have structure III since the species must result from the addition of a single ligand to structure I or II which represent species D, and the simplest way for this to occur is for a second ligand to displace one of the sulfur atoms of the bidentate dithiophosphinate of structure I or II to make it a monodentate ligand in structure III. However, to explain the conductance and infrared results cited above, the structure III species must be in equilibrium with ionized species in which one or both dithiophosphinates are displaced from the first coordination sphere of the vanadyl ion and ionized. All species giving rise to a singlet esr spectrum apparently have very similar magnetic parameters since only one singlet species was resolved in the esr spectrum.

The temperature dependence of the equilibrium between species S and D warrants some comments since the esr spectra of the vanadyl dithiophosphinate complexes in pyridine, HMP, or DMF solution exhibit a temperature dependence. At +30°, the spectrum of the methyl complex in pyridine (see Figure 4) consists of eight well-resolved lines with no evidence of phosphorus hyperfine splittings. At higher temperatures, doublets appear in the esr spectrum. This result is consistent with the decrease in the dielectric constant of pyridine as the temperature increases. The lower dielectric constant destabilizes the dissociated form and drives the equilibrium to the D side. Similar esr results are obtained for the ethoxy and phenyl complexes with the doublets appearing at lower temperatures in the methyl and ethoxy complexes than in the phenyl complexes. This may result from the greater stabilization of the diphenyldithiophosphinate anion due to charge delocalization to the phenyl groups. Obviously there are numerous structures possible for the species containing two or more ligand molecules per dithiophosphinate and still yielding a singlet hyperfine esr pattern. However, their magnetic parameters would be similar and separate esr lines for each would not be resolved.

In DMF, the phenyl and ethoxy complexes show singlet esr spectra over the complete temperature range of the liquid, while the methyl complex gives a mixture of doublets and singlets above 60°. Attempts to gain further insight into the coordination of DMF at the vanadyl ion were made by studying the paramagnetic broadening of the nmr lines of the DMF solvent. The line-broadening results for the phenyl complex in DMF were similar to those for $VO(DMF)_5(ClO_4)_2$ in DMF.[26,29] We therefore conclude that in DMF, the diphenyldithiophosphinate chelates are completely displaced from the first coordination sphere of the vanadyl ion. Furthermore, the conductance of the DMF solution was linear in the concentration of phenyl complex. The persistence of the dissociated form for phenyl and ethoxy complexes even at high temperatures is attributed to the high dielectric constant of DMF (36.1) relative to that of pyridine (12.3). The esr spectra of the complexes in HMP solution are similar to those in DMF. This is expected since the dielectric constants of HMP (30.0) and DMF are similar.

The esr spectra of the phenyl and methyl complexes in 5% DMF-toluene solution at 25° are predominantly triplets, while the spectra of the complexes in 5% pyridine-CS_2 or 5% HMP-toluene solutions are predominantly doublets. This difference in the solvent systems is due primarily to the differences in the electron donor properties of the ligands.[30] The observation of adduct formation of the ethoxy complex at lower ligand concentrations than those required for formation of analogous adducts with the methyl or phenyl complex indicates that the ethoxy complex is a stronger Lewis acid than the methyl or phenyl complexes.

^{31}P Hyperfine Interactions. The mechanism of the hyperfine interaction between the ^{31}P nuclei in the dithiophosphinate chelates with the unpaired electron on the vanadium atom is believed to be through a σ interaction between the vanadium $d_{x^2-y^2}$ orbital and an appropriate linear combination of the two P-S σ-bonding orbitals.[22] The hyperfine splittings will be influenced by the amount of phosphorus 3s character in the P-S σ bonds. The coefficient C_{3s}^P, of the phosphorus 3s atomic orbital in the molecular orbital containing the unpaired electron, is related to the phosphorus hyperfine splitting by[31]

$$a^P = 3636|C_{3s}^P|^2 \qquad (11)$$

The values of C_{3s}^P calculated from the observed ^{31}P hyperfine splittings in the phenyl and ethoxy complexes in toluene solutions are 0.095 and 0.117, respectively. The large difference in the coefficients and phosphorus splittings in these two complexes can be attributed to the difference in the amount of phosphorus s character in the P-S bonds of the dithiophosphinate and dithiophosphate moieties. In the dithiophosphate complex, the P-S bonds are shorter and have more s character than in the dithiophosphinate complexes. Infrared[32] and X-ray[33] evidence for differences in P-S bonding in these complexes has been reported.

When a Lewis base displaces one of the sulfur atoms of the

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(29) G. A. Miller and R. E. D. McClung, *J. Chem. Phys.*, 58, 4358 (1973).

(30) V. Gutmann, *Rec. Chem. Progr.*, 30, 169 (1969).

(31) P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen and Co. Ltd., London, 1967, pp 438-439.

(32) R. A. Chittenden and L. S. Thomas, *Spectrochim. Acta*, 20, 1679 (1964).

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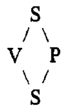
dithiophosphinate or dithiophosphate from its coordination to the vanadium atom, the ^{31}P nucleus of this chelate no longer experiences significant hyperfine interactions because the spatial arrangement leads to a substantial decrease in the interaction between the vanadium $d_{x^2-y^2}$ orbital and the P-S σ orbitals. The hyperfine splitting of the ^{31}P nucleus of the dithiophosphinate chelate which has not been displaced is altered because the bonding in the



grouping will be modified by the asymmetry of the coordination at the other equatorial sites. In the species D which result from the phenyl and ethoxy complexes in solutions containing low concentrations of pyridine, $C_{3s}{}^P$ has the value 0.084 and 0.100, respectively. It would appear that changes in the coordination trans to the dithiophosphinate chelate lead to lengthening of one or both of the P-S bonds and a decrease in the amount of phosphorus s character in the P-S σ bonds. The HMP adducts of the phenyl and ethoxy complexes show smaller ^{31}P hyperfine splittings than the pyridine adducts. This may be attributable to differences in the effects of oxygen and nitrogen ligand coordination on the V-S and, hence, the P-S bonding.

Registry No. Bis(dimethyldithiophosphinato)oxovanadium(IV), 41523-86-8; bis(diphenyldithiophosphinato)oxovanadium(IV), 38298-50-9; bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV), 35944-43-5; hexamethylphosphoramide, 680-31-9; pyridine, 110-86-1; dimethylformamide, 68-12-2.

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Oxidative Dehydrogenation of Ethylenediamine Complexes of Ruthenium(II)

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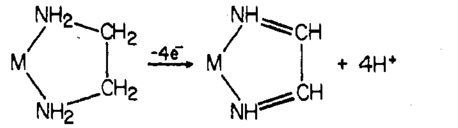
Ethylenediamine coordinated to ruthenium(II) is readily oxidized to the coordinated diimine ligand (diim = NH=CHCH=NH). The new complexes $[Ru(phen)_2diim]I_2$ and $[Ru(en)_2phen]I_2$ have been characterized by elemental analyses, visible absorption spectra, and analysis of their 220-MHz pmr spectra. Improved procedures are reported for the preparation of $[Ru(phen)_2en]I_2$ and $[Ru(en)_2diim]I_2$. The electrochemical properties of these complexes have been investigated by redox titration and cyclic voltammetry. A correlation between the oxidative dehydrogenation reaction and the formal reduction potential of the ruthenium(III)-ruthenium(II) couple is observed.

Introduction

The oxidative dehydrogenation of coordinated macrocyclic ligands has been examined;[2-4] recently examples have been reported of the analogous reactions of coordinated diamines and monoamines. The four-electron oxidation of ethylenediamine to α-diimine (diim) has been observed for



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both tris(ethylenediamine)ruthenium(II)[5] and tetracyanoethylenediamineferrate(II)[6] ions; similarly, oxidation of hexakis(methylamine)ruthenium(II) ion produces coordinated cyanide.[7] In each case the oxidized ligand remains coordinated in the metal complex.

We report here some preparative and electrochemical studies of further examples of oxidative dehydrogenation of ethylenediamine coordinated to ruthenium(II) which permit a correlation between the ease of the reaction and the electrochemical properties of the reactant complex.

Experimental Section

Preparation of Complexes. $[Ru(phen)_2en]I_2$. An improved procedure was developed for the synthesis of this complex which results in a better yield in a much shorter period of time than the original method.[8] The procedure of Liu, Liu, and Bailar[9] was used to prepare $Ru(phen)_2ox$. This was converted to $Ru(phen)_2Cl_2$ by suspension in concentrated HCl (5 ml of HCl/g of $Ru(phen)_2ox$) for 4-6 hr at room temperature. The crude product was then recrystallized from 1:1 water-ethanol.[10] Conversion to the desired product followed a procedure similar to that of Dwyer.[8] In a typical preparation 0.5 g of $Ru(phen)_2Cl_2$ was refluxed in 100 ml of 1:1 water-ethanol. After dissolution the hot solution was filtered and the ethanol was removed by heating the filtrate on a steam bath. A solution of 0.5 ml of 96% ethylenediamine in 10 ml of methanol was added to the resulting solution. This solution was heated for a further 10-20 min during which time the color changed from brown to bright red-orange. After cooling, 0.6 g of NaI in 2 ml of water was added to form a dark red precipitate. This product was collected on a filter, washed with water followed by ethanol, and recrystallized from 1:1 0.01 *M* trifluoroacetic acid-methanol. The final product was collected by filtration, washed with water, ethanol, and ether, and dried. The complex is not stable indefinitely in air, but decomposes slowly, presumably to the diimine analog. *Anal.* Calcd for $RuC_{26}H_{24}N_6I_2$: C, 40.3; H, 3.12; N, 10.8; Ru, 13.0; I, 32.7. Found: C, 40.3; H, 2.98; N, 11.0; Ru, $\geqslant$12.6; I, 32.4.

$[Ru(phen)_2diim]I_2$. A mixture of freshly precipitated AgCl and 1 g of $[Ru(phen)_2en]I_2 \cdot 2H_2O$ was stirred in 100 ml of H_2O for 20 min at room temperature. The resulting mixture was filtered,

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