Electron Paramagnetic Resonance Spectra of Some Oxovanadium(IV) Chelates

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X-Band e.p.r. spectra of magnetically dilute glasses at 77 K show that ethanol and pyridine form weak complexes with vanadyl chelates and that vanadium(IV) in solutions of these chelates is readily oxidised to vanadium(V). A method which enables spin Hamiltonian parameters to be extracted from systems which have C_{2v} symmetry is described, and the magnetic and optical properties of some five- and six-membered ring chelates of the VO^{2+} ion, and of their complexes with ethanol and with pyridine, are listed. The principal values of the hyperfine tensor components and the isotropic contribution to hyperfine coupling can be used to distinguish five- from six-membered ring chelates. Spin Hamiltonian parameters are equated to the atomic orbital coefficients in some of the molecular orbitals involved in bonding in these chelates. The weak C_{2v} component of the ligand field mixes the vanadium $3d_{x^2-y^2}$, $3d_{z^2}$, and $4s$ orbitals and the magnetic resonance data is used to estimate the extent of this mixing. Mixing $3d_{z^2}$ character into the orbital containing the unpaired electron accounts for 'in-plane anisotropy' in the g-tensor components. Mixing $4s$ character accounts for characteristic differences between hyperfine tensor components observed for five- and six-membered ring chelates and for the changes which occur in the magnetic properties of these compounds when additional complexing with solvent molecules takes place.

THE oxometallate ion, oxovanadium(IV), has been extensively studied: theoretical methods,[1-5] spectrophotometric techniques,[1,6-8] X-ray crystallographic analyses,[9-11] and electron paramagnetic resonance methods [2-5,12-15] have all been employed in characterising it. In its chelates the ligand field has dominant C_{4v} symmetry but this is reduced to C_{2v} or even to C_2 by bidentate ligands.[5,9-11,16,17] Although several e.p.r. studies [5,16,17] of doped single-crystals containing the VO^{2+} ion report this reduction in symmetry, to our knowledge there has only been one report [3] of the effects of these lower symmetries on the e.p.r. spectra of vanadyl chelates dispersed in magnetically dilute glasses, although numerous reports of analyses of such systems with apparent C_{4v} symmetry have been made.[12-15] Several computational techniques have been developed to enable spin Hamiltonian parameters to be extracted from spectra of VO^{2+} species with C_{4v} symmetry [12,18-21] but so far none have been reported for species with C_{2v} symmetry. Some e.p.r. spectra of vanadyl chelates which have this lower symmetry are therefore reported below and a method which can be used to quickly analyse spectra obtained from their dilute solutions in glasses is described.

EXPERIMENTAL

The vanadyl chelates (I)—(VI) were prepared by mixing, in 2 : 1 molar ratios, the appropriate enols, or their sodium salts, and an aqueous solution of vanadyl sulphate. Where necessary, the pH of the solution was then adjusted with sodium hydroxide to pH *ca.* 5. After refluxing for several minutes, the resultant aqueous mixture was then allowed to cool and the vanadyl chelates were filtered off and dried.

The chelates form stable solids but their solutions in alcohol and in some cases in water, are all unstable in the presence of oxygen, the six-membered ring species (I) and (II) being slowly oxidised,[22] the five-membered ring chelates (III)—(VI) reacting rapidly. When the maltolate, (V), for example, is dissolved in commercial chloroform containing 2% of ethanol, within a few minutes the *d–d* transitions in its visible spectrum are quickly masked by the development of an intense red colour. At the same time the solution slowly becomes diamagnetic, its e.p.r. spectrum gradually disappears, and its sharp i.r. absorption at 990 cm^{-1}, characteristic of the vanadyl V=O stretching vibration, is slowly replaced by a new absorption at 960 cm^{-1}. These all imply that an oxovanadium(V) complex is being formed and that reaction (1) is taking place. The corresponding reaction, (2), in aqueous solution is reversible.

$$2VO(maltolate)_2 + 2ROH + \tfrac{1}{2}O_2 \longrightarrow 2VO(maltolate)_2OR + H_2O \quad (1)$$

$$2VO(maltolate)_2 + H_2O + \tfrac{1}{2}O_2 \rightleftharpoons 2VO(maltolate)_2OH \quad (2)$$

A freshly prepared, green, aqueous solution of vanadyl

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[1] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 111.

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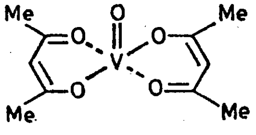
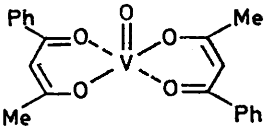
[21] L. D. Rollmann and S. I. Chan, 'Electron Spin Resonance of Metal Complexes,' ed., T. F. Yen, Adam Hilger, London, 1969, p. 175.

[22] T. R. Ortolano, J. Selbin, and S. P. McGlynn, *J. Chem. Phys.*, 1964, **41**, 262.

maltolate turns red when it is allowed to stand in contact with air. When this red solution is boiled it turns green, the colour change being reversed when the solution is cooled. Furthermore, at pH 5, a 1 : 2 molar aqueous mixture of ammonium metavanadate and maltol is red. On boiling this mixture its colour changes to green and vanadyl maltolate is precipitated.



(I)



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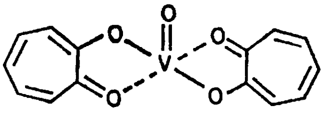
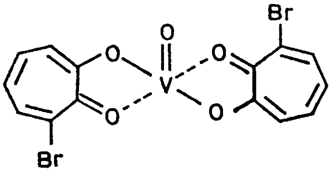
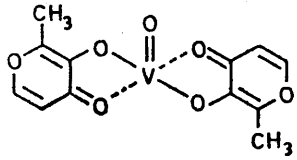


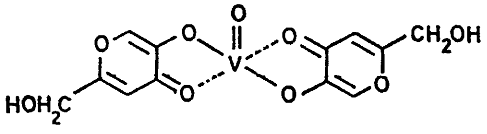
(III)



(IV)



(V)



(VI)

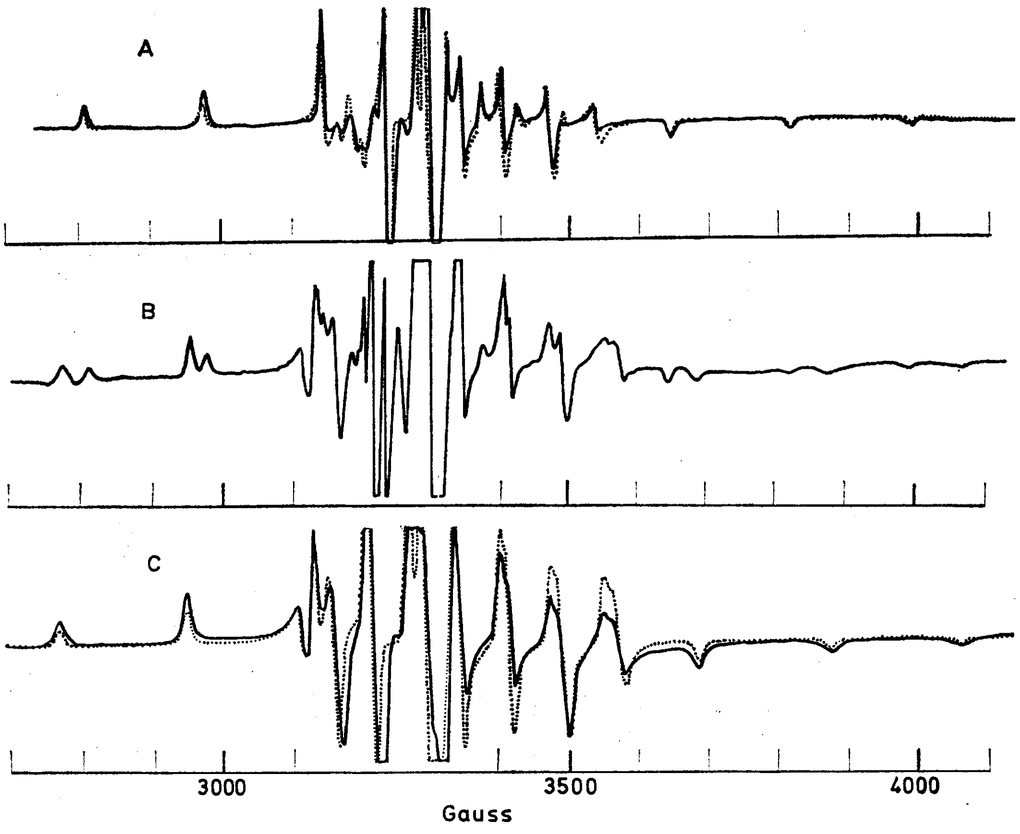


FIGURE 1 Observed (——) and calculated (· · · ·) e.p.r. spectra of vanadyl tropolonate (III). Spectrum A is obtained from a 10^{-3}M-solution of (III) in chloroform–toluene glass (60 : 40) at 77 K and spectrum B is obtained when 2% of ethanol is added to this solution. Spectrum C is obtained from the ethanolic adduct of (III)

Thoroughly out-gassed 10^{-3}M-solutions of the complexes (I)—(VI) in chloroform–toluene glasses (chloroform : toluene = 3 : 2), and in similar glasses to which a small quantity of ethanol or pyridine had been added, were examined at 77 K in a Decca X3 spectrometer combined with a Newport Instruments 11-in magnet system. All resonant fields were calibrated by standard proton magnetic resonance techniques. We have not found any evidence for dimer formation.[23] Typical spectra are shown in Figure 1.

Analysis of Spectra.—In d^1 vanadyl complexes which

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[23] T. D. Smith, T. Lund, J. R. Pilbrow, and J. H. Pryce, *J. Chem. Soc.* (*A*), 1971, 2936.

have at least C_{2v} symmetry the g- and T-tensors coincide and the spin Hamiltonian can therefore be written [24] in the diagonal form

$$\mathscr{H} = \beta[g_{xx}H_xS_x + g_{yy}H_yS_y + g_{zz}H_zS_z] + T_{xx}I_xS_x + T_{yy}I_yS_y + T_{zz}I_zS_z + Q'[I_z^2 - (1/3)I(I+1)] - (g_{zz})_N\beta_N H_z \quad (1)$$

where x, y, and z are the principal axes of the g- and T-tensors and use has been made of the fact that in vanadyl chelates the ^{51}V quadrupolar and Zeeman interactions are both small.

It can be shown [25] that the intensities of the transitions '$\Delta m_S = \pm 1$, $\Delta m_I = \pm 1$' and '$\Delta m_S = \pm 1$, $\Delta m_I = \pm 2$' are very weak in vanadyl chelates and hence it is only necessary to consider '$\Delta m_S = \pm 1$, $\Delta m_I = 0$' transitions in order to account for the e.p.r. spectra of compounds (I)—(VI).

In magnetically dilute polycrystalline samples, each of the randomly oriented paramagnetic molecules separately contributes eight transitions of the form '$\Delta m_S = \pm 1$, $\Delta m_I = 0$' ($m_I = +\frac{7}{2} \ldots -\frac{7}{2}$) to the observed e.p.r. spectrum which therefore consists of a superposition of the spectra associated with each orientation, weighted in proportion to the probability of finding the complex at that particular orientation. Furthermore in vanadyl chelates which have at least C_{2v} symmetry, for each value of m_I the variation [12,16,26] in resonant field position with orientation can be described by the Kneubühl function,[27] $S(H)$, multiplied by an appropriate broadening function. If the transition probability is assumed to be independent of orientation and the broadening function is assumed to have a Gaussian form, then the line-shape function, $F(H')$, which defines the absorption spectrum as a function of the observed field, H', can be written in the form

$$F(H') = (2\pi)^{-\frac{1}{2}} \sum_{m_I=-\frac{7}{2}}^{m_I=+\frac{7}{2}} \int_{H=-\infty}^{+\infty} \beta^{-1}S_{m_I}(H) \exp[-(H'-H)^2(2\beta^2)^{-1}]\mathrm{d}H \quad (2)$$

Except for the case in which $m_I = -\frac{1}{2}$, if H_1, H_2, and H_3 are resonant field values for paramagnetic molecules in which the applied field lies along one of the three principal axis directions ($H_1 < H_2 < H_3$), then in the field range $H_1 \leqslant H \leqslant H_2$

$$S_{m_I}(H) = 2(\pi)^{-1} . H_1H_2H_3H^{-2} . [(H_3^2 - H^2)(H_2^2 - H_1^2)]^{-\frac{1}{2}}K(k) \quad (3)$$

where

$$k = [(H_3^2 - H_2^2)(H^2 - H_1^2)]^{\frac{1}{2}}[(H_3^2 - H^2)(H_2^2 - H_1^2)]^{-\frac{1}{2}}$$

and $K(k)$ is the elliptic integral $\int_0^{\pi/2} (1 - k^2 \sin^2 x)^{-\frac{1}{2}}\mathrm{d}x$.

In the field range $H_2 \leqslant H \leqslant H_3$

$$S_{m_I}(H) = 2(\pi)^{-1} . H_1H_2H_3H^{-2} . [(H_3^2 - H_2^2)(H^2 - H_1^2)]^{-\frac{1}{2}}K(k') \quad (3')$$

where

$$k' = [(H_3^2 - H^2)(H_2^2 - H_1^2)]^{\frac{1}{2}}[H_3^2 - H_2^2)(H^2 - H_1^2)]^{-\frac{1}{2}}$$

and $K(k')$ is the elliptic integral $\int_0^{\pi/2} [1 - (k')^2 \sin^2 x]^{-\frac{1}{2}}\mathrm{d}x$.

For certain inter-relationships of the spin Hamiltonian parameters it can be shown [12,26] that the resonant field does not vary smoothly with orientation, and then singularities are obtained in the Kneubühl functions, $S(H)$, in addition to those observed when the field lies along the principal axes directions. A singularity of this kind is observed in the e.p.r. spectrum of vanadyl chelates in which $m_I = -\frac{1}{2}$, and in that case the observed spectrum can be simulated by taking H_1 to be the resonant field when the applied field is along the z-axis of the g-tensor, H_3 to be the resonant field when the applied field is along the x- or y-axis directions, and H_2 is the magnitude of the resonant field at the singularity.

Reasonable sets of values of H_1, H_2, and H_3 for each value of m_I can be taken directly from the experimental spectrum and iterative computational procedures then used to obtain the best match of the derivative of the calculated function $F(H')$ to the observed spectrum. When the resonant field values H_x, H_y, and H_z obtained when the magnetic field lies along the principal x, y, and z directions are known, then the principal g- and T-tensor components, and the ^{51}V nuclear quadrupole coupling parameter, Q', can be obtained from the relationships

$$H_z = h\nu(g_{zz}\beta)^{-1} - hc(g_{zz}\beta)^{-1}T_{zz}m_I - hc^2(4g_{zz}\beta\nu)^{-1}[T_{xx}^2 + T_{yy}^2][I(I+1) - m_I^2] \quad (4)$$

$$H_x = h\nu(g_{xx}\beta)^{-1} - hc(g_{xx}\beta)^{-1}T_{xx}m_I - hc^2(4g_{xx}\beta\nu)^{-1}[T_{yy}^2 + T_{zz}^2][I(I+1) - m_I^2] - hc(2g_{xx}\beta T_{xx})^{-1}(Q')^2[2I(I+1) - 2m_I^2 - 1]m_I \quad (5)$$

where ν is the frequency of the microwave radiation used in recording the e.p.r. spectrum, and T-tensor components are in units of cm^{-1}. H_y Is obtained from (5) by interchanging subscripts x and y.

RESULTS AND DISCUSSION

Spin Hamiltonian parameters extracted from the e.p.r. spectra of chelates (I)—(VI) are listed in Table 1. Spectra computed for vanadyl tropolonate, (III), using the data in Table 1 are shown in Figure 1. Table 1 shows that the magnitudes of the principal values of the hyperfine tensor components in chloroform–toluene (3 : 2) glass can be used to distinguish six-membered from five-membered ring chelates of the oxovanadium(IV) ion: g-tensor components cannot be used for this purpose. The two kinds of chelate cannot be distinguished if solvent molecules complex with the chelate; solvent complexing decreases the magnitudes of the T-tensor components of six-membered ring chelates and increases them in five-membered ring systems. In the five-membered ring chelates, spin-Hamiltonian parameters of the ethanol and pyridine complexes are so similar that the two kinds of complex must be similar: the oxygen atom of the ethanol molecule must, therefore, be able to co-ordinate to the sixth position of the vanadyl chelates. The effects of ethanol on the magnetic parameters of the six-membered ring chelates are markedly greater than the corresponding effects of pyridine. Since ethanol is known to be a weaker donor than pyridine the changes in electron distribution caused by

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[24] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.* (*A*), 1951, **205**, 135.

[25] B. Bleaney, *Phil. Mag.*, 1951, **42**, 441.

[26] R. Neiman and D. Kivelson, *J. Chem. Phys.*, 1961, **35**, 156.

[27] F. K. Kneubühl, *J. Chem. Phys.*, 1960, **33**, 1074.

incorporating the ethanol molecule into the sixth position round the vanadium atom must be supplemented in some way, for example by a 'push–pull' effect obtained by simultaneous hydrogen bonding of another molecule of ethanol to the V=O oxygen.[8]

TABLE 1

Spin Hamiltonian parameters for the vanadyl chelates (I)—(VI) and for their complexes with ethanol and with pyridine. All tensor components refer to chelates at 77 K except for $\langle g' \rangle$ and a' which are the isotropic g-factor and ^{51}V hyperfine coupling parameters at 290 K. Solubility problems prevented data from being obtained in cases marked *. In †, inaccuracies in data prevented a value for Q' from being estimated. All hyperfine tensor components are in units of cm^{-1}. Limits of error are g_{xx} and $g_{yy} = \pm 0{\cdot}001$, $g_{zz} = \pm 0{\cdot}0005$, T_{xx} and $T_{yy} = \pm 0{\cdot}00005$, $T_{zz} = \pm 0{\cdot}00002$, $Q' = \pm 0{\cdot}0001$

	Compd.	g_{xx}	g_{yy}	g_{zz}	T_{xx}	T_{yy}	T_{zz}	$\langle g \rangle$	a	$\langle g' \rangle$	a'	Q'
Uncomplexed	(I)	1·984	1·981	1·942	−0·00630	−0·00642	−0·01734	1·969	−0·01007	1·970	−0·00999	0·0002
chelate in	(II)	1·984	1·981	1·941	−0·00627	−0·00650	−0·01744	1·969	−0·01011	1·970	−0·00994	0·0001
chloroform–toluene	(III)	1·986	1·979	1·950	−0·00416	−0·00527	−0·01538	1·972	−0·00831	1·972	−0·00856	0·0001
(60 : 40) glass	(V)	1·986	1·979	1·948	−0·00483	−0·00574	−0·01611	1·971	−0·00895	1·972	−0·00913	0·0000
Ethanol-chelate	(I)	1·978	1·973	1·947	−0·00543	−0·00594	−0·01670	1·967	−0·00939	1·968	−0·00940	0·0003
complex in	(II)	1·978	1·973	1·947	−0·00533	−0·00594	−0·01667	1·967	−0·00936	1·968	−0·00940	0·0003
chloroform–toluene	(III)	1·983	1·978	1·941	−0·00562	−0·00599	−0·01679	1·967	−0·00950	*	*	0·0003
(60 : 40) glass	(IV)	1·983	1·978	1·941	−0·00556	−0·00596	−0·01671	1·968	−0·00947	*	*	0·0003
	(V)	1·981	1·977	1·943	−0·00566	−0·00605	−0·01685	1·967	−0·00957	*	*	0·0003
Pyridine-chelate	(I)	1·980	1·980	1·945	−0·00618	−0·00618	−0·01674	1·969	−0·00974	1·972	−0·00963	†
complex in	(II)	1·981	1·978	1·944	−0·00590	−0·00617	−0·01672	1·970	−0·00965	1·970	−0·00957	0·0002
pyridine–toluene	(III)	1·984	1·986	1·944	−0·00550	−0·00572	−0·01614	1·969	−0·00917	1·971	−0·00915	0·0002
glass	(IV)	1·984	1·980	1·945	−0·00557	−0·00580	−0·01625	1·970	−0·00924	1·971	−0·00916	0·0002
	(V)	1·982	1·979	1·945	−0·00563	−0·00589	−0·01654	1·969	−0·00943	1·972	−0·00913	0·0002
	(VI)	1·980	1·978	1·945	−0·00562	−0·00585	−0·01647	1·969	−0·00935	1·970	−0·00933	0·0002

Bonding in Chelates of Oxovanadium(IV).—In crystal-field theory, the weak effective C_{2v} perturbation of the dominant C_{4v} field in oxovanadium(IV) chelates mixes the vanadium $3d_{x^2-y^2}$, $3d_{z^2}$, and $4s$ orbitals so that, with the co-ordinate system shown in Figure 2, in the ground state the unpaired electron is in the orbital described by the linear combination

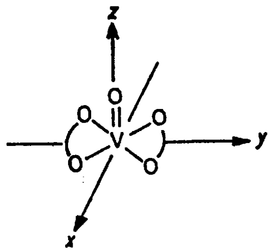

FIGURE 2

$$\psi = ad_{x^2-y^2} + bd_{z^2} + cs \qquad (6)$$

Since the effective C_{2v} component of the crystal field is relatively weak $a \gg b,c$. In ligand-field theory this metal ion orbital combines with a ligand group orbital of appropriate symmetry and the unpaired electron is in the antibonding orbital $\psi(A_1)$ where the analytical forms of $\psi(A_1)$ and of the other magnetically important antibonding molecular orbitals are given by (7):

$$\begin{aligned}\psi(A_1) &= \beta_2{}^*(ad_{x^2-y^2} + bd_{z^2} + cs) - (\beta_2{}^*)'\phi_{L_1}\\ \psi(A_2) &= \beta_1{}^*d_{xy} - (\beta_1{}^*)'\phi_{L_2}\\ \psi(B_1) &= (e_\pi{}^*)_{xz}d_{xz} - (e_\pi{}^*)_{xz}'\phi_{L_3}\\ \psi(B_2) &= (e_\pi{}^*)_{yz}d_{yz} - (e_\pi{}^*)'_{yz}\phi_{L_4}\end{aligned} \qquad (7)$$

Spin-orbit coupling, Zeeman interactions, and hyperfine interactions all perturb these basis functions and if the matrix elements of these interactions are equated with those of the spin Hamiltonian (1) then the spin Hamiltonian parameters can be expressed as functions of the coefficients of the antibonding orbitals (7). These functions have been shown [13,17,24] to be

$$g_{zz} = 2{\cdot}0023 - (\Delta E_{xy})^{-1}[8a^2(\beta_2{}^*)^2P_{m\sigma}{}^*\xi] \qquad (8)$$

$$g_{xx} = 2{\cdot}0023 - (\Delta E_{xz})^{-1}[2a(a + 2\sqrt{3}b)(\beta_2{}^*)^2(P_{m\pi}{}^*)_{xz}\xi] \qquad (9)$$

$$g_{yy} = 2{\cdot}0023 - (\Delta E_{yz})^{-1}[2a(a - 2\sqrt{3}b)(\beta_2{}^*)^2(P_{m\pi}{}^*)_{yz}\xi] \qquad (10)$$

$$T_{zz} = P\left\{-\kappa - \frac{4}{7}\,a^2(\beta_2{}^*)^2 - \frac{1}{14}\frac{(3a + b\sqrt{3})}{(a - b\sqrt{3})}(2{\cdot}0023 - g_{yy}) - \frac{1}{14}\frac{(3a - b\sqrt{3})}{(a + b\sqrt{3})}(2{\cdot}0023 - g_{xx}) - (2{\cdot}0023 - g_{zz})\right\} \qquad (11)$$

$$T_{xx} = P\left\{-\kappa + \frac{2}{7}a^2(\beta_2{}^*)^2 - 4\,\frac{\sqrt{3}}{7}ab - (2{\cdot}0023 - g_{xx}) + \frac{1}{14}\frac{(3a + b\sqrt{3})}{(a - b\sqrt{3})}(2{\cdot}0023 - g_{yy}) - \frac{1}{7}\frac{b}{a}(2{\cdot}0023 - g_{zz})\right\} \qquad (12)$$

$$T_{yy} = P\left\{-\kappa + \frac{2}{7}a^2(\beta_2{}^*)^2 + 4\,\frac{\sqrt{3}}{7}ab - (2{\cdot}0023 - g_{yy}) + \frac{1}{14}\frac{(3a - b\sqrt{3})}{(a + b\sqrt{3})}(2{\cdot}0023 - g_{xx}) + \frac{1}{7}\frac{b}{a}(2{\cdot}0023 - g_{zz})\right\} \qquad (13)$$

where $P_{m\sigma}{}^*$ and $P_{m\pi}{}^*$ are metal orbital populations in the in-plane σ and out-of-plane π antibonding molecular orbitals, respectively, and small terms in b^2 have been ignored. $P = 2{\cdot}0023\beta_e\beta_N g\langle d_{x^2-y^2}|r^{-3}|d_{x^2-y^2}\rangle$ And has been estimated by McGarvey,[28] using the Hartree–Fock calculations of Freeman and Watson,[29] to be 0·0128 cm^{-1}. ξ Is the spin-orbit coupling constant for the vanadium ion in the valence state appropriate to the vanadyl chelates, *i.e.* to vanadium in a V^+ ($3d^3 4s^{\frac{1}{2}} 4p^{\frac{1}{2}}$) state, and has been shown [2] to be 170 cm^{-1}.

Adding equations (11), (12), and (13) and dividing each side by three gives

$$a = -P\kappa - [2{\cdot}0023 - \langle g\rangle]P \qquad (14)$$

where $\langle g\rangle = 1/3(g_{xx} + g_{yy} + g_{zz})$ and $a = 1/3(T_{xx} + T_{yy} + T_{zz})$.

In-plane π-Bonding.—Values of κ and of the bonding parameters $(\beta_2{}^*)^2$, $|b|$, and $|c|$ can be estimated from equations (11)—(14) and are listed in Table 2. They show that, (i) in-plane π-bonding can be ignored; the unpaired electron is localised on the vanadium ion, and solvents have little effect on the nature of in-plane π-bonding.

TABLE 2

Molecular orbital coefficients and metal orbital populations for compounds (I)—(VI) and for their ethanol and pyridine complexes

	Compound	κ	$(\beta_2{}^*)^2$	$\lvert b\rvert$	$P_{m\sigma}{}^*$	$(\beta_1{}^*)^2$	$(P_{m\pi}{}^*)_{xz}$	$(P_{m\pi}{}^*)_{yz}$
Uncomplexed chelate in chloroform–toluene (60 : 40) glass	(I)	0·77	0·989	0·0034	0·75	0·90	0·83	0·94
	(II)	0·78	0·995	0·0094	0·76	0·91	0·83	0·90
	(III)	0·64	0·965	0·041	0·76	0·90	0·95	0·83
	(V)	0·68	0·984	0·033	0·74	0·89	0·91	0·84
Ethanol-chelate complex in chloroform–toluene (60 : 40) glass	(I)	0·72	0·985	0·0180	0·72	0·87	0·99	1·02
	(II)	0·72	0·995	0·022	0·71	0·86	0·99	1·01
	(III)	0·73	0·979	0·013	0·76	0·91	0·80	0·82
	(IV)	0·72	0·982	0·013	0·75	0·90	0·80	0·82
	(V)	0·73	0·989	0·014	0·72	0·87	0·87	0·84
Pyridine–chelate complex in pyridine–toluene glass	(I)	0·74	0·972		0·74	0·89	0·89	0·89
	(II)	0·74	0·965	0·0078	0·76	0·91	0·87	0·94
	(III)	0·70	0·950	0·0068	0·74	0·89	0·77	0·79
	(IV)	0·71	0·953	0·0072	0·73	0·88	0·77	0·79
	(V)	0·72	0·970	0·009	0·71	0·86	0·83	0·81
	(VI)	0·72	0·970	0·008	0·71	0·86	0·90	0·84

(ii) In the five-membered ring chelates, the contribution from the metal ion $3d_{z^2}$ orbital, (b^2), to $\psi(A_1)$ is considerably larger than the corresponding contribution in the six-membered ring systems. When a solvent molecule is incorporated into the sixth co-ordination position of the vanadium ion, this contribution is increased in the six-membered ring chelates and is reduced in the five-membered ring systems.

(iii) $|c^2|$ Is less than 0·01. $|c|$ Values can be estimated from the isotropic contributions, a, to ^{51}V hyperfine coupling listed in Table 1: a values for five-membered ring chelates are markedly smaller than those for six-membered ring species and they can be used to distinguish the two types of chelate. The first term on the right of equation (14) is the isotropic contribution to hyperfine coupling. The second term, the indirect dipolar contribution, arises from the fact that both the ^{51}V nuclear spin and the spin of the unpaired electron are coupled to the orbital motion of the electron.[28] It contributes approximately −0·0004 cm^{-1} to the isotropic coupling, and hence the contact contributions are about −0·0105 and −0·0090 cm^{-1} for six- and five-membered ring chelates respectively. The near constancy of the $(\beta_2{}^*)^2$ values in Table 2 shows that the difference in these contact contributions is not due to different degrees of delocalisation of the unpaired electron on to the ligands in five- as compared with six-membered ring species.

The different contact contributions can be accounted for if the five-membered ring chelates have an additional amount of 4*s* character in the $\psi(A_1)$, orbital. This additional, direct, 4*s* contribution to hyperfine coupling is positive and opposes the negative contribution due to spin polarisation by the *d*-character in this orbital. If it is assumed that the spin polarisation contributes −0·0100 cm^{-1} in all of the uncomplexed chelates, then the direct 4*s* contributions in compounds (III) and (V) are *ca.* +0·0017 and +0·0010 cm^{-1} respectively. Clementi's wave functions [30] lead to direct contributions per 4*s* electron of 0·0850 and 0·1560 cm^{-1} respectively, for the vanadium configurations V ($\cdots 3d^3 4s^2$) and V^+ ($\cdots 3d^2 4s^2$). Hence the 4*s* contribution to hyperfine coupling in the configuration appropriate to the vanadyl chelates is *ca.* +0·1100 cm^{-1}. The $\psi(A_1)$ orbital in the five-membered ring chelates therefore contains a maximum of 1% 4*s* character, *i.e.* $(c^2) < 0{\cdot}01$. The $3d_{z^2}$ and the 4*s* contributions to the $\psi(A_1)$ orbital are both due to the C_{2v} component of the ligand fields in these systems, and so it is reasonable to expect that the five-membered ring complexes which exhibit largest in-plane anisotropy in the spin Hamiltonian should also have larger 4*s* contributions to hyperfine coupling, and hence have smaller $|a|$ values, as is observed. In this context it is significant that solvation decreases the

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anisotropy in the five-membered ring systems, reduces the amount of 4*s* character in the $\psi(A_1)$ orbital, and increases the $|a|$ values in these compounds.

In-plane σ-Bonding: Estimation of $(\beta_1{}^*)^2$.—The metal orbital population, $(P_{m\sigma}{}^*)$, can be deduced from (8) provided the energy, ΔE_{xy}, for the transition $\psi(A_2) \leftarrow \psi(A_1)$ is known. $(\beta_1{}^*)^2$ Can then be obtained from the relationships

$$P_{m\sigma}{}^* = (\beta_1{}^*)^2 - (\beta_1{}^*)(\beta_1{}^*)'S$$

and
$$(\beta_1{}^*)^2 + (\beta_1{}^{*\prime})^2 - 2(\beta_1{}^*)(\beta_1{}^*)'S = 1$$

where S is the group overlap integral for the in-plane σ-bond. In vanadyl acetylacetonate, S has been shown [2] to be 0·25 and we have assumed that this value is also valid for compounds (II)—(VI). The frequencies of the band maxima observed in the visible-u.v. absorption spectra of compounds (I)—(VI) are given in Table 3. There appears to be some confusion in the literature about the nature of these maxima [17,31,32] and so we have used equation (8) to assign them to the electronic transitions available to vanadyl chelates. This procedure is valid since solvent molecules only slightly affect the in-plane π-bond and they can therefore exert only a minor influence on the nature of the in-plane σ-bond. We have found that, for the six-membered ring chelates (I) and (II), ΔE_{xy} must therefore be equated to the energies in the column headed ΔE_3 in Table 3: assigning either ΔE_1 or ΔE_2 to this transition results in unacceptably large changes in the estimated metal orbital populations and in unreasonably large delocalisation of the electrons in the σ-bonds on solvation. Assignment of the band maxima ΔE_3 to the transition energies ΔE_{xy} for the five-membered ring chelates then yields metal orbital population values, $P_{m\sigma}{}^*$, which are similar to those deduced for the six-membered ring species: any other assignment leads to very large differences in the metal orbital populations. Values of $P_{m\sigma}{}^*$ and of $(\beta_1{}^*)^2$ obtained for complexes (I)—(VI) are in Table 2. There is more delocalisation of electrons in the in-plane σ-bonds than in the in-plane π-bonds.

TABLE 3

Band maxima (cm^{-1}) in the visible-u.v. absorption spectra of compounds (I)—(VI). Solubility problems prevented some spectra in toluene and in ethanol from being observed

Compound	Solvent	ΔE_1	ΔE_2	ΔE_3	ΔE_4
(I)	Toluene	15,100		16,800	25,400
(II)	,,	14,800		16,800	21,500
(I)	Chloroform	15,000		16,800	25,600
(II)	,,	14,800		16,900	21,500
(III)	,,	13,300	16,600	18,500	
(IV)	,,	13,300	16,600	18,500	
(V)	,,	13,300	16,600	18,200	
(VI)	,,	13,300	16,600	18,200	
(I)	Ethanol	12,800		17,200	26,000
(II)	,,	12,700		17,200	21,500
(I)	Pyridine	13,000		17,200	
(II)	,,	13,000		17,300	21,500
(III)	,,	11,900	13,000	16,400	
(IV)	,,	11,900	13,000	16,400	
(V)	,,	11,800	13,000	16,400	21,000
(VI)	,,	11,800	13,000	16,400	21,000

Out-of-plane π-Bonding.—The metal orbital populations $(P_{m\pi}{}^*)_{xz}$ and $(P_{m\pi}{}^*)_{yz}$ for out-of-plane π-bonding in the *xz* and *yz* planes can be estimated from equations (9) and (10) provided the energies ΔE_{xz} and ΔE_{yz} for the transitions $\psi(B_1) \leftarrow \psi(A_1)$ and $\psi(B_2) \leftarrow \psi(A_1)$ are known. Assigning ΔE_1 and ΔE_2 in Table 3 to ΔE_{yz} and ΔE_{xz} respectively, yields the $(P_{m\pi}{}^*)_{xz}$ and $(P_{m\pi}{}^*)_{yz}$ values listed in Table 2. These are individually reliable to ±0·05 and there is therefore no measured difference in the degree of π-bonding in the *xz* and *yz* planes. Although differences in $P_{m\pi}{}^*$ values may exert a minor influence, (9) and (10) show that the differences in the tensor components g_{xx} and g_{yy} are essentially due to a combination of effects which arise from the small contributions from the vanadium $3d_{z^2}$ orbital to the $\psi(A_1)$ orbital which contains the unpaired electron and from differences in the transition energies ΔE_{xz} and ΔE_{yz}. Our mean $P_{m\pi}{}^*$ values are rather larger than the values of 0·74 calculated from the data obtained by Ballhausen and Gray [1] in their molecular orbital analysis of the $VO(H_2O)_5{}^{2+}$ ion, but are consistent with their picture of substantial π-bonding in the V=O fragments in these chelates. The data in Table 2 show that the mean $P_{m\pi}{}^*$ value is reduced when a sixth ligand is co-ordinated to the five-membered ring chelates, *i.e.* the mean $P_{m\pi}$ value of the corresponding bonding orbitals is then increased. In the five-membered ring complexes, π-bonding of the vanadium ion to its ligands is therefore enhanced when a sixth ligand is co-ordinated.

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