Electron Spin Resonance Studies on some Perfluoropinacolates of Vanadium(IV) and Chromium(V)

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E.s.r. and optical spectral measurements of solutions of the perfluoropinacolate(2−) (pfp) derivatives of vanadium(IV) and chromium(V), $[VO(pfp)_2]^{2-}$ and $[CrO(pfp)_2]^-$, in a range of solvents have been carried out. Analysis of the bonding parameters suggests strong hydrogen bonding in water between the vanadyl or chromyl oxygen atom and the solvent, with the water molecule bonded in the vertical plane which does not include the pfp ligand. There is negligible solvent interaction with the vacant sixth co-ordination position. The choice of values for the spin–orbit coupling parameter ξ and the hyperfine parameter P for use in the calculations of bonding parameters is discussed.

THE existence of complexes of chromium(V) with halogens of the type $[CrOX_5]^{2-}$ is now well established. However, no alkoxides of chromium(V) have, until recently,[1] been described despite their existence with chromium(IV). Chromates readily react in acid solution with perfluoropinacol, $(F_3C)_2C(OH)C(OH)(CF_3)_2$ (H_2pfp), to yield blue or purple salts of the type $M[CrO(pfp)_2]$ ($M = K^+$, Cs^+, or $[Et_4N]^+$). The corresponding salts of V^{IV} and Cu^{II}, $K_2[VO(pfp)_2]$ and $K_2[Cu(pfp)_2]$, have also been prepared. The colour and optical spectrum of the chromium complex is rather different from that normally expected for Cr^V. We decided, therefore, to investigate the optical and e.s.r. spectra of the chromium and vanadium complexes and to monitor their solvent dependence with a view to understanding more of the structure and bonding in the complexes.

EXPERIMENTAL

The complexes were prepared as described in the preliminary publication.[1] E.s.r. spectra were recorded at 77 K on a Varian E3 spectrometer using diphenylpicrylhydrazide as a g marker, and at Q-band frequencies. Optical spectra were recorded on a Unicam SP 700 spectrophotometer and the spectra analysed using a Dupont curve resolver. Diffuse-reflectance spectra were recorded on a Beckman DK-2B spectrophotometer. Solvents used were

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[1] C. J. Willis, *J.C.S. Chem. Comm.*, 1972, 944.

the best commercially available and dried with molecular sieves. The complexes were only soluble in the more-polar solvents.

RESULTS AND DISCUSSION

Vanadyl Complex.—Frozen-solution e.s.r. spectra of the complex in a range of solvents could all be interpreted in terms of a species having axial symmetry and hyperfine coupling arising from interaction of an unpaired electron with a nucleus having $I = \frac{7}{2}$ (^{51}V). Hyperfine couplings were corrected to second order and a summary of the experimental $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, and $A_{\perp}$ values is given in Table 1. The absence of any splitting of the perpendicular feature was confirmed by recording the spectrum at *Q*-band frequencies. The optical spectra measured at room temperature consisted of four resolved peaks which were centred around 14 000, 16 000, 18 000, and 25 000 cm^{-1}. The spectra were all solvent dependent and the positions of the absorption maxima are summarised in Table 1 for each solvent. The spectrum differs from that of many other vanadyl complexes in that four rather than three absorptions are observed.[2-5] This is interpreted in terms of a splitting of the lowest-energy absorption, which is usually degenerate, because of the reduced symmetry of the molecule. However, it should be emphasised that no splitting of the perpendicular features in the e.s.r. spectrum was detected and hence the splitting of the lowest-energy absorption is likely to be only small.

TABLE 1

E.s.r. and optical data for $K_2[VO(pfp)_2]$ in various solvents

Solvent	E_T	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$/ 10^{-4} cm^{-1}	$A_{\perp}$/ 10^{-4} cm^{-1}	ΔE_{yz}/ cm^{-1}	ΔE_{xz}/ cm^{-1}	ΔE_{xy}/ cm^{-1}	E_4/ cm^{-1}
H_2O	63·1	1·957	1·968	144	39·1	13 200	15 400	18 100	24 700
MeOH	55·5	1·951	1·978	141	41·7	13 500	15 700	18 300	24 600
EtOH	51·9	1·955	1·981	143	42·5	14 200	15 900	18 300	24 900
Pr^{n}OH	50·7	1·947	1·976	148	45·1	13 800	16 000	18 500	25 200
CH_3CN	46·0	1·955	1·975	153	39·8	14 200	15 900	18 100	25 400
dmf [a]	43·8	1·951	1·980	143	44·5	14 000	15 850	17 900	25 200
C_5H_5N	40·2	1·948	1·979	151	46·2	14 750	16 450	18 700	25 800
Et_2O	34·6	1·949	1·982	155	47·3	14 350	16 450	18 700	25 800

[a] Dimethylformamide.

The e.s.r. and optical spectra may readily be interpreted in terms of the single unpaired electron in an A_1 molecular orbital (m.o.) which is predominantly $d_{x^2-y^2}$. The axis notation is given in Figure 1 where the *z* axis goes through the vanadyl group and the *y* axis bisects the chelate ligands. The point group is C_{2v}, being a weak perturbation of the dominant C_{4v} point group of many vanadyl complexes. With the unpaired electron in A_1, spin–orbit coupling will mix the orbitals such that $g_{\parallel} < g_{\perp} < 2$.[6] Furthermore, the signs of the vanadium hyperfine splittings must be negative in order to make both A_{aniso} and A_{iso} negative. The optical spectrum is readily assigned by comparison with that of many related vanadyl complexes which have been thoroughly analysed.[2-5] The three lowest-energy transitions are thus assigned ΔE_{yz} ($E_{d_{yz}} - E_{d_{x^2-y^2}}$), ΔE_{xz} ($E_{d_{xz}} - E_{d_{x^2-y^2}}$), and ΔE_{xy} ($E_{d_{xy}} - E_{d_{x^2-y^2}}$). There is some doubt about the assignment of the fourth transition, E_4, it being either $E_{d_{x^2-y^2}} \rightarrow E_{d_{z^2}}$ or a charge-transfer (c.t.) band.[2-4] In either case it does not feature in any of the subsequent calculations.

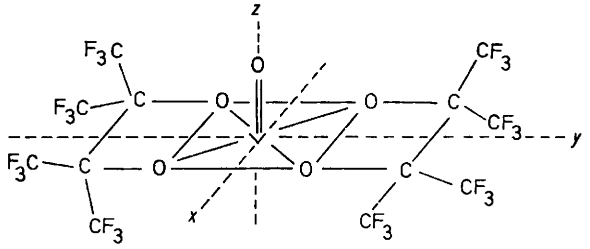

FIGURE 1 Axis notation for $[VO(pfp)_2]^{2-}$

Bonding parameters: theory. Although the unpaired electron is in a predominantly metal $d_{x^2-y^2}$ orbital, the symmetry is such that the metal $3d_{z^2}$ and $4s$ orbitals can also mix with it. Hence the ground state should best be described by the linear combination (1), where

$$\psi = ad_{x^2-y^2} + bd_{z^2} + cs \qquad (1)$$

$a \gg b,c$. In m.o. theory, this metal-ion orbital combines with ligand-group orbitals of appropriate symmetry, and the unpaired electron is in the $\psi(A_1)$ antibonding orbital. This and the other magnetically relevant antibonding m.o.s are given in equations (2)—(5). These basic functions are all perturbed by spin–orbit coupling, Zeeman and hyperfine interactions. The e.s.r. parameters may be expressed as functions of the coefficients of the orbitals (2)—(5). These functions have been shown to be [7] as in equations (6)—(11) where

$$\psi(A_1) = \beta_2^*(ad_{x^2-y^2} + bd_{z^2} + cs) - \beta_2^{*\prime}\psi_{L1} \qquad (2)$$

$$\psi(A_2) = \beta_1^*d_{xy} - \beta_1^{*\prime}\psi_{L2} \qquad (3)$$

$$\psi(B_1) = e_{\pi x}^*d_{xz} - e_{\pi x}^{*\prime}\psi_{L3} \qquad (4)$$

$$\psi(B_2) = e_{\pi y}^*d_{yz} - e_{\pi y}^{*\prime}\psi_{L4} \qquad (5)$$

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[2] See, for example, H. Kon and N. E. Sharpless, *J. Phys. Chem.*, 1966, **70**, 105.

[3] C. M. Guzy, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1969, 2791.

[4] D. Kivelson and S. K. Lee, *J. Chem. Phys.*, 1964, **41**, 1896.

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

[6] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

[7] B. R. McGarvey, *Transition-metal Chem.*, 1966, **3**, 89; M. A. Hitchman and R. L. Belford, *Inorg. Chem.*, 1969, **8**, 958.

P_σ^* and $P_{\pi x,y}^*$ are m.o. populations in the in-plane σ (xy plane) and out-of-plane π antibonding m.o.s

$$g_{zz} = 2{\cdot}0023 - (\Delta E_{xy})^{-1}[8a^2(\beta_2^*)^2 P_\sigma^* \xi] \qquad (6)$$

$$g_{xx} = 2{\cdot}0023 - (\Delta E_{xz})^{-1}[2a(a + 2\sqrt{3}b)(\beta_2^*)^2(P_{\pi x}^*)\xi] \qquad (7)$$

$$g_{yy} = 2{\cdot}0023 - (\Delta E_{yz})^{-1}[2a(a - 2\sqrt{3}b)(\beta_2^*)^2(P_{\pi y}^*)\xi] \qquad (8)$$

$$A_{zz} = P\left\{- \kappa - \frac{4}{7} a^2(\beta_2^*)^2 - \frac{1}{14}\frac{(3a + b\sqrt{3})}{(a - b\sqrt{3})}(2{\cdot}0023 - g_{yy}) - \frac{1}{14}\frac{(3a - b\sqrt{3})}{(a + b\sqrt{3})}(2{\cdot}0023 - g_{xx}) - (2{\cdot}0023 - g_{zz})\right\} \qquad (9)$$

$$A_{xx} = P\left\{- \kappa + \frac{2}{7} a^2(\beta_2^*)^2 - 4\frac{\sqrt{3}}{7} ab - (2{\cdot}0023 - g_{xx}) + \frac{1}{14}\frac{(3a + b\sqrt{3})}{(a - b\sqrt{3})}(2{\cdot}0023 - g_{yy}) - \frac{1b}{7a}(2{\cdot}0023 - g_{zz})\right\} \qquad (10)$$

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

respectively, $P = g_e\beta_e g_N\beta_N\langle d_{x^2-y^2}|r^{-3}|d_{x^2-y^2}\rangle$, and ξ is the spin–orbit coupling constant for vanadium. The choice of values for P and ξ will be discussed later. Equations (6)—(11) can be solved by substituting experimental values for g, A, and the energies (*e.g.* $\Delta E_{xy} = E_{xy} - E_{x^2-y^2}$). Since the maximum value of c^2 was 0·02, and the bonding parameters were not significantly changed when c was put equal to zero, we took $c = 0$ for all subsequent calculations.

The σ-bonding parameter P_σ^* was deduced from the further relations (12) and (13) where S is the group

$$P_\sigma^* = (\beta_1^*)^2 - \beta_1^*\beta_1^{*\prime}S \qquad (12)$$

$$(\beta_1^*)^2 + (\beta_1^{*\prime})^2 + 2\beta_1^*\beta_1^{*\prime}S = 1 \qquad (13)$$

overlap integral for the in-plane σ-bond. In vanadyl pentane-2,4-dionate, S has been shown [4] to be 0·25 and we have assumed that this value is appropriate for our complex. The only remaining problem is the choice of values to be taken for P and ξ. This is not an easy matter because both parameters appear to be affected by covalency in the complex. Many attempts have been made to relate quantitatively the magnitude of the reduction in ξ and P with covalency. Owen [8] has shown experimentally that ξ is typically reduced 20—30% when the first-order equations for g are used, and that these should be modified to include the m.o. coefficients, *e.g.* P_σ and β_2^2 (in-plane π-bonding), as in (14).

$$g_z = 2 - (8P_\sigma\beta_2^2\xi/\Delta E_{xy}) \qquad (14)$$

Because of the relation between ξ and Z/r^3, where Z is the effective nuclear charge and r the distance of the electron from the nucleus, it was thought reasonable to use a smaller value for ξ such that $\xi' = k\xi_{(\text{free ion})}$.[9] It is not certain whether the whole of the observed reduction is caused by covalency, or whether there is a contribution from the natural expansion of the d-wave function due to a screening effect by the ligands.[10]

When the equations for g involve the bonding coefficients and ξ, the value of ξ to be used must be close to that of the charge of the free ion since ξ is being effectively reduced by the bonding coefficients. It is unlikely to be the value appropriate for the effective valence state of the metal in the complex as suggested, for example, by Stewart and Porte,[11] or Ballhausen and Gray,[5] which would involve a net reduction of the free-ion value of ξ twice. Whilst it could be argued that the bonding coefficient need not be the sole parameter for reducing ξ, it is probably the major one, and it is reasonable to use a value close to the free-ion value of ξ.

It may be appropriate to regard the problem in a different fashion. Our choice of basis states (2)—(5) takes into account, to a first approximation, the effect of covalency on the spin-Hamiltonian parameters (6)—(11) *via* the bonding coefficients. However, the radial dependence of the metal $d_{x^2-y^2}$ orbital will now be different from that of the free ion and it may be best to regard ξ, which is proportional to the expectation value $\langle d_{x^2-y^2}|\frac{1}{r}\frac{\partial V}{\partial r}|d_{x^2-y^2}\rangle$, as a parameter to be determined experimentally. It is our opinion that the value of ξ is close to that for the free 4+ ion, and we may surmise that the bulk of the contribution to the expectation value $\langle\frac{1}{r}\frac{\partial V}{\partial r}\rangle$ comes from a region where the electric field is such that the positively charged vanadium ion surrounded by the negatively charged ligands, looks, to the $3d$ electron, like V^{4+} in free space.

The parameter P, on the other hand, is proportional to $\langle r^{-3}\rangle$; ξ is only proportional to $\langle r^{-3}\rangle$ if the effective charge Z may be considered constant over the radial extent of the $3d$ function, and thus may be expected in fact to depend on higher inverse powers of r. Although $\langle r^{-3}\rangle$ has been used in the expression for P to absorb some other factors and complications,[12] it will still be determined mainly by the form of the $3d$ wave function at higher values of r than those which have the greatest effect on ξ, and where the screening of the nuclear charge by ligand electrons is greater. Thus the value of P is found to be close to free-ion values for lower charge. As we shall see later, the bonding parameters are very sensitive to the value of P chosen and, indeed, the value of P may vary from one compound to another

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[8] J. Owen, *Proc. Roy. Soc.*, 1955, **A227**, 183.

[9] K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, 1965, **42**, 1019.

[10] W. Marshall and R. Stuart, *Phys. Rev.*, 1961, **123**, 2048.

[11] C. P. Stewart and A. L. Porte, *J.C.S. Dalton*, 1972, 1661.

[12] A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions,' Clarendon Press, Oxford, 1970, p. 710.

even if the formal oxidation state remains constant. In the calculations on the vanadyl complex, ξ was taken as 248 cm^{-1} (V^{4+})[13] and $P = 0{\cdot}0110$ cm^{-1}.

Experimental bonding parameters. Initially, the value of P used was that appropriate for an ion with charge two less than the nominal charge (0·0128 cm^{-1}).[6] However, this yielded values of $P_{\pi x}{}^*$ for water as solvent in excess of one. By reducing P to 0·0110 cm^{-1}, then $P_{\pi x}{}^*$ was reduced from 1·16 to 0·99. This value was used in all calculations. The range of computed values, for the vanadyl complex in various solvents, were $P_\sigma{}^*$ 0·37—0·50, $P_{\pi x}{}^*$ 0·62—0·99, $P_{\pi y}{}^*$ 0·54—0·85; $\beta_2{}^*$ was close to one for all solvents. The values are recorded in Table 2. In general, low values of $P_\sigma{}^*$ are associated with high values of $P_{\pi x}{}^*$ and $P_{\pi y}{}^*$. In water, the values of $P_{\pi x}{}^*$ and $P_{\pi y}{}^*$ were significantly higher than those for other solvents. There was no clear relation between bonding parameter and solvent for the remaining solvents, the range of values being only slightly larger than the error (±0·05).

TABLE 2

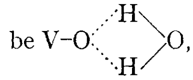
Molecular orbital coefficients and metal orbital populations of $K_2[VO(pfp)_2]$ in various solvents

Solvent	In-plane σ P_σ	In-plane π $\beta_2{}^2$	Out-of-plane π_x $P_{\pi x}$	Out-of-plane π_y $P_{\pi y}$
H_2O	0·38	1·05	0·99	0·85
MeOH	0·47	1·00	0·77	0·66
EtOH	0·43	1·02	0·67	0·60
Pr^{n}OH	0·50	1·04	0·82	0·71
CH_3CN	0·37	1·05	0·76	0·68
dmf [a]	0·47	0·99	0·72	0·63
C_5H_5N	0·48	1·05	0·73	0·65
Et_2O	0·46	1·05	0·62	0·54

[a] Dimethylformamide.

In-plane π-bonding. The value of $(\beta_2{}^*)^2$ is close to one for all solvents and shows that in-plane π-bonding can be ignored. The absence of in-plane π-bonding shows that the $V(O{-}C)_4$ fragments of the complex are planar with a V–O–C bond angle close to 120° (sp^2 hybridised oxygen). Were the angle to be significantly different from 120°, there would be some p orbital in the xy plane available for π-bonding. This situation is similar to that found in copper phthalocyanin.[14] The unpaired electron is localised on the vanadium ion and solvents, not unreasonably, have no effect on the nature of in-plane π-bonding.

σ-Bonding. There is considerable covalency in the metal–ligand σ-bond and, like the in-plane π-bond, it is not very dependent on solvent, the range of values being almost within experimental error.

Out-of-plane π-bonding. The computed values of $P_{\pi x,y}{}^*$ represent the metal orbital populations in the π-antibonding orbitals. The population in the chemically more relevant π-bonding m.o.s, $P_{\pi x,y}$, cannot be readily deduced from these values, but, in general, a large value of $P_{\pi x,y}{}^*$ would be associated with a small value of $P_{\pi x,y}$. With water as solvent, $P_{\pi x}{}^* = 0{\cdot}99$ and $P_{\pi y}{}^* = 0{\cdot}85$. It follows that the value of $P_{\pi x}$ will be close to zero and $P_{\pi y}$ rather small. These results indicate that there is very little π-bonding and that the electrons which are potentially involved in π-bonding are localised on the ligand, in this case the vanadyl oxygen atom. In contrast, in other solvents there is much more π-bonding with $P_{\pi y}$ probably greater than $P_{\pi x}$. The considerable effect water has as a solvent on the bonding in the vanadyl complex can be readily attributed to hydrogen bonding at the vanadyl oxygen atom. The orientation of the water molecule could be  $\mathrm{V{-}O}\begin{matrix}\cdots\mathrm{H}\\ \cdots\mathrm{H}\end{matrix}\mathrm{O}$, with the water mainly in the xz plane where it can have greatest effect and where it results in minimum π-bonding. This is also the most sterically favoured orientation, since the chelating ligands will almost certainly have the effect of reducing the intrachelate O–V–O bond angle below 90°, by analogy with oxalate complexes where the intrachelate O–M–O bond angle is typically 75—77°.[15] The result is that the equatorial oxygen atoms form a rectangle rather than a square.

The absence of significant solvent effects with solvents other than water reflects their weaker H-bonding capabilities and the absence of significant interaction of solvent in the vacant sixth co-ordination position. It is interesting to note that in pyridine the bonding parameters are not significantly different from those in *NN*-dimethylformamide (dmf) or methanol. This contrasts with the usual behaviour of pyridine which can co-ordinate strongly, and where actual adducts can often be isolated.[3,16] We attribute the absence of adduct formation to steric crowding of the vacant sixth co-ordination position by the perfluoromethyl groups.

The first and second optical absorptions are slightly solvent dependent, as illustrated by Figure 2 where they are plotted against the E_T value of the solvent.[17] Both absorptions decrease in energy as E_T increases. Hydrogen bonding and other strongly solvating solvents with large E_T interact with the vanadyl oxygen atom and reduce the π-bonding of the oxygen $p_{x,y}$ orbitals with the metal $d_{xz,yz}$ orbitals. The result is that the B_1 and B_2 bonding m.o.s are destabilised and the corresponding $B_1{}^*$ and $B_2{}^*$ antibonding m.o.s are stabilised. The effects are small and are not reflected in the calculated values of $P_\pi{}^*$ because of the uncertainty in $P_\pi{}^*$.

Choice of values for ξ and P. Because of the controversy over the choice of values for ξ and P, we decided to compute values for the bonding parameters for different values of ξ and P appropriate for differing effective charges on the metal ion. The results are given in Table 3 for the case of the vanadyl complex in water and varying the effective ionic charge from 4+ to 1+. Only with the combination of ξ for 4+ and

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[13] T. M. Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441.

[14] C. M. Guzy, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1969, 2229.

[15] W. B. Scheidt, C. Tsai, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1971, **93**, 3867; R. Deyreux and A. Peneloux, *Bull. Soc. chim. France*, 1969, 2675.

[16] R. L. Carlin and F. A. Walker, *J. Amer. Chem. Soc.*, 1965, **87**, 2128; M. M. Jones, *ibid.*, 1954, **76**, 5995.

[17] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

P for 1+ or 2+ does an acceptable group of bonding parameters appear, *i.e.* acceptable in that all values are close to or less than one. This supports our earlier assertions that the value chosen for ξ should be near that of the formal charge on the ion and that for P near the value appropriate for the effective charge on the ion. We are clearly unable to justify exactly what value of P to select, and we have arbitrarily chosen 0·0110 cm^{-1}. While the absolute value of bonding parameters for a family of complexes may be unreliable, the relative values are meaningful *provided that* P remains constant from one molecule to another, an assumption which is not necessarily valid. It is pointless comparing our results with those of other workers, since often different assumptions have been made concerning the value of ξ or P to be used. Furthermore, since the magnitude of bonding parameters can vary so dramatically if different values of ξ and P are selected, then many of the published bonding parameters could be worthless.

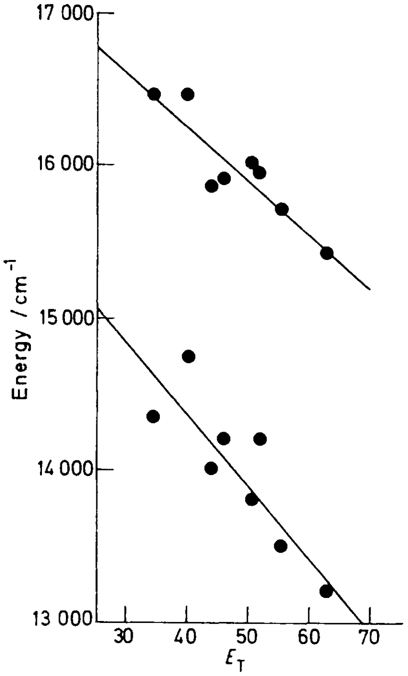

FIGURE 2 Solvent dependence of the first two optical absorptions as a function of E_T value. The straight lines are drawn from least-squares calculations

TABLE 3

Variation of the bonding parameters with ξ and P for the vanadyl complex in water

Spin–orbit coupling constant ξ cm^{-1}	Hyperfine coupling parameter, P/cm^{-1}			
	0·0172 (4+)	0·0150 (3+)	0·0128 (2+)	0·0108 (1+)
248	0·61 [b]	0·53	0·45	0·38
(4+) [a]	1·58 [c]	1·37	1·16	0·97
	1·36 [d]	1·17	0·99	0·83
	0·67 [e]	0·78	0·92	1·09
210	0·73	0·63	0·53	0·45
(3+)	1·87	1·62	1·37	1·15
	1·60	1·39	1·17	0·98
	0·67	0·78	0·92	1·09
170	0·90	0·78	0·66	0·55
(2+)	2·31	2·00	1·69	1·42
	1·98	1·71	1·45	1·22
	0·67	0·78	0·92	1·09
136	1·12	0·97	0·82	0·69
(1+)	2·89	2·50	2·12	1·77
	2·47	2·14	1·81	1·52
	0·67	0·78	0·92	1·09

[a] Number in parentheses is the charge on the metal atom appropriate to the value of ξ or P given. [b-e] are, respectively, P_σ^*, $P_{\pi x}^*$, $P_{\pi y}^*$, and $(\beta^*)^2$.

Chromyl Complex.—E.s.r. measurements on the complex in a range of solvents at 77 K yielded poorly resolved spectra, and it was only possible to get a well resolved spectrum in dmf. The spectrum differed considerably from that of the vanadyl complex in that three well separated g features were apparent. On either side of two of the features, satellite lines arising from interaction of the unpaired electron with the ^{53}Cr nucleus ($I = \frac{3}{2}$, 9·54%) were detected. The spectrum was characterised by having $g_z = 1·9737$, $g_x = 1·9852$, and $g_y = 1·9772$ (which is consistent with $g_{av} = 1·9794$ obtained in fluid solution at room temperature). Hyperfine coupling was observed on g_z and g_x and equalled 35·1 and 14·8 G respectively. No hyperfine splitting on the y feature was detected and this suggested a very small value. Since the isotropic hyperfine coupling was 15·66 G, then A_y could be deduced, assuming A_{iso} is negative and A_z and A_x are also both negative, to give a value of +3·1 G. This was confirmed by a computer simulation of the spectrum and by recording the spectrum at Q-band frequencies. The optical spectrum consisted of four peaks at *ca.* 17 000, 26 000, 28 500, and 32 000 cm^{-1}. The position of the 28 500 and 32 000 cm^{-1} absorption maxima were solvent dependent but that of the 17 000 and 26 000 cm^{-1} absorptions were not. The results are summarised in Table 4.

TABLE 4

Optical data for K[CrO(pfp)$_2$] in various solvents

Solvent	Transitions/cm^{-1}
H_2O	17 550, 26 000, 28 700
MeOH	17 300, 25 800, 28 750
EtOH	17 100, 25 700, 28 300
Pr^{n}OH	17 300, 25 700, 27 950
CH_3CN	17 100, 25 750, 28 300
dmf	17 300, 25 450, 28 800
C_5H_5N	17 100, 26 100, 29 000
Et_2O	17 500, 25 650, 29 000

The e.s.r. parameters and optical absorptions for the chromyl complex are much more difficult to interpret than those for the vanadyl complex. It is apparent that there is considerable distortion in the xy plane such that the degeneracy of $g_\perp$ and $A_\perp$ has been completely removed. It follows, further, that the optical spectrum is not easily interpreted by analogy with the vanadyl complex. It is not possible to analyse the optical spectra simply by comparison with that of related chromyl complexes since no single-crystal study has been carried out on any chromyl(V) complex. The few attempts at interpretation of chromyl spectra have involved complexes with C_{4v} symmetry, *e.g.* $[CrOCl_5]^{2-}$.[18]

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[18] H. Kon and N. E. Sharpless, *J. Chem. Phys.*, 1965, **42**, 906.

Since 17 000 and 26 000 cm^{-1} absorptions in our complex are not solvent dependent *and* have related absorptions in $[CrOCl_5]^{2-}$, then we assign them to the same transitions, namely $A_2(d_{xy})\rightarrow A_1(d_{x^2-y^2})$ and $A_1(d_{x^2-y^2})\rightarrow A_2{}^*(d_{xy})$ where $A_2(d_{xy})$ is a filled bonding m.o. These transitions for $[CrOCl_5]^{2-}$ seem reasonable and have been accepted by others. We propose that the transition equivalent to that at 13 200 in $[CrOCl_5]^{2-}$ has been split by the reduced symmetry such that the upper level is at *ca.* 28 500 cm^{-1} and the lower level is <7 000 cm^{-1} (above the ground state) and not actually observed. This proposal is supported by the observation that the 28 500 cm^{-1} transition is solvent dependent. This is a large splitting, but is entirely consistent with the large separation of g_x and g_y. The transition at *ca.* 32 000 cm^{-1} could be the $A_1(d_{x^2-y^2})\rightarrow A_1{}'^*(d_{z^2})$, but does not feature in the calculations.

The bonding parameters. Reasonable values of the bonding parameters (*i.e.* all values $\leqslant 1$) can be obtained for $P = 0{\cdot}00343$ cm^{-1} (ref. 6) (appropriate for Cr^{2+}) if $\Delta E_{yz} \leqslant 1\,800$ cm^{-1}, or for $P = 0{\cdot}00394$ cm^{-1} (appropriate for Cr^{3+}) if $\Delta E_{yz} \leqslant 4\,500$ cm^{-1}, with in both cases $\xi = 380$ cm^{-1}. Since it is impossible to be precise about the exact magnitude of P, then we cannot estimate ΔE_{yz} more precisely than $\leqslant 4\,500$ cm^{-1}. Unfortunately, inspection of the diffuse-reflectance spectrum did not help because of the presence of several features in the 4 000 cm^{-1} region which could have been overtones of vibrations. If we take $P = 0{\cdot}00394$ cm^{-1} and $\Delta E_{yz} = 4\,000$ cm^{-1}, then we can calculate the following values for the bonding coefficients $P_\sigma{}^*$, $P_{\pi x}{}^*$, $P_{\pi y}{}^*$, $(\beta_2{}^*)^2$, namely 0·31, 0·48, 0·87, and 0·80. Small changes in P or ΔE_{yz} will modify these values slightly, but not alter their relative magnitudes. No other combination of e.s.r. data with the optical absorption, nor a reduction in the value of ξ from the free-ion value, yielded acceptable bonding parameters.

These values may be compared with the corresponding values for the vanadyl complex in the same solvent, dmf (Table 2). The bonding σ-electrons are more on the metal (P_σ is higher) and this presumably arises because of the higher charge on the metal attracting the electrons. The unpaired electron is somewhat delocalised over the equatorial ligand atoms. We postulate that this arises, not from a radial expansion of the electron wave function, but from the opportunity of direct overlap with part of an in-plane p orbital on each oxygen. This could be present if the Cr–O–C bond angle is increased so that the hybridisation at the O is $sp^{<2}$, thus leaving some p orbital available for overlap. It is interesting that the total amount of π-bonding ($P_{\pi x}{}^* + P_{\pi y}{}^*$) is the same in both the vanadyl and chromyl complexes. However, the relative distribution is very different. There is more π-bonding in the xz plane (almost perfectly covalent), but in the yz plane $P_{\pi y}$ is now very much smaller, probably arising from elongation of the ligand because of the increase in the Cr–O–C bond angle. This would have the effect of making the p_z oxygen orbitals further away from the chromium and less amenable to overlap.

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