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Electron Spin Resonance Spectra of Dibromo- and Dichloro-complexes of Vanadium(IV)

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Reactions of $SOCl_2$ or $SOBr_2$ with a range of 20 vanadyl complexes, $[VO(L_4)]\cdot$ (L_4 = quadridentate or two bidentate ligands), yield solutions containing *cis*- or *trans*-dihalogen vanadium(IV) complexes $[VX_2(L_4)]$. They are characterised by their e.s.r. spectra and in most cases the unpaired electron is in a $d_{x^2-y^2}$ orbital. In some cases both *cis* and *trans* isomers can be detected and characterised, because of significant differences in e.s.r. parameters. In the case of $[VX_2(L_4)]$ [X = Cl or Br, L_4 = tropolonate or perfluoropinacolate], the unpaired electron is in a d_{z^2} orbital and the structure is thought to be trigonal prismatic.

THE chemistry of vanadium(IV) is dominated by the stable VO^{2+} ion which forms a wide variety of complexes in which the VO^{2+} unit maintains a discrete existence. Most complexes are of the type $[VO(L/_4)]$ (L_4 = quadridentate or two bidentate ligands) which may weakly add a fifth ligand in basic solvents. Six-co-ordinate complexes of the simple V^{4+} ion are uncommon and have been little studied. Recently it was found that direct reaction of vanadyl complexes with thionyl bromide or thionyl chloride readily yielded *trans*-dibromo- or -dichlorovanadium(IV) complexes respectively.[1] We have measured the e.s.r. spectra of 20 complexes of this type with a wide range of equatorial ligands. Detailed analysis of the spin-Hamiltonian parameters has yielded bonding parameters and a description of the ground-state molecular orbital for each complex. We have compared these parameters with those for the corresponding VO^{2+} complex.

EXPERIMENTAL

All the vanadyl complexes were prepared by standard methods, the references being given in Table 1. Dibromo- and dichloro-derivatives were prepared by dissolving the corresponding vanadyl complex directly in $SOBr_2$ or $SOCl_2$, or by dissolving the complex in an organic solvent and adding various proportions of $SOBr_2$ or $SOCl_2$. Thionyl bromide was prepared by reaction of $SOCl_2$ with KBr in liquid SO_2.[2] In the case of Schiff-base complexes and $[VO(acac)_2]$, $[VO(bzac)_2]$, $[VO(dbm)_2]$, $[VO(dbms)_2]$, and $[VO(trop)_2]$, the dichloro-derivatives precipitate from benzene solutions after addition of stoicheiometric amounts of $SOCl_2$. These are dark coloured substances, rapidly hydrolysed in air to vanadyl complexes. E.s.r. spectra were measured at temperatures between −40 and 20 °C, the optimum temperature varying with the complex, and also as frozen solutions at 77 K. Spectra were recorded on a Varian E3 *X*-band spectrometer and some also at *Q*-band frequencies. The spectra of the parent $[VO(L_4)]$ complexes in the same organic solvent as for $[VCl_2(L_4)]$ and $[VBr_2(L_4)]$ were also recorded so that a self-consistent set of results could be obtained. Conductivity measurements were carried out in $SOCl_2$–CH_2Cl_2, $SOBr_2$–CH_2Cl_2, $CHCl_3$, or toluene solution on a model OK–102/1 conductivity bridge. In all cases, no electrical conductivity could be detected.

RESULTS AND DISCUSSION

Ease of Reaction with $SOCl_2$.—Upon addition of $SOCl_2$ to vanadyl complexes, there was usually a rapid reaction to form a dark green or blue solution. In the case of bi- and quadri-dentate Schiff-base complexes, and with acac, bzac, dbm, dbms, pfp, and trop ligands, there was always reaction to completion in both pure $SOCl_2$ and with $SOCl_2$–organic solvent mixtures. The choice of organic solvent was important, however. Reaction only took place if the solvent was toluene, benzene, 1,2-dichloroethane, chloroform, nitrobenzene, dimethylformamide (dmf), diethylformamide (def), dimethylacetamide (dma), or diethylacetamide (dea). With strong bases such as pyridine, quinoline, isoquinoline, or picoline there was no visible reaction, yet the e.s.r. signal of the parent vanadyl complex was destroyed. With weaker bases such as alcohols, acetone, tetrahydrofuran (thf), dioxan, acetonitrile, ethyl acetate, triethyl phosphate, nitromethane, and diethyl ether, reaction, as judged by the e.s.r.

spectrum of a frozen solution, yielded an equilibrium mixture of unchanged [VO(L$_4$)] and [VCl$_2$(L$_4$)]. With hexane, heptane, and light petroleum, the vanadyl complexes were practically insoluble and no reaction took place. In dimethyl sulphoxide (dmso), there appeared to be a reaction of SOCl$_2$ with the solvent, since the solution boiled on addition of SOCl$_2$.

Reaction of vanadyl complexes of tfacac, hfacac, phen, and bipy with SOCl$_2$ was slow and could only be completed, even in pure SOCl$_2$, after boiling. With [VO(S$_2$CNEt$_2$)$_2$] the product solution was very unstable.

In all cases, excess of SOCl$_2$ was necessary to prevent hydrolysis of [VCl$_2$(L$_4$)] to [VO(L$_4$)] in mixtures with organic solvents even if all solvents were dried with molecular sieves. This was apparent if [VCl$_2$(L$_4$)] had been isolated from SOCl$_2$ and subsequently dissolved in a dried solvent; the e.s.r. spectrum always showed some VO^{2+} species to be present.

No reaction appeared to take place (or the reaction product was instantly destroyed) with the following vanadyl complexes, all of which would be described as having weak ligands: [VO(O$_2$CMe)$_2$], [VO(C$_2$O$_4$)]·2H$_2$O, [VO(SO$_4$)]·*n*H$_2$O, [VO(dmso)$_5$][ClO$_4$]$_2$, [VO(NC$_5$H$_5$)$_3$(NCS)$_2$], [VO][ClO$_{42}$·*n*H]$_2$O; Cs$_3$[VO(CN)$_5$] and [VO(bzim)$_4$][SO$_4$]·*n*H$_2$O (bzim = benzimidazole) were both insoluble in SOCl$_2$ and the solvents tried.

Reaction with SOBr$_2$.—In general, reaction of the vanadyl complexes with SOBr$_2$ was slower or incomplete. With [VO(acac)$_2$], [VO(bzac)$_2$], [VO(dbm)$_2$], [VO(salen)], [VO(acacen)], and [VO(phen)$_2$][SO$_4$], there was always some unchanged vanadyl complex, as judged by the e.s.r. spectrum. There was no evidence of reaction with [VO(tfacac)$_2$] and [VO(salphen)].

Treatment of Spectral Parameters.—Analysis of the e.s.r. spectra showed that there were basically two types. One, characterised by having all g values <2 and A_z large, was typical of a d^1 ion with the unpaired electron largely in a $d_{x^2-y^2}$ orbital. The other had one g value *ca.* 2 and the others <2, A_z small, and A_x and A_y large. This was typical of a d^1 ion with the unpaired electron mainly in a d_{z^2} orbital. In the following discussion, we take the symmetry of the *trans*-[VCl$_2$(L$_4$)] complexes as being C_s and so the unpaired electron is in an orbital of A' symmetry. The wavefunction of the ground state is given by equations (1) and (2). The frozen-solution

$$|\psi\rangle_0 = a|d_{z^2}\rangle + b|d_{x^2-y^2}\rangle \qquad (1)$$

$$a^2 + b^2 = 1 \qquad (2)$$

spectra were analysed using the expressions (3)—(8) derived from second-order perturbation theory by McGarvey [3] and presented in this format by Evans *et al.*[4]

$$A_x = -\kappa P + P[\alpha_x - (g_0 - g_x)] \qquad (3)$$

$$A_y = -\kappa P + P[\alpha_y - (g_0 - g_y)] \qquad (4)$$

$$A_z = -\kappa P + P[\alpha_z - (g_0 - g_z)] \qquad (5)$$

Thus from equations (2)—(8), the four unknowns a, b, P, and κ can be deduced. The orbital coefficients a and b allow us to make fruitful comparisons between [VO(L$_4$)] and [VCl$_2$(L$_4$)] species, as does the anisotropic hyperfine parameter $P = g_0 g_n \gamma_e \gamma_n \langle r^{-3} \rangle$ which gives direct information about electron delocalisation and covalency.

$$\alpha_x = \frac{-2}{7}(a^2 - b^2) - \frac{4 \times 3^{\frac{1}{2}}ab}{7}\left[1 - \frac{(g_0 - g_z)}{8b^2}\right] - \frac{3^{\frac{1}{2}}}{14}\frac{(a + b \times 3^{\frac{1}{2}})(g_0 - g_y)}{(a \times 3^{\frac{1}{2}} - b)} \qquad (6)$$

$$\alpha_y = \frac{-2}{7}(a^2 - b^2) + \frac{4 \times 3^{\frac{1}{2}}ab}{7}\left[1 - \frac{(g_0 - g_z)}{8b^2}\right] - \frac{3^{\frac{1}{2}}}{14}\frac{(a - b \times 3^{\frac{1}{2}})(g_0 - g_x)}{(a \times 3^{\frac{1}{2}} + b)} \qquad (7)$$

$$\alpha_z = \frac{4}{7}(a^2 - b^2) + \frac{3^{\frac{1}{2}}}{14}\left[\frac{(a + b \times 3^{\frac{1}{2}})(g_0 - g_y)}{(a \times 3^{\frac{1}{2}} - b)} + \frac{(a - b \times 3^{\frac{1}{2}})(g_0 - g_x)}{(a \times 3^{\frac{1}{2}} + b)}\right] \qquad (8)$$

The spin-polarisation parameter κ relates to $A_{\text{iso.}} = -\kappa P + (g_{\text{iso.}} - g_e)P$.

Complexes with Quadridentate Schiff Bases (N$_2$O$_2$).—The solutions from the reaction of SOCl$_2$ with [VO(acacen)], [VO(salen)], and [VO(salphen)] each yielded e.s.r. spectra at 77 K with sets of eight lines arising from interaction of the unpaired electron with a ^{51}V nucleus with $A_z > A_x = A_y$ and $g_z < g_x = g_y$. There was no observed splitting of the x and y features (Figure 1). The parameters are given in Table 2. There was no evidence for unreacted [VO(L$_4$)]. Spectra in SOBr$_2$ were almost identical, and with both the dichloro- and dibromo-forms the spectral parameters were almost independent of solvent, except that there was a lowering of g_x and g_y by 0.003 in dmf and other amide solvents. This lack of solvent dependence of the e.s.r. parameters has been observed before for vanadyl Schiff-base complexes [5] in contrast to [VO(acac)$_2$] where the e.s.r. parameters are very solvent dependent.[6] The e.s.r. para-

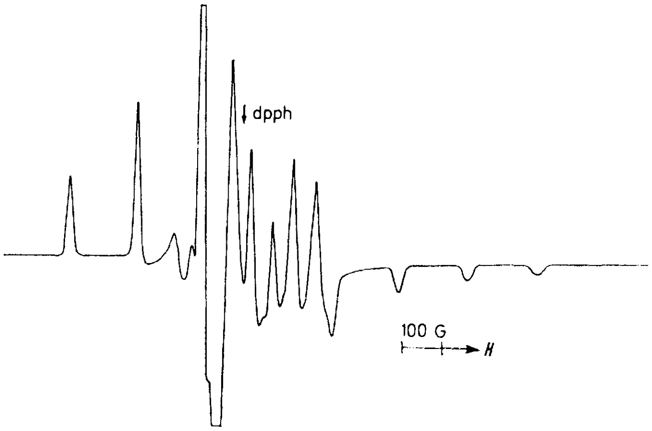
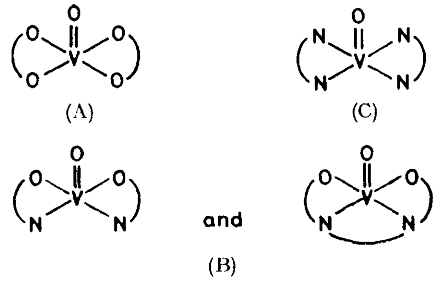


FIGURE 1 E.s.r. spectrum of a frozen solution of [VCl$_2$(acacen)$_2$] in toluene–CH$_2$Cl$_2$–SOCl$_2$ (3 : 7 : 10). dpph = Diphenylpicrylhydrazyl

meters and the absence of differences in the spectra of the dichloro- and dibromo-complexes strongly suggests a *trans* dihalide structure for the complexes having approximately C_s symmetry. The unpaired electron is in an A' orbital having entirely $d_{x^2-y^2}$ character, where we define the axes as in Figure 2. The changes in the e.s.r. experimental and derived parameters upon going from $[VO(L_4)]$ to $[VCl_2(L_4)]$ type complexes (L_4 are equatorial ligands) are as follows: g_z decreases from *ca.* 1.96 to 1.90, A_z decreases from *ca.* 165 to 145 ($\times 10^{-4}$ cm^{-1}), $A_{x,y}$ decreases from *ca.* 56 to 45 ($\times 10^{-4}$ cm^{-1}), P decreases from *ca.* 122 to 105 ($\times 10^{-4}$ cm^{-1}), and $g_{x,y}$ remains unchanged.

TABLE 1

List of complexes studied $[VO(L_4)]$



Structure type (A)

Ligands

acac = Acetylacetonate [a]
bzac = Benzoylacetonate [a]
dbm = Dibenzoylmethanate [a]
tfacac = Triflouroacetylacetonate [b]
hfacac = Hexafluoroacetylacetonate [c]
dbms = Thiodibenzoylmethanate [d]
pfp = Perfluoropinacolate [e]
trop = Tropolonate [f]
S_2CNEt_2 = Diethyldithiocarbamate [g]

Structure type (B)

acacen = *NN'*-Ethylenebis(acetylacetoneiminate) [h]
salen = *NN'*-Ethylenebis(salicylideneiminate) [i]
salphen = *o*-Phenylenebis(salicylideneiminate) [i]
Busaln = Butylsalicylideneiminate [b]
Phsaln = Phenylsalicylideneiminate [b]
salox = Salicylaldoximate [j]

Structure type (C)

bipy = 2,2'-Bipyridyl [k]
phen = 1,10-Phenanthroline [k]
hbzim = Benzimidazol-2-olate [l]
(bipy)(SO_4) [k]
(phen)(SO_4) [k]

[a] R. A. Rowe and M. M. Jones, *Inorg. Synth.*, 1957, **5**, 115. [b] K. Ramaiah and D. F. Martin, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1663. [c] J. Selbin, G. Maus, and D. L. Johnson, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1735. [d] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pick, and J. S. Shannon, *Austral. J. Chem.*, 1965, **18**, 673; R. A. Bozis and B. J. McCormick, *Inorg. Chem.*, 1970, **9**, 1541. [e] C. J. Willis, *J.C.S. Chem. Comm.*, 1972, 944. [f] C. P. Stewart and A. L. Porte, *J.C.S. Dalton*, 1972, 1661. [g] B. J. McCormick, *Inorg. Chem.*, 1968, **7**, 1965. [h] P. J. McCarthy, R. J. Hovey, K. Veno, and A. E. Martell, *J. Amer. Chem. Soc.*, 1955, **77**, 5820; L. J. Boucher, E. C. Tynam, and T. F. Yen, *Inorg. Chem.*, 1968, **7**, 731. [i] P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl, and H. Thiebert, *J. Prakt. Chem.*, 1937, **149**, 217. [j] H. J. Bielig and H. Möllinger, *Liebigs Ann. Chem.*, 1957, **605**, 117. [k] J. Selbin and L. H. Holmes, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1111. [l] R. L. Dutte and S. Lahiry, *Sci. Cult.*, 1960, **26**, 139.

In the $[VO(L_4)]$ complexes the V atom is considerably out of the plane of the equatorial ligands, but with the $[VCl_2(L_4)]$ and $[VBr_2(L_4)]$ derivatives the V atom will be in the equatorial plane. The effect of this is to make a small increase in the equatorial σ bonding and to considerably increase the in-plane π bonding. Thus the σ-bonding d_{xy} orbital, Figure 3, will be slightly stabilised and the π-bonding $d_{x^2-y^2}$ orbital strongly stabilised. The corresponding antibonding orbitals with which we are concerned for e.s.r. purposes will be destabilised. Thus the energy of the orbital containing the unpaired electron will be considerably raised. The change in g_z suggests a narrowing of the $d_{x^2-y^2} \rightarrow d_{xy}$ energy gap by about one half.

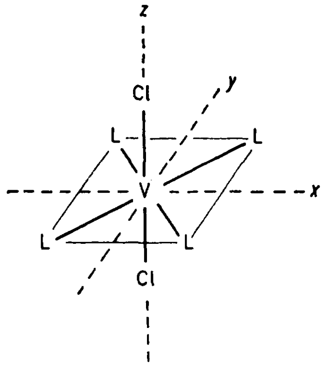


FIGURE 2 Axis notation for *trans*-$[VCl_2(L_4)]$ complexes (L represents N, O, or S)

Changes in the axial σ-bond strength on going from $[VO(L_4)]$ to $[VCl_2(L_4)]$ affect the energy of the d_{z^2} orbital, but this has little effect upon the g tensor. However, the increased π bonding expected must be such as to raise the energy of the $d_{xz,yz}$ pair of orbitals by about the same amount as $d_{x^2-y^2}$ is raised, since $g_{x,y}$ stays approximately constant. The halogeno-complexes are more covalent as shown by the reduction in the value of P. This is entirely consistent with the changes in energy of the orbitals described above.

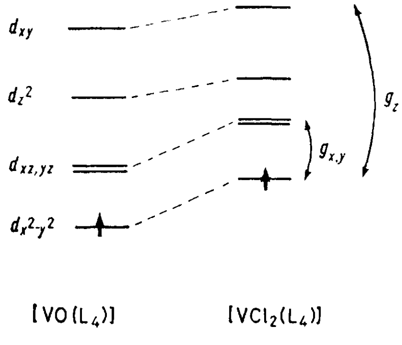


FIGURE 3 Relative energies of the metal orbitals in $[VO(L_4)]$ and *trans*-$[VCl_2(L_4)]$ where L_4 = quadridentate Schiff base

Complexes with Bidentate Ligands (N_2O_2).—The solution from the reaction of $SOCl_2$ or $SOBr_2$ with $[VO(Busaln)_2]$ and $[VO(Phsaln)_2]$ (both bidentate Schiff-base ligands) and with $[VO(salox)_2]$ yielded e.s.r. spectra at 77 K which closely resemble those reported for quadridentate Schiff bases. There were, however, a number of significant differences Whilst the vanadyl complexes with bidentate Schiff bases had similar e.s.r. parameters to those with quadridentate Schiff bases, the dichloro- and dibromo-complexes had quite different e.s.r. parameters for the two kinds of Schiff base. The hyperfine couplings were similar to those for quadridentate Schiff bases, but $g_{x,y}$ values were now reduced from about 1.98 to 1.95 whilst g_z tended to increase. Furthermore, at least three distinct species differing mainly in g_z were observed which varied in intensity as the solution aged [Figure 4(*a*) and (*b*)]. The parameters for the dichloro- and dibromo-derivatives differed, in contrast to the quadridentate Schiff bases, but only one species of the dibromo-complex was present in solution.

The different spectral parameters observed with the dichloro- and dibromo-complexes together with the large change in $g_{x,y}$ strongly suggests that one halide at least is in the equatorial plane of the complex. This is mechanistically quite possible since vanadyl complexes of bidentate Schiff bases are strongly distorted and are nearer trigonal-bipyramidal in shape.[7] Thus after the vanadyl-oxygen atom has been replaced, an incoming chlorine atom will enter into an equatorial position. There are several positions at which this may take place and so several isomers are possible. Subsequent rearrangements may occur to form *trans* dichloro-complexes. Our spectra show no evidence of such species, since their e.s.r. parameters would be similar to those of the quadridentate Schiff bases. Only three isomers are possible with *cis*-dichloro-complexes [(I)—(III)], and we assign the three species seen in the e.s.r. spectra [Figure 4(*a*) and (*b*)] to these isomers. Since $g_{x,z}$ is dependent upon the energy separation $\Delta E(d_{xz,yz} - d_{x^2-y^2})$, the in-

TABLE 2

Electron spin resonance results ($A_{x,y,z}$, P, and κP in units of 10^{-4} cm^{-1})

Complex	$-A_x$	$-A_y$	$-A_z$	g_x	g_y	g_z	$-A_{iso.}$	$g_{iso.}$	a^2	b^2	P	κ	κP
[VO(acacen)$_2$]	55	55	164	1.987	1.987	1.956	91	1.978	0	1	121	0.727	88
[VO(salen)]	56	55	166	1.986	1.989	1.955	92	1.977	0	1	123	0.726	89
[VO(salphen)]	58	56	167	1.985	1.989	1.955	93	1.976	0	1	122	0.739	90
[VO(Busaln)$_2$]	56	54	167	1.983	1.987	1.951	92	1.974	0	1	124	0.715	89
[VO(Phsaln)$_2$]	55	55	168	1.985	1.985	1.950	93	1.974	0	1	125	0.712	89
[VO(salox)$_2$]	57	57	164	1.984	1.984	1.952	93	1.975	0	1	119	0.751	89
[VO(acac)$_2$]	62	60	174	1.983	1.987	1.944	99	1.970	0	1	124	0.763	95
[VO(bzac)$_2$]	62	60	174	1.983	1.987	1.944	99	1.970	0	1	124	0.763	95
[VO(dbm)$_2$]	62	60	174	1.983	1.987	1.944	99	1.970	0	1	125	0.757	94
[VO(tfacac)$_2$]	64	61	174	1.982	1.987	1.944	100	1.970	0	1	123	0.775	95
[VO(hfacac)$_2$]	67	66	178	1.982	1.983	1.934	103	1.967	0	1	123	0.805	99
[VO(dbms)$_2$]	55	55	161	1.983	1.983	1.956	90	1.975	0	1	119	0.723	86
[VO(trop)$_2$]	50	40	155	1.981	1.989	1.950	82	1.972	0.001	0.999	122	0.640	78
[VO(pfp)$_2$]$^{2-}$	46	46	152	1.979	1.979	1.950	79	1.972	0	1	118	0.658	77
[VO(S$_2$CNEt$_2$)$_2$]	51	48	150	1.987	1.992	1.967	83	1.983	0	1	113	0.713	81
[VO(bipy)$_2$][SO$_4$]	66	66	179	1.984	1.984	1.941			0	1	124	0.804	100
[VO(phen)$_2$][SO$_4$]	65	65	178	1.984	1.984	1.945			0	1	124	0.794	99
[VO(hbzim)$_2$]	65	65	178	1.982	1.982	1.945			0	1	125	0.792	99
trans-[VCl$_2$(acacen)]	45	45	144	1.987	1.987	1.908	75	1.961	0	1	105	0.703	74
trans-[VCl$_2$(salen)]	48	48	149	1.980	1.980	1.900	76	1.950	0	1	106	0.720	76
trans-[VCl$_2$(salphen)]	47	47	147	1.984	1.984	1.903	75	1.953	0	1	105	0.718	76
cis-[VCl$_2$(Busaln)$_2$] [a]	47	47	148	1.953	1.953	1.950			0	1	113	0.662	75
b	47	47	148	1.953	1.953	1.966			0	1	115	0.655	75
c	47	47	147	1.953	1.953	1.977	76	1.957	0	1	116	0.654	76
cis[VCl$_2$(Phsaln)$_2$] [a]	47	47	148	1.954	1.954	1.950			0	1	113	0.663	75
b	47	47	148	1.954	1.954	1.965			0	1	115	0.656	76
c	47	47	147	1.954	1.954	1.977	77	1.960	0	1	116	0.654	76
trans-[VCl$_2$(salox)$_2$]	44	44	138	1.962	1.962	1.959			0	1	106	0.680	71
cis-[VCl$_2$(acac)$_2$] [d]	44	44	151	1.940	1.940	1.920			0	1	117	0.614	72
trans-[VCl$_2$(acac)$_2$]	48	48	154	1.968	1.968	1.862	76	1.930	0	1	108	0.705	76
trans-[VCl$_2$(bzac)$_2$]	48	48	155	1.968	1.968	1.860	77	1.930	0	1	108	0.702	76
trans-[VCl$_2$(dbm)$_2$]	48	48	157	1.968	1.968	1.856	77	1.929	0	1	110	0.695	76
trans-[VCl$_2$(tfacac)$_2$]	50	50	130	1.970	1.970	1.899			0	1	84	0.853	72
trans-[VCl$_2$(dbms)$_2$]	50	50	158	1.970	1.970	1.801	77	1.900	0	1	103	0.745	77
[VCl$_2$(trop)$_2$]	110	102	1 [e]	1.938	1.944	1.996	71	1.959	0.997	0.003	105	0.656	69
[VCl$_2$(pfp)$_2$]$^{2-}$	131	131		1.903	1.903								
cis-[VCl$_2$(phen)$_2$] [f]	60	60	129	1.760	1.760	1.931			0	1	82	0.827	68
trans-[VCl$_2$(S$_2$CNEt$_2$)$_2$]	61	61	173	1.983	1.983	1.953			0	1	125	0.760	95
trans-[VBr$_2$(acacen)]	45	45	143	1.986	1.986	1.912	74	1.960	0	1	104	0.705	73
trans-[VBr$_2$(salen)]	47	47	147	1.979	1.979	1.907	80	1.955	0	1	106	0.711	75
cis-[VBr$_2$(Busaln)$_2$]	45	45	140	1.956	1.956	1.962	72	1.956	0	1	108	0.667	72
cis-[VBr$_2$(Phsaln)$_2$]	45	45	140	1.962	1.962	1.961	72	1.959	0	1	107	0.673	72
trans-[VBr$_2$(salox)$_2$]	44	44	138	1.962	1.962	1.959			0	1	106	0.680	71
cis-[VBr$_2$(acac)$_2$]	42	42	142	1.962	1.969	1.969	75	1.963	0	1	114	0.620	71
cis-[VBr$_2$(bzac)$_2$]	42	42	142	1.960	1.960	1.969	75	1.963	0	1	114	0.620	71
cis-[VBr$_2$(dbm)$_2$]	41	41	143	1.958	1.958	1.968	75	1.961	0	1	116	0.603	70
[VBr$_2$(trop)$_2$]	105	105	3 [e]	1.942	1.942	1.990	71	1.958	0	1	119	0.532	63
cis-[VBr$_2$(phen)$_2$] [f]	60	60	129	1.760	1.760	1.931			0	1	82	0.827	68

[a] Fresh solution. [b] Above complex after 2 min. [c] Above complex after 2 h. [d] *cis*-[VCl$_2$(L$_4$)] where (L$_4$) = (bzac)$_2$, (dbm)$_2$, (tfac)$_2$, and (dbms)$_2$ have same parameters. [e] Calculated from $A_{iso.} = \frac{1}{3}(A_x + A_y + A_z)$. [f] Complexes derived from [VO(bipy)$_2$][SO$_4$], [VO(bipy)(SO$_4$)], [VO(phen)(SO$_4$)], and [VO(hbzim)$_2$] have same parameters.

plane π bonding will be stabilised more than the axial π bonding because of the presence of an equatorial chlorine and only one chlorine on the axis (relative to the vanadyl complex). It follows that the antibonding $d_{x^2-y^2}$ orbital containing the unpaired electron will be raised more in energy than the $d_{xz,yz}$ pair. The progressive increase in g_z with time means that $\Delta E(d_{xy} - d_{x^2-y^2})$ is getting larger, and this is probably associated with d_{xy} becoming progressively more destabilised because of changing equatorial σ bonding. This is associated with a small increase in P which reflects decreased covalency in the complex.

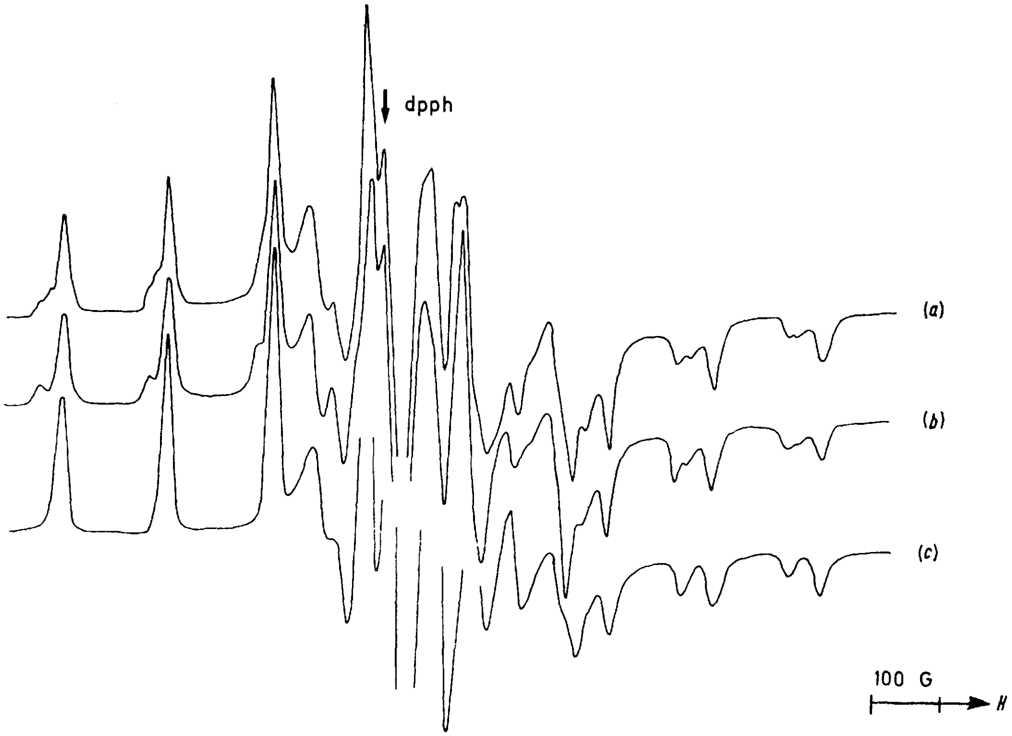
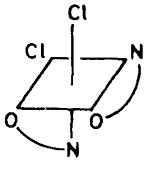
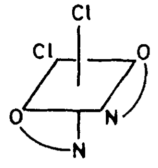


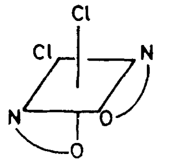
FIGURE 4 E.s.r. spectrum of a frozen solution of [$VCl_2(Busaln)_2$]: (a) in 80% benzene–20% $SOCl_2$ (fresh); (b) after 5 min; (c) in 80% diethylacetamide–20% $SOCl_2$ (fresh)



(I)



(II)

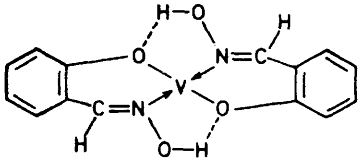


(III)

The dibromo-complexes show changes in e.s.r. parameters expected for a more covalent system. Thus P decreases from *ca.* 0.011 5 to 0.010 7 cm^{-1} on going from the dichloro- to the dibromo-complexes and κ increases from *ca.* 0.66 to 0.67.

In the presence of an excess of strong base (dmf, def, dma, and dea) only two species are seen in solution [Figure 4(*c*)]. One species has A_z lowered from 0.014 8 to 0.014 2 ($\times 10^{-4}$ cm^{-1}) with a corresponding reduction in P which correlates well with the increase in covalency expected when the equatorial chlorine is solvated by the base. The second species has parameters very similar to the original.

Reaction of [$VO(salox)_2$] with $SOCl_2$ and $SOBr_2$ yields solutions whose e.s.r. spectra have parameters which are almost identical. Only one species appears to be present in solution. This suggests that ***trans*** complexes are formed and this may occur in contrast to that formed with the bidentate Schiff bases because of the potentially strong equatorial hydrogen bonds forcing a rigidly planar framework [structure (IV)].



(IV)

Complexes with β-Diketonate Ligands (' O_4 ' *and* ' O_2S_2 ' *Complexes with Six-membered Rings*).—The solution from the reaction of $SOCl_2$ with [$VO(acac)_2$], [$VO(bzac)_2$], [$VO(dbm)_2$], [$VO(tfacac)_2$], [$VO(hfacac)_2$], and [$VO(dbms)_2$] yielded e.s.r. spectra at 77 K which in most cases were from a mixture of two species, the relative abundances of which were solvent dependent (Figure 5). One species, existing in greater abundance in non-polar solvent, has parameters closely resembling those from quadridentate Schiff bases, *i.e.* with a very low value of g_z (*ca.* 1.86). We assign these species to *trans*-dichloro-complexes. The abundance of this form decreases with the ligands tfacac > acac > bzac > dbm, and is also associated with progressively decreasing covalency through this series (P changing from 0.008 4 to 0.011 0 cm^{-1}). With dbms ligand, the drop in g_z was even greater (to 1.801) and this reflects the increased covalency and stability of the equatorial σ bonds and shows itself in a reduced value of P relative to [VCl$_2$(dbm)$_2$].

The other species, existing in greater abundance in polar solvents, has e.s.r. parameters resembling those of bidentate Schiff-base complexes and we assign a *cis*-dichloro-structure to them. The parameters were almost identical for each complex. The solvent dependence of *cis* and *trans* isomers is well documented and our observations correlate well with those of Von Dreele and Fay.[8] It is noteworthy that this is one of the few authentic cases in which *cis* and *trans* isomers have been identified and detected by e.s.r. spectroscopy.

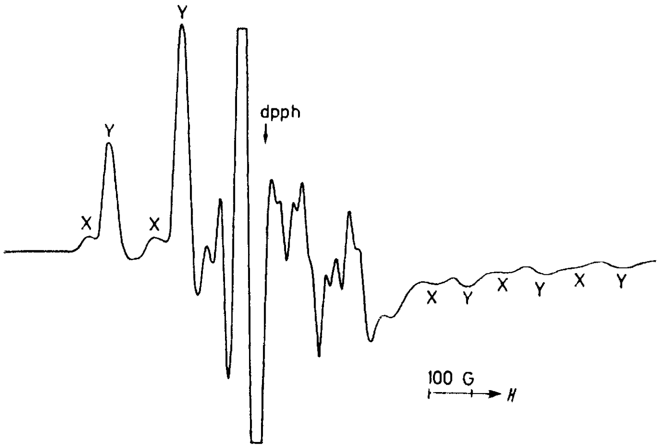


FIGURE 5 E.s.r. spectrum of a frozen solution of [VCl$_2$(acac)$_2$] in 80% CHCl$_3$–20% SOCl$_2$ showing lines from two isomers, *cis* (X) and *trans* (Y)

The species in solution from the reaction with SOBr$_2$ was predominately the *cis* isomer (in almost 100% abundance in the case of dbm and bzac ligands).

Complexes Co-ordinated via O *but having Five-membered Rings.*—The solution from reaction of SOCl$_2$ or SOBr$_2$ with [VO(trop)$_2$] and [VO(pfp)$_2$]$^{2-}$ yielded quite different e.s.r. spectra at 77 K (Figure 6). The main differences were that now $g_z > g_x = g_y$ and $A_z < A_x = A_y$. This pattern of e.s.r. parameters is typical of that shown by systems with a d_{z^2} ground state. In the case of the trop complexes, the spectra were very well resolved and very similar for the dichloro- and dibromo-complexes. Spectra measured at Q-band frequencies confirmed the above assignment and showed in addition a very small splitting of the x and y features. In the case of the pfp complexes very poor solubility in all solvents tried made the spectrum weaker and the lines were very broad, but the main features were almost the same. We could not resolve A_z for [VCl$_2$(trop)$_2$] and [VBr$_2$(trop)$_2$] but a value was estimated from the isotropic data. This switch in ground state was surprising and only occurred with complexes having five-membered rings incorporating the V atom. The extra strain in the ring, compared with that for six-membered rings, must have a dramatic effect upon the structure with consequent reordering of energy levels. The only other six-co-ordinate vanadium(IV) complexes with a d_{z^2} ground state are [V(mnt)$_3$]$^{2-}$ (mnt = maleonitriledithiolate),[9] and [VL$_2$] (L = pentane-2,4-dione benzoylhydrazonate or 4-phenylbutane-2,4-dione benzoylhydrazonate).[10] In both these complexes, the structures involve five-membered rings and are close to trigonal-prismatic geometry. We predict that the structures of [VX$_2$(trop)$_2$] and [VX$_2$(pfp)$_2$]$^{2-}$ (X = Cl or Br) are likewise trigonal prismatic with the chelate ligands occupying two vertical edges of a trigonal prism, and the halogen atoms at the co-ordination sites of the other vertical edge. Support for this type of structure comes from the observation that the dibromo- and dichloro-complexes have almost identical e.s.r. parameters. This would be expected since the d_{z^2} orbital does not interact with ligand atoms in a trigonal-

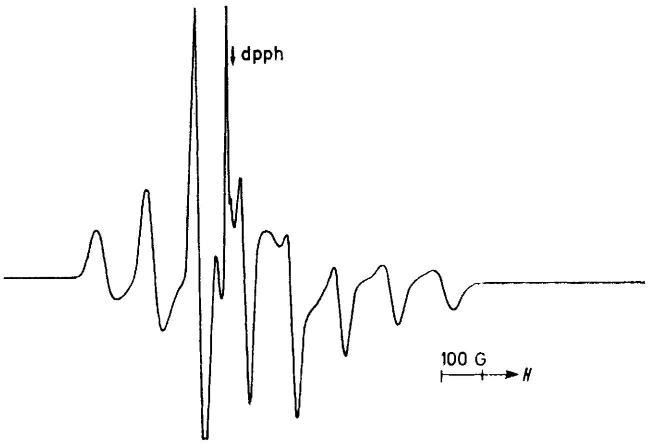


FIGURE 6 E.s.r. spectrum of a frozen solution of [VCl$_2$(trop)$_2$] in 80% diethylacetamide–20% SOCl$_2$

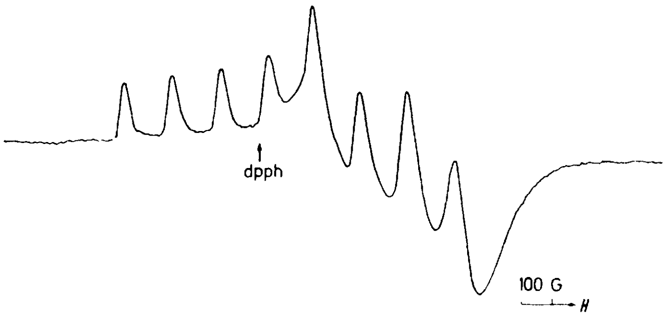


FIGURE 7 E.s.r. spectrum of a frozen solution of *cis*-[VCl$_2$(bipy)$_2$] in SOCl$_2$

prismatic structure. Interaction with the d_{z^2} orbital would however occur in *cis* or *trans* octahedral structures, with consequent effects upon the e.s.r. parameters. Furthermore, the complex in $SOCl_2$–$CHCl_3$, $SOCl_2$–CH_2Cl_2, or toluene solution exhibited (like all the others studied) no detectable electrical conductivity, showing that ionic species were absent and supporting a neutral $[VX_2(trop)_2]$ type formulation. We tried reaction of $SOCl_2$ with other vanadyl complexes having ligands with five-membered rings, *e.g.* $[VO(C_2O_4)_2]^{2-}$, but no reaction occurred.

Complexes with ' N_4 ' Ligands.—The solution from the reaction of $SOCl_2$ or $SOBr_2$ with $[VO(bipy)_2][SO_4]$, $[VO(bipy)(SO_4)]$, $[VO(phen)_2][SO_4]$, $[VO(phen)(SO_4)]$, and $[VO(bzim)_2]^{2+}$ each gave similar e.s.r. spectra after several hours refluxing. Frequently there was evidence of unchanged parent vanadyl complex in the e.s.r. spectrum. The spectrum at 77 K was deceptively simple (Figure 7) and was analysed with the help of a *Q*-band spectrum and computer simulation. The spectrum could only be interpreted assuming axial symmetry. The value of $A_\perp$ cannot be measured very accurately and the value quoted has an error of about ± 5 G.* Unfortunately, the value could not be checked using the spectrum of a fluid solution because it was so weak. The glass spectrum is noteworthy in that $g_\perp$ is particularly low, and analysis of the spin-Hamiltonian parameters shows that P is also lower than that for other complexes. The complexes so formed are almost certainly *cis*-dihalogenovanadium dichelates since it is well known [11] that *trans*-bipyridyl and *trans*-1,10-phenanthroline complexes are never formed because of steric hindrance due to the α-protons of the chelates. Although the complex strictly has C_2 symmetry, it does have effective axial symmetry since the atoms on the x and y axes are identical showing that the complex is particularly covalent.

Complex with $[VO(S_2CNEt_2)_2]$.—The product of reaction of $SOCl_2$ with $[VO(S_2CNEt_2)_2]$ yielded a solution having a weak e.s.r. spectrum. There was evidence of rapid decomposition. The e.s.r. parameters were similar to those of the quadridentate Schiff bases and suggested that a *trans*-dichloro-complex was formed. In contrast, however, the e.s.r. parameters showed an increase in P from 0.001 3 to 0.012 5 on going from $[VO(S_2CNEt_2)_2]$ to $[VCl_2(S_2CNEt_2)_2]$. There must be considerable strain in this molecule and the weak bonding and low stability may reflect an apparently more ionic structure.

Electronic Spectra.—The optical spectra of all dihalogeno-complexes were dominated by intense bands at *ca.* 470—480 nm and at *ca.* 640—700 nm each with ε *ca.* 4 500—6 000 $dm^3\ mol^{-1}\ cm^{-1}$, and correlate well with those obtained for other dichloro-complexes.[8] These charge-transfer bands masked the *d–d* transitions and so no correlation between these and the e.s.r. spectra was possible.

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* Throughout this paper: 1 G = 10^{-4} T.

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