Electronic Absorption Spectra of Some Oxovanadium(IV) Compounds

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Single-crystal polarised electronic absorption spectra at 298 and 5 K, in the range 5 000—30 000 cm^{-1}, of [VOX$_2$(tmu)$_2$] (tmu = tetramethylurea, X = Cl or Br), [NEt$_4$]$_2$[VOCl$_4$], and [AsPh$_4$]$_2$[VO(NCS)$_4$], and similar spectra of poly(dimethylsiloxane) mulls of [VOCl$_2$(tmtu)$_2$], [VOCl$_2$(tppo)$_2$], [VOCl$_2$(hmpa)$_2$], K$_3$[VO(CN)$_5$], [NH$_4$]$_3$[VOF$_5$], and [NMe$_4$]$_2$[VO(NCS)$_4$(OH$_2$)] (tmtu = tetramethylthiourea, tppo = triphenylphosphine oxide, and hmpa = hexamethylphosphoramide) are reported. The absorption bands have been assigned based on a combination of their observed polarisation, relative intensities, vibrational fine structure, and changes in positions with changes in the in-plane ligands. For the five-co-ordinate complexes *all* of the expected *d–d* type transitions occur below 30 000 cm^{-1}, the electronic bands at 5 K for $(3d_{xy}^*)\rightarrow(3d_{xz}^*, 3d_{yz}^*)$ being in the range 12 860—15 100 cm^{-1}, for $(3d_{xy}^*)\rightarrow(3d_{z^2}^*)$ in the range 21 000—22 600 cm^{-1}, whilst the $(3d_{xy}^*)\rightarrow(3d_{x^2-y^2}^*)$ transition varies in energy as expected from the changes in the in-plane ligands. For the six-co-ordinate complexes only the $(3d_{xy}^*)\rightarrow(3d_{xz}^*, 3d_{yz}^*)$ and $(3d_{xy}^*)\rightarrow(3d_{x^2y^2}^*)$ transitions are observed below 30 000 cm^{-1}. It is suggested that in these latter complexes the $(3d_{xy}^*)\rightarrow(3d_{z^2}^*)$ transition lies above 30 000 cm^{-1} its energy being increased due to an increase in the ligand-field strength along the molecular *z* axis.

SINCE the initial work of Ballhausen and Gray [1] on the electronic structure of vanadyl sulphate, compounds containing the VO^{2+} group have been the subject of considerable theoretical and experimental work. The assignments of the electronic absorption spectra based on a number of theoretical calculations [1-5] show a wide divergence of opinion concerning the energies of both *d–d* and charge-transfer type transitions. Similarly, a number of experimental studies based on data obtained from solution, mull, KBr disc, or single-crystal studies have afforded a variety of assignments for the observed spectra.[6-9] Although it seems unlikely that one single rigid assignment scheme will apply to all the vanadyl compounds studied, the wide variety of schemes proposed also seems unreasonable. One of the major contributory factors to this somewhat confused situation is the lack of well resolved polarised single-crystal data over a wide range of temperature. Although a few such studies have been reported,[6-10] the data are limited due to either difficulties in aligning the crystals so that suitable molecular orientations can be achieved, or to lack of resolution resulting from inadequate cooling of the samples. In view of this we report the single-crystal polarised electronic absorption spectra of four compounds, for which favourable molecular orientations are possible, over the energy range 5 000—30 000 cm^{-1}, and at 298 and 5 K. These data are supplemented by the mull spectra of a number of other compounds over the same temperature and energy ranges. The compounds studied give a range of ligand-field strengths from that of cyanide to that of bromide.

EXPERIMENTAL

Electronic Absorption Spectra.—These were obtained on suitably thinned and oriented (by standard *X*-ray techniques) single crystals mounted on a silica substrate and poly(dimethylsiloxane) mulls, at room temperature and 5 K on equipment described previously.[11]

Vibrational Spectra.—Infrared spectra in the range 200—4 000 cm^{-1} were obtained as Nujol mulls between CsI plates on a Perkin-Elmer 225 spectrophotometer. A Raman spectrum of solid [VOCl$_2$(tmu)$_2$] was obtained using a Cary 81 spectrometer.

Preparation of Compounds.—The compounds [VOX$_2$(tmu)$_2$] (X = Cl or Br; tmu = tetramethylurea) were prepared according to the method of Du Preez and Sadie.[12] Crystals of the chloro-compound were grown by slow evaporation of a solution of the compound in dry CH$_2$Cl$_2$–CCl$_4$ (1 : 1), whilst crystals of the bromo-analogue were grown from dry MeCN solution.

The compound [VOCl$_2$(tmtu)$_2$] (tmtu = tetramethylthiourea) was prepared by the method of Du Preez and Gibson; [13] [VOCl$_2$(hmpa)$_2$] (hmpa = hexamethylphosphoramide) was kindly supplied by Dr. K. R. Seddon.

The compound [VOCl(tppo)$_2$] (tppo = triphenylphosphine oxide) was prepared as a powder by concentrating a hot reduced solution of V$_2$O$_5$ (1 g) in concentrated HCl–EtOH (50 cm of 1 : 1 mixture) and tppo (6 g) on a steam-bath.

The salt [NEt$_4$]$_2$[VOCl$_4$] was prepared as crystals from a solution of VOCl$_2$ and [NEt$_4$]Cl (1 : 2 mol ratio) in dry MeCN, K$_3$[VO(CN)$_5$] was prepared by the method of Nicholls and Bennett,[14] [NH$_4$]$_3$[VOF$_5$] was obtained, as small crystals, by the slow evaporation of an aqueous solution of [VO][SO$_4$]·5H$_2$O and [NH$_4$]F (1 : 5 mol ratio), and [AsPh$_4$]$_2$[VO(NCS)$_4$] and [NMe$_4$]$_2$[VO(NCS)$_4$(OH$_2$)] were prepared according to the method which Selbin and Holmes [15] used to obtain [NMe$_4$]$_3$[VO(NCS)$_5$].

Analytical data on all of the above compounds were consistent with their formulations.

RESULTS

Since the assignment of the electronic absorption spectra are based almost entirely on the low-temperature measurements we will describe these in some detail and merely present the room-temperature data diagrammatically for comparison.

Single-crystal Spectra.—[VOX$_2$(tmu)$_2$]. The compound [VOCl$_2$(tmu)$_2$] crystallises in the monoclinic space group *C*2/*c*, with the terminal V–O vectors of all the molecules in the unit cell parallel to the crystal *b* axis.[16] We have shown that the chloro- and bromo-compounds are isomorphous. The molecules of the chloro-compound have an approximate square-pyramidal geometry with the chlorides essentially mutually *trans*, and they possess C_2 point symmetry. In both compounds we have grown crystals which enable the electric vector of the incident radiation to be polarised parallel to the crystal *b* axis [*i.e.* parallel to V–O (terminal), which defines the molecular *z* axis], and also parallel to the crystal *c* axis. This latter direction is close to the V–O (tmu) vector. However, since we have been unable to grow crystals suitable for obtaining absorption spectra in the *ac* plane, and e.s.r. measurements show that the system is nearly isotropic in this plane, we designate the absorption spectrum obtained with the radiation polarised along *c* as the molecular *x,y* spectrum. The results of the spectra obtained are shown in Figures 1 and 2, whilst those obtained at 5 K are summarised in Table 1.

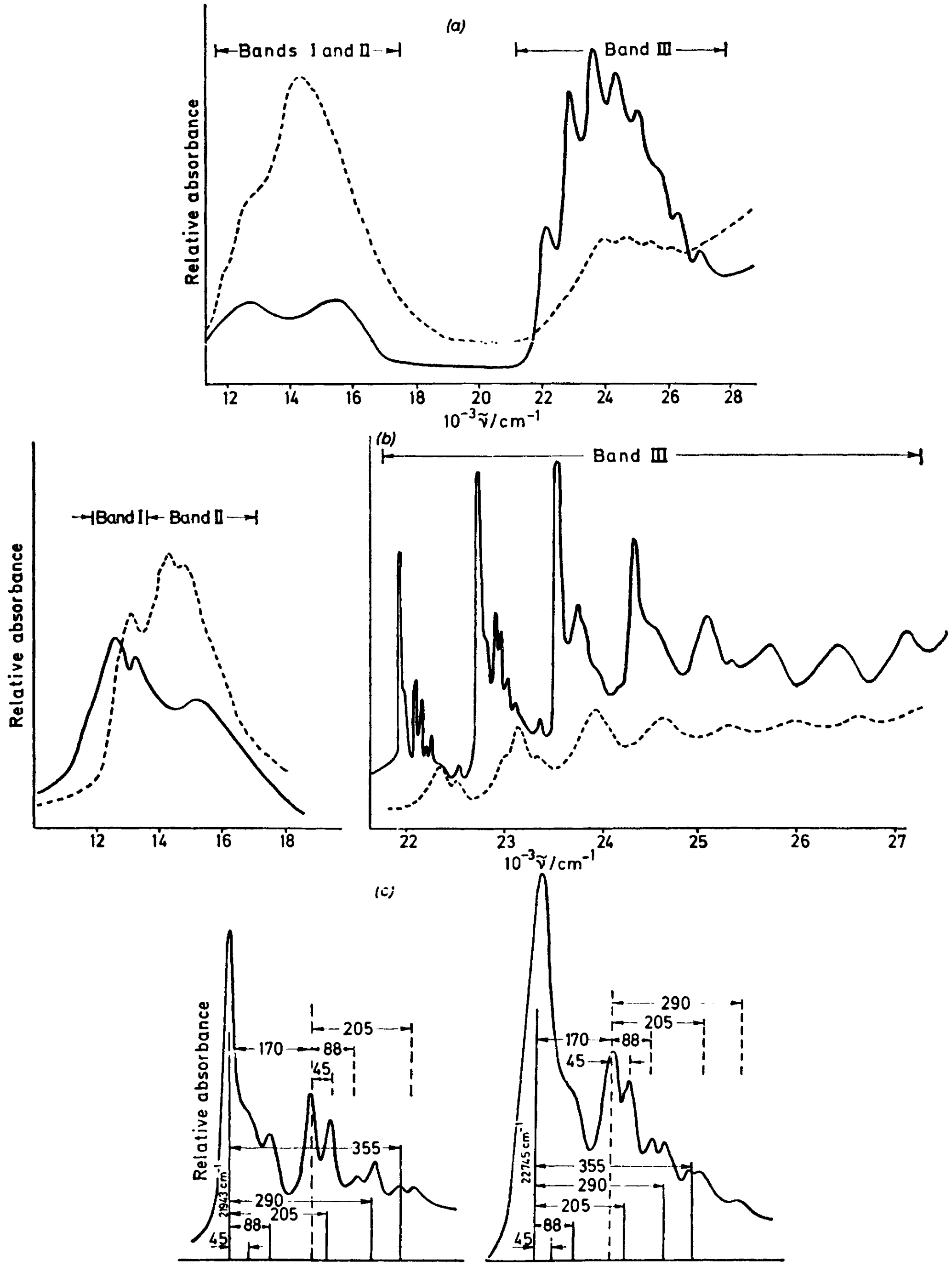

FIGURE 1 Polarised single-crystal electronic absorption spectrum of [VOCl$_2$(tmu)$_2$] at (*a*) 298, (*b*) 5 K, (*c*) expanded representation of the first two components of band III in *z* polarisation at 5 K. (———), *z* Polarisation; (– – – –), *x,y* polarisation

Cooling the crystals to 5 K affords some resolution of the low-energy band system and a very marked improvement in the resolution of the high-energy band system in both compounds. The low-energy band system is clearly resolved into two major components. The first of these (designated as band I) appears in z polarisation as absorption maxima at 12 570 and 12 270 cm^{-1} in the chloro- and bromo-compounds respectively. The x,y components of these bands are *ca.* 480 and *ca.* 530 cm^{-1} higher in energy in the chloro- and bromo-compounds respectively. The second component of the low-energy band system (designated as band II) shows some extra structure, particularly for the bromo-compound. In this case the structure appears as a partially resolved four-membered progression with an average separation between the members of *ca.* 800 cm^{-1}, with the first component at 14 020 cm^{-1}. Similar, but less well resolved, features are also observed for the chloro-compound. In contrast to the above behaviour there is a considerable improvement in resolution for the high-energy band system (designated as band III) on cooling. In both the chloro- and bromo-compounds the z-polarised spectrum is now clearly resolved into a major seven- or eight-membered progression, each member being separated by *ca.* 800 cm^{-1}. The first few members of this major progression have superimposed on them a further repeating splitting pattern (see, for an example, the insets to Figures 1 and 2). The x,y-polarised spectrum of the chloro-compound is not as well resolved as the corresponding z-polarised spectrum. However, it again consists of a six-membered progression with mean separations of *ca.* 770 cm^{-1}, but in this case the first member of the progression is at 22 343 cm^{-1}, *i.e.* 400 cm^{-1} higher in energy than the first member of the z-polarised spectrum. In the bromo-compound the x,y-polarised spectrum also appears as a six-membered progression with an average separation of *ca.* 800 cm^{-1}, the maximum intensity occurring for an absorption *ca.* 350 cm^{-1} higher in energy than the first member of the corresponding band in the z-polarised spectrum. Also there are a number of weak but well resolved features on the low-energy side of each of these main absorptions, see Figure 2. Features similar to these were not resolved for the chloro-compound.

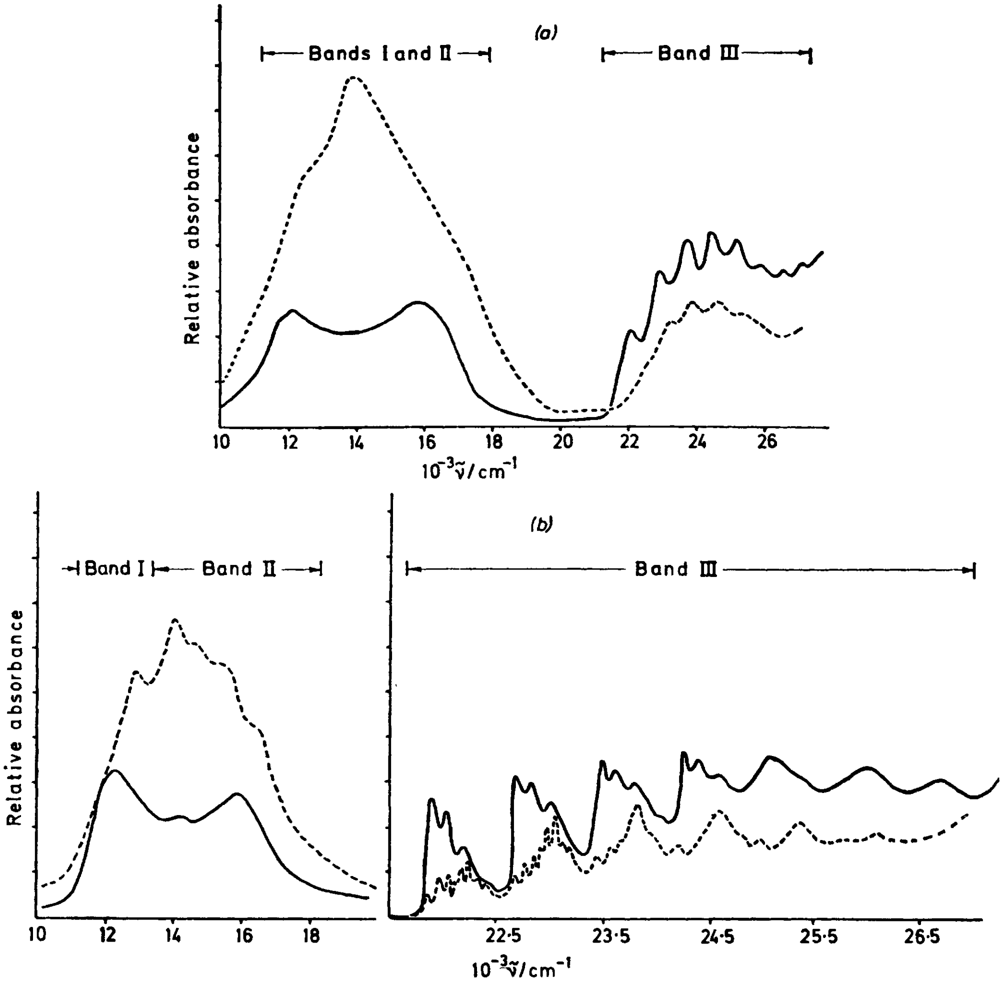

FIGURE 2 Polarised single-crystal electronic absorption spectrum of [VOBr$_2$(tmu)$_2$] at (*a*) 298 and (*b*) 5 K. Key as in Figure 1

[NEt$_4$]$_2$[VOCl$_4$]. This compound has been shown to crystallise in a tetragonal space group,[17] and to contain discrete square-pyramidal [VOCl$_4$]$^{2-}$ ions with C_{4v} symmetry. The single-crystal polarised absorption spectrum has previously [7] been reported at 296 and 77 K. As in this previous report, we also found that the spectrum at room temperature was considerably more intense in xy than in z polarisation, see Figure 3. Cooling the crystals to 5 K resulted in an improvement in the resolution of the xy-polarised spectrum but no significant change in the z polarised spectrum. In the xy spectrum there is a band maximum at 11 910 cm^{-1} which is clearly resolved from a six-membered progression (band II) the members of which decrease in intensity as their energy increases. The first member of this progression is at 13 067 cm^{-1} and the average separation between them is 795 cm^{-1}. The third band system in the spectrum (band III) shows considerable resolution, and consists of a seven-membered progression with the first absorption at 21 383 cm^{-1}. The average separation between the members is 790 cm^{-1}. There is a small increase in intensity as we go from the first to the second and third members of the progression, but thereafter the intensities decrease.

TABLE 1

Band positions (cm^{-1}) for the single-crystal polarised electronic absorption spectrum of [VOX$_2$(tmu)$_2$] at 5 K *

	[VOCl$_2$(tmu)$_2$] Polarisation		[VOBr$_2$(tmu)$_2$] Polarisation	
Band	z	x,y	z	x,y
I	12 570s	13 090s	12 268m	12 783s
	13 200s			
		14 280s	14 027m	14 020s
II	15 310s			14 694 (sh)
		14 770s	15 800m	15 521 (sh)
				16 351 (sh)
III	21 943s		21 875m	21 852w
	21 982 (sh)		22 035m	21 950w
	22 024m		22 095m	22 041w
	22 109m		22 187 (sh)	22 093w
	22 151m	22 145 (sh)		22 150w
	22 203w			22 224w
	22 245w	22 210 (sh)		22 317w
	22 293w			22 392 (sh)
	22 327w	22 343w	22 677m	22 659w
	22 535w	22 498w	22 815m	22 757w
			23 000m	22 845w
	22 745s			22 903w
	22 800 (sh)			22 955m
	22 828 (sh)			23 028m
	22 914m	22 910 (sh)		23 110w
	22 954m			23 184w
	23 008w			
	23 039w	23 050 (sh)	23 455m	23 437w
	23 107w	23 121m	23 602m	23 548w
	23 131w	23 288m	23 766m	23 647 (sh)
	23 200w			23 759 (sh)
	23 350w			23 822m
				23 949 (sh)
	23 545s			
	23 731m	23 742 (sh)	24 236m	24 207w
	23 882 (sh)	23 880w	24 332m	24 577m
	24 306 (sh)	24 059 (sh)	24 552w	24 766 (sh)
	24 437s		25 042	24 958w
	24 544 (sh)	24 505 (sh)		25 309w
	24 703 (sh)	24 651w		
	25 047m	24 841 (sh)	25 757w	
	25 145 (sh)	25 188 (sh)	26 390w	26 057w
	25 718w	25 372w	27 038w	
			27 702w	
	26 379m	26 076w	28 327w	
	27 058m	26 678w		
	27 740m			
	28 456w			

* s = Strong, m = medium, w = weak, and sh = shoulder.

[AsPh$_4$]$_2$[VO(NCS)$_4$]. There are no single-crystal X-ray structural data available for this compound. The crystals developed as large almost hexagonal thin plates, which exhibited sharp extinctions under the polarising microscope. Electron spin resonance measurements showed that there was a minimum g value along one of these extinction directions, whilst in the plane perpendicular to this direction the crystals showed only a small anisotropy. By analogy with the e.s.r. behaviour of the other systems studied here, the direction of the minimum g value is assumed to be close to the terminal V–O direction of the complex anion. In view of the formulation of the compound and its e.s.r. behaviour we assume that this anion has C_{4v} symmetry. The electronic absorption spectra were obtained with the electric vector polarised parallel to each of the above extinction directions. The resulting spectra are assumed to approximate closely to those of the molecular z and xy directions.

At room temperature the xy-polarised spectrum is the more intense and consists of three bands none of which shows any fine structure, see Figure 4. In z polarisation we have so far only observed a single broad band corresponding to the lowest energy band in the xy-polarised spectrum, the other two bands being too weak to be observed in our experiments. Cooling the crystals to 5 K made the distinction between the band at 14 060 cm^{-1} (band II) and that at 17 720 cm^{-1} (band I) in xy polarisation clearer, but no further structure was resolved. The third band in xy polarisation (band III) was partially resolved into a five-membered progression with separations of *ca.* 750 cm^{-1}, see Figure 4 and Table 2. The intensity distribution of the individual members of this progression is similar to that observed on the corresponding band in [NEt$_4$]$_2$[VOCl$_4$].

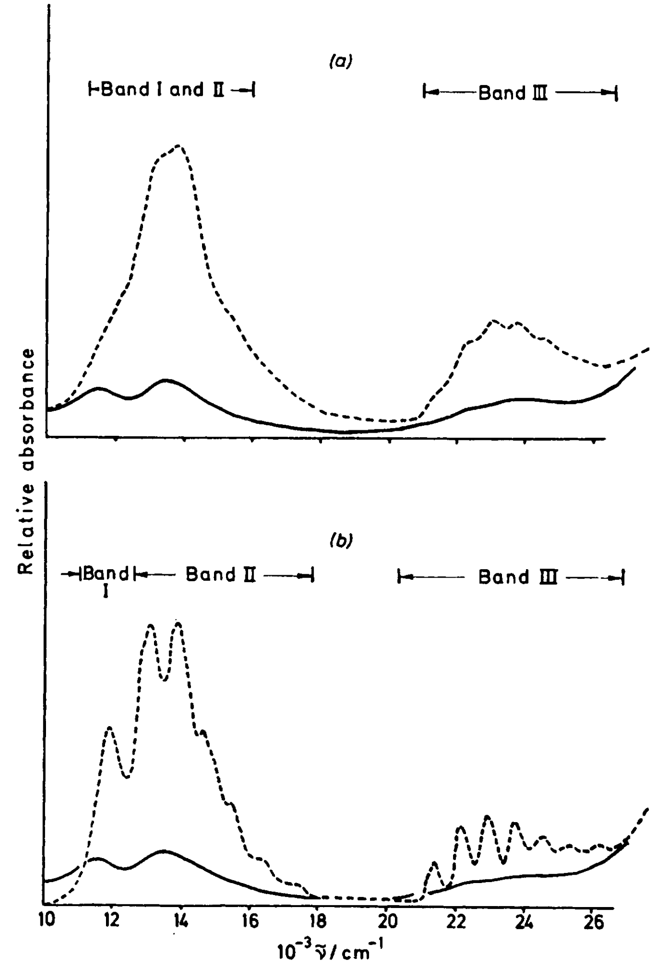

FIGURE 3 Polarised single-crystal electronic absorption spectrum of [NEt$_4$]$_2$[VOCl$_4$] at (*a*) 298, and (*b*) 5 K. Key as in Figure 1

Mull Spectra.—We have obtained the electronic absorption spectra of a number of compounds as poly(dimethylsiloxane) mulls at both room temperature and 5 K, for which we have so far been unable to grow suitable single crystals. The data obtained at low temperatures are shown in Table 3, and selected examples of the spectra are shown in Figure 5.

It is convenient to divide the compounds into two groups which are known or suspected (from their stoicheiometries) to be (*a*) five- or (*b*) six-co-ordinate. The group of five-co-ordinate compounds is made up of $[VOCl_2(hmpa)_2]$, which has been characterised by *X*-ray crystallography,[18] and $[VOCl_2(tmtu)_2]$ and $[VOCl_2(tppo)_2]$. The mull spectra of this group of compounds are characterised by absorptions at room temperature in the regions 11 500—15 500 and 21 000—29 000 cm^{-1}. Cooling the samples to 5 K gave some indication of resolution within the low-energy band system, whilst the absorption in the 21 000—25 000 cm^{-1} region showed somewhat better resolution into what is clearly a vibrational progression based on an energy separation of *ca.* 800 cm^{-1}, see Table 3. The six-co-ordinate group consists of $K_3[VO(CN)_5]$, which is known to be six-co-ordinate,[19] $[NMe_4]_2[VO(NCS)_4(OH_2)]$,* $[VO(SMe_2O)_5][ClO_4]_2$, and $[NH_4]_3[VOF_5]$. The mull spectra of this group of compounds, at both room temperature and 5 K, consist of relatively intense absorptions in the range 10 000—16 000 cm^{-1}. However, in contrast to the five-co-ordinate group, they lack an absorption in the region 21 000—25 000 cm^{-1}, which shows a vibrational progression involving intervals of *ca.* 800 cm^{-1}.

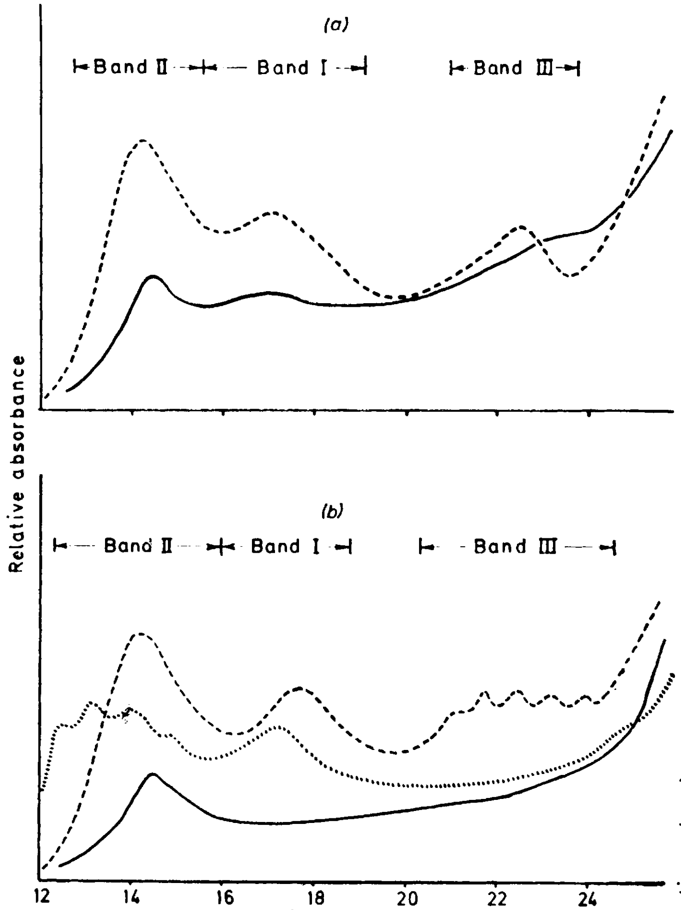

FIGURE 4 Polarised single-crystal electronic absorption spectrum of $[AsPh_4]_2[VO(NCS)_4]$ at (*a*) 298, and (*b*) 5 K. (· · · ·), Poly(dimethylsiloxane) mull of $[NMe_4]_2[VO(NCS)_4(OH_2)]$ at 5 K; other details as in Figure 1

TABLE 2

Band positions (cm^{-1}) for single-crystal polarised absorption spectra of $[NEt_4]_2[VOCl_4]$ and $[AsPh_4]_2[VO(NCS)_4]$ at 5 K

	$[NEt_4]_2[VOCl_4]$ Polarisation			$[AsPh_4]_2[VO(NCS)_4]$ Polarisation	
Band	*z*	*xy*	Band	*z*	*xy*
I	11 600w	11 909s	II	14 420w	14 060s
II		13 067s			
		13 095s	I	*	17 720m
	13 700w	14 644s			
		15 382 (sh)	III		21 030 (sh)
		16 245 (sh)			21 760w
		17 211w (sh)		*	22 490w
III		21 383w			23 270w
	*	22 204w			24 050w
		22 984w			
		23 784w			
		24 587w			
		25 346w			

* The spectra in this region consisted of very weak, broad, ill defined absorptions.

DISCUSSION

We have attempted to assign the single-crystal polarised absorption spectra purely on the basis of the experimental data, without recourse to any predictions relying on calculations. Thus our arguments are based on the appropriate selection rules, coupled with relative band intensities and any vibrational fine structure which may be observed. The required selection rules for electric dipole transitions are summarised in Table 5. The electronic ground state for these compounds is assumed to be that of an unpaired electron in a primarily metal-based $3d_{xy}$ antibonding molecular orbital. The discussion will be structured around the designation of

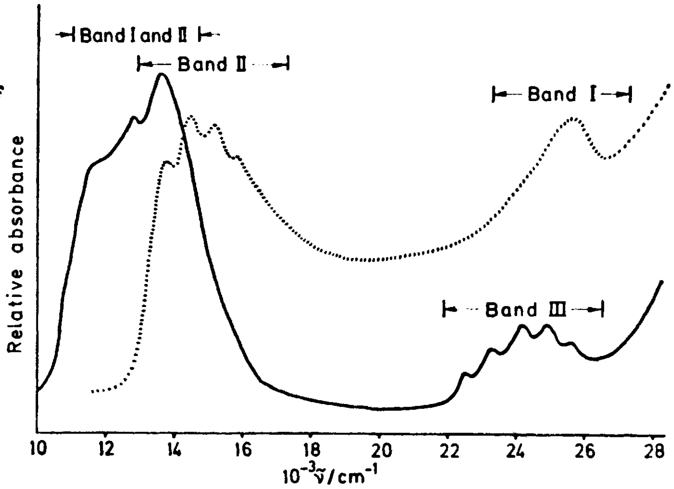

FIGURE 5 Poly(dimethylsiloxane) mull spectra at 5 K of $[VOCl_2(hmpa)_2]$ (—), and $K_3[VO(CN)_5]$ (· · · ·)

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* The $[VO(NCS)_4(OH_2)]^{2-}$ ion has been characterised in $[NH_4]_2[VO(NCS)_4(OH_2)]\cdot 4H_2O$ (A. C. Hazell, *J. Chem. Soc.*, 1963, 5745).

absorptions into bands I, II, and III introduced in the Experimental section.

TABLE 3

Band positions for mull spectra at 5 K

Compound	Absorption maxima (10^3 cm^{-1}) Band I	Band II	Band III	Other bands
[VOCl$_2$(tmtu)$_2$]	$\longleftarrow$ 15.10 $\longrightarrow$		21.72, 22.54, 23.27, 24.01, 24.80	
[VOCl$_2$(hmpa)$_2$]	$\longleftarrow$ 11.76, 12.86, 13.64 $\longrightarrow$		22.58, 23.37, 24.11, 24.96, 25.76	
[VOCl$_2$(tppo)$_2$]	$\longleftarrow$ 12.03, 12.86, 13.89 $\longrightarrow$		22.21, 23.18, 23.90, 24.63, 25.58 26.35	28.09, 28.59, 28.96
[NMe$_4$]$_2$[VO(NCS)$_4$(OH$_2$)]	17.40	12.45, 13.27, 14.03, 14.81		25.3
[NH$_4$]$_3$[VOF$_5$]	15.50	10.30		
K$_3$[VO(CN)$_5$]	25.47	13.72, 14.44, 15.17, 15.87		
[VO(SMe$_2$O)$_5$][ClO$_4$]$_2$ *	15.10	12.52		

* Room-temperature spectrum only.

Band I.—We propose that absorptions labelled under this heading are attributable to the one-electron promotion $3d_{xy}{}^* \rightarrow 3d_{x^2-y^2}{}^*$. However, this assignment is not clear cut when based on polarisation arguments alone. The transition is formally forbidden in C_{4v} symmetry, but we find that bands which we assign to this transition appear to be more intense in *xy* than in *z* polarisation. In contrast to this the transition is electronically allowed in *z* polarisation in C_2 symmetry, but forbidden in *x,y* polarisation, whereas the experimental observation is that the proposed band is comparable in intensity in both polarisations. The inclusion of spin–orbit coupling does relax the selection rules for all polarisations in each symmetry, but in view of the small value of the free-ion spin–orbit coupling constant of vanadium(IV) (250 cm^{-1}) [20] it seems unlikely that this effect alone would account for the observed intensities. In view of this we base our assignment on two other factors. First, the successful assignment of the other bands in the spectra to the other *d–d* promotions makes it seem likely that the remaining bands have the origins suggested. Secondly, and more importantly, the bands assigned to this particular promotion change in energy in the expected manner as the nature of the in-plane ligands is changed. Thus there are band maxima at 11 909, 17 720, 13 090, and 12 783 cm^{-1} in *xy*, polarisation for [VOCl$_4$]$^{2-}$, [VO(NCS)$_4$]$^{2-}$, [VOCl$_2$(tmu)$_2$], and [VOBr$_2$(tmu)$_2$] respectively. These observations are reinforced by the mull data, where we suggest that the absorptions listed under band I in Table 3 arise from the electronic promotion $3d_{xy}{}^* \rightarrow 3d_{x^2-y^2}{}^*$. This assignment is compatible with the expected order of the ligand-field strengths of the ligands concerned.

TABLE 4

Vibrational spectral data (cm^{-1}) for the compounds at room temperature

Compound	ν(V=O)	ν(V–X)	ν(V-tmu)
K$_3$[VO(CN)$_5$]	930		
[NH$_4$]$_3$[VOF$_5$]	943		
[NMe$_4$]$_2$[VO(NCS)$_4$(OH$_2$)]	960		
[VOCl$_2$(tmtu)$_2$]	990		
[VOCl$_2$(tmu)$_2$]	995	380	425
[VOBr$_2$(tmu)$_2$]	1 000	335	425
[NEt$_4$]$_2$[VOCl$_4$]	1 000	350	
[VOCl$_2$(tppo)$_2$]	1 010		
[AsPh$_4$]$_2$[VO(NCS)$_4$]	1 015		

Attempts have been made to obtain the Raman spectra of [VOX$_2$(tmu)$_2$] and [NEt$_4$]$_2$[VOCl$_4$]. These compounds decomposed in the exciting radiation giving unsatisfactory results except for a weak spectrum of [VOCl$_2$(tmu)$_2$] which below 250 cm^{-1} gave absorptions at 245, 115, 55, and 35 cm^{-1}.

In the [VOX$_2$(tmu)$_2$] compounds the band which we assign to the $3d_{xy}{}^* \rightarrow 3d_{x^2-y^2}$ promotion occurs 520 cm^{-1} to lower energy in *z* polarisation. Examination of the selection rules show that this is compatible with this transition being essentially vibronically allowed in *x,y* polarisation, the wavenumber of the allowing vibration being 520 cm^{-1}. There are two vibrations of this order of magnitude (566 and 586 cm^{-1}) in the complexes which appear to be ligand vibrations since they are also present in the free ligand. Either of these may correspond to the allowing vibration, but due to the lack of resolution on band I the precise wavenumbers may differ from 520 cm^{-1}.

Band II.—Absorption bands under this heading are proposed to arise from the electronic excitation $3d_{xy}{}^* \rightarrow 3d_{xz}{}^*, 3d_{yz}{}^*$. These correspond to the band systems in *x,y* polarisation at 5 K which have electronic origins at 13 097, 14 280, and 14 020 cm^{-1} in [VOCl$_4$]$^{2-}$, [VOCl$_2$(tmu)$_2$], and [VOBr$_2$(tmu)$_2$] respectively, and the unresolved band centred on 14 060 cm^{-1} in [AsPh$_4$]$_2$[VO(NCS)$_4$]. The assignment is based on two factors. The observation that these particular bands are more intense

TABLE 5

Selection rules for electric dipole transitions

Transition	C_{4v} Polarisation *z*	C_{4v} Polarisation *xy*	C_{4v}' Polarisation *z*	C_{4v}' Polarisation *xy*
$(xy)b_2 \rightarrow a_1(z^2)$	F(B_2)	F(E)	F(E,B_2,B_1)	A
$\rightarrow b_1(x^2 - y^2)$	F(A_2)	F(E)	A	A
			A	A
$\rightarrow e(xz,yz)$	F(E)	A		
			F(E_1,B_2,B_1)	A
	C_2 Polarisation *z*	C_2 Polarisation *x,y*	C_2' Polarisation *z*	C_2' Polarisation *x,y*
$(xy)a \rightarrow a(z^2,x^2 - y^2)$	A	F(B)	A	A
$\rightarrow b(xz,yz)$	F(B)	A	A	A

F = Forbidden, A = allowed. The symmetry of the vibration which will make an electronically forbidden band allowed is given in parentheses.

in x,y than in z polarisation is compatible with the selection rules for this assignment. In addition there are vibrational progressions involving vibrational quanta of 800 and 795 cm^{-1} for $[VOBr_2(tmu)_2]$ and $[VOCl_4]^{2-}$ respectively, which are attributable to the totally symmetric V–O(terminal) stretching vibration in the excited state. The involvement of the ν[V–O(terminal)] is compatible with electron promotion into the $3d_{xz}$*, $3d_{yz}$* orbitals, since they are involved in π bonding to the terminal oxo-group. A reduction in the frequency of the excited state vibration relative to that in the ground state (1 000 cm^{-1} for both of the above compounds, Table 4) would be expected for such a transition, since it concerns the promotion of an electron into an antibonding molecular orbital, thus weakening this bond. The lower but non-zero intensity of the z-polarised spectra may be attributed to a relaxation of the selection rules by either vibronic coupling or by spin–orbit coupling. The poor resolution so far obtained in z polarisation does not enable us to comment on this point.

Band III.—The third band system in each of the single-crystal studies shows much more resolution at 5 K than any of the other bands. The similarities in the energies of the first members of band III, and the occurrence of similar vibrational fine structure, suggests that for each compound band III has a common assignment. In the compounds with C_2 symmetry the greater intensity in z polarisation coupled with the similar intensity of the z-polarised band to that of the allowed x,y-polarised band II suggests that band III is electronically allowed in z polarisation. This is compatible with it being an $A \rightarrow A$ transition. This conclusion is reinforced by the observation that the strongest features in x,y polarisation are *ca.* 400 and 350 cm^{-1} higher in energy than the strongest features in z polarisation in $[VOCl_2(tmu)_2]$ and $[VOBr_2(tmu)_2]$ respectively, see Figures 1 and 2. This indicates that the major source of intensity in x,y polarisation is due to vibronic coupling, presumably with vibrations in the electronic excited states. The differing energies of these allowing vibrations suggest that they are probably metal–halogen vibrations in the excited state. The corresponding vibrations in the electronic ground state are 380 and 350 cm^{-1} for the chloro- and bromo-complexes respectively, although it is possible that they could be ν[V–O(tmu)] vibrations which are reduced in frequency compared with the analogous vibration in the ground state (425 cm^{-1} for each compound). However the major progressions in both polarisations involve vibrational quanta of *ca.* 800 cm^{-1}, which we attribute to ν[V–O(terminal)] in the electronic excited state. A comparison of the intensities of bands II and III for the ions with C_{4v} symmetry suggests that band III in these systems is due to an electronically forbidden transition, *i.e.* it is either $B_2 \rightarrow A_1$, $B_2 \rightarrow B_1$, or $B_2 \rightarrow A_2$ in character. However there are progressions involving energy separations of *ca.* 790 and 750 cm^{-1} for $[VOCl_4]^{2-}$ and $[VO(NCS)_4]^{2-}$ respectively, which indicate coupling with ν[V–O(terminal)] in the electronic excited state. This suggests that in the electronic excited state the electron is occupying an orbital which is involved in bonding with the terminal oxygen atom. It is also noticeable that the electronic origins of band III in all the five-co-ordinate compounds studied lie in the narrow range 21 000—22 600 cm^{-1} for a variety of in-plane ligands. In addition there is a marked difference in the spectra in the region of band III between $[VO(NCS)_4]^{2-}$ and $[VO(NCS)_4(OH_2)]^{2-}$. Because excited states with B_1 or A_2 symmetry would involve promotion of an electron from π orbitals of the in-plane ligands the above observations collectively seem to make these assignments unlikely. This leaves the $B_2 \rightarrow A_1$ type of promotion as the most probable assignment of band III in the C_{4v} system.

Although the experimental data establish the symmetry of the excited state in both the C_2 and C_{4v} systems with a reasonable degree of confidence, there still remains the problem concerning which molecular-orbital configurations are involved. There are three types of electron promotion which could give rise to an excited state of A_1 symmetry (we confine ourselves to the nomenclature of C_{4v} symmetry for simplicity): (*i*) the *d–d* type of promotion $3d_{xy}^* \rightarrow 3d_{z^2}^*$; (*ii*) a charge-transfer process involving the promotion of a single electron from a doubly occupied molecular orbital of a_1 symmetry into the already singly occupied $3d_{xy}$* orbital, *e.g.* $(3d_{z^2})^2(3d_{xy}^*)^1 \rightarrow (3d_{z^2})^1(3d_{xy}^*)^2$; (*iii*) a charge-transfer type of transition involving single-electron promotion from a doubly occupied molecular orbital into an appropriate empty antibonding orbital, *e.g.* $(3d_{xy})^2(3d_{xy}^*) \rightarrow (3d_{xy})^1(3d_{xy}^*)^1(3d_{z^2}^*)^1$ or $(e)^4(3d_{xy}^*)^1 \rightarrow (e)^3(3d_{xy})^1(e^*)^1$. The experimental data readily preclude $(e)^4(3d_{xy}^*)^1 \rightarrow (e)^3(3d_{xy}^*)^1(e^*)^1$ on the following grounds. If the e orbitals involved are the bonding orbitals involving $3d_{xz}, 3d_{yz}$, then the promotion of one of these bonding electrons into a similar antibonding molecular orbital would be expected to cause a dramatic weakening of the V–O(terminal) bond, with a concomitant large reduction in its vibrational frequency. However the observed frequency is very similar in magnitude to that associated with the $(3d_{xy}^*) \rightarrow (3d_{xz}^*, 3d_{yz}^*)$ transition. Similarly if the e orbitals were a non-bonding ligand combination then we would not have expected such a dramatic difference in the spectrum in the region of band III between $[VO(NCS)_4]^{2-}$ and $[VO(NCS)_4(OH_2)]^{2-}$, or so little variation in the position of the electronic origin of band III as the in-plane ligands are varied.

It is more difficult to choose between the other possibilities based on the magnitudes of the excited state V–O vibrations, since it seems likely that they could be of similar size in each of the three situations. However, the magnitudes of the allowing vibration in x,y polarisation in the $[VOX_2(tmu)_2]$ compounds seem to offer the possibility of making a choice. These excited-state vibrations are different in magnitude for the chloro- and bromo-compounds suggesting that they are essentially metal–halide in character. Also these values are equal to or greater than the corresponding ground-state vibrations. These observations strongly suggest that the electron promotion $(3d_{xy}{*})\rightarrow(3d_{z^2}{*})$ is the correct one since this involves removing an electron from an in-plane *antibonding* molecular orbital thus strengthening the in-plane bonding. On the other hand, the excitations $(3d_{z^2})^2(3d_{xy}{*})^1\rightarrow(3d_{z^2})^1(3d_{xy}{*})^2$ and $(3d_{xy})^2(3d_{xy})^1\rightarrow(3d_{xy})^1$-$(3d_{xy}{*})^1(3d_{z^2}{*})$ involve the *addition* of an in-plane *antibonding* electron and the *removal* of an in-plane *bonding* electron respectively. In each case we would expect a weakening of the in-plane bonding and hence a reduction in ν(V–X).

The assignment of band III to the promotion $(3d_{xy}{*})\rightarrow(3d_{z^2}{*})$ is also compatible with our data on six-co-ordinate vanadyl complexes and the single-crystal studies on $[VO][SO_4]\cdot5H_2O$.[10] There is not a great deal of difference between the terminal V–O bond lengths in the five- and six-co-ordinate complexes.[10,16,18,19,21] Thus the addition of a sixth ligand *trans* to V–O would be expected to increase the ligand-field strength in this direction with the result that the $(3d_{xy}{*})\rightarrow(3d_{z^2}{*})$ transition would move to higher energy. Our observations indicate that this transition occurs at $>30\,000$ cm^{-1} in six-co-ordinate vanadyl species.

The discussion so far has involved the interpretation of the strongest features in the spectra. Although further resolution is desirable in order to define the fine structure more accurately, we offer a brief comment on such fine structure that has been resolved on band III for the $[VOX_2(tmu)_2]$ compounds. The most detailed information is for the first three major components of the *z*-polarised spectrum of $[VOCl_2(tmu)_2]$. As illustrated in Figure 1(*c*) this structure can be accounted for by two superimposed band systems, one built off the intense absorption, and the second off the next most intense feature, 170 ± 5 cm^{-1} higher in energy. The occurrence and the frequency of this latter feature are compatible with it being due to a terminal oxovanadium in-plane ligand bending vibration in the excited state. For example bands at 186 and 195 cm^{-1} in the i.r. spectra of $Cs_2[VOCl_5]$ and $Cs_2[CrOCl_5]$ have been assigned to a symmetric O–M–Cl bending vibration.[22] After ν[V–O-(terminal)] such a bending vibration may be expected to be the most likely to couple with the electronic excited state involving the electron in $3d_{z^2}{*}$. The extra fine structure involves separations of 45 ± 10, 88 ± 5, 205 ± 5, 290 ± 5, and 355 ± 5 cm^{-1}. The assignment of these frequencies to particular electronic excited-state vibrational modes is at present uncertain.

In contrast to the chloro-analogue the *z*-polarised spectrum of $[VOBr_2(tmu)_2]$ shows relatively poor resolution. The only definable features are at 150 ± 10 and 315 ± 10 cm^{-1} higher in energy than the major absorptions. These are ascribed to vibrational fine structure. On the other hand, the *x,y*-polarised spectrum of the bromo-compound, although weak, shows much better resolution than that obtained for the same polarisation in the chloro-analogue. Although there appears to be a *ca.* 20 cm^{-1} shift, for which we so far have no explanation, the features on the low-energy side of what we have assigned as the vibronically allowed bands can be reasonably well accounted for by extra vibrational splittings of 98 ± 5, 187 ± 5, 243 ± 5, 297 ± 5, and 370 ± 5 cm^{-1} off the corresponding most intense features in the *z*-polarised spectrum, see Figure 2(*b*).

The present study has provided more detailed polarisation data and better resolved electronic absorption spectra on a wider range of oxovanadium(IV) compounds than has hitherto been available. Our interpretation of these spectra, which places all the *d–d* transitions below 30 000 cm^{-1} for the five-co-ordinate species, is in general agreement with similar studies on $[VO(acac)_2]$ [6] (acac = acetylacetonate) and $[NEt_4]_2[VOCl_4]$,[7] and with molecular-orbital calculations on $[VOCl_4]^{2-}$ (ref. 4) and $[VOCl_2(tmu)_2]$.[23] However, we disagree with these molecular-orbital calculations in that we find the $d_{xy}{*}\rightarrow d_{x^2-y^2}{*}$ transition at lower energy than the $d_{xy}{*}\rightarrow d_{xz}{*},d_{yz}{*}$ transition in these two particular species. On the other hand, we find no support for the proposal that bands from 20 000 cm^{-1} upwards are charge-transfer in origin,[3,8] or that in general the $d_{xy}{*}\rightarrow d_{z^2}{*}$ is in the region 35 000—50 000 cm^{-1}, although this may be valid for six-co-ordinate oxovanadium(IV) compounds.

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