Magnetic Circular Dichroism Spectroscopy of the Vanadyl Ion

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Magnetic circular dichroism (m.c.d.) spectra of a series of vanadyl complexes with tetragonal symmetry have been measured in order to confirm the assignment of the *d–d* spectrum and to provide an estimate of the angular momentum of the excited ^2E state. The spectra of the ions $[VO(H_2O)_5]^{2+}$ and $[VO(NCS)_5]^{3-}$ show the presence of the expected *A* term with the correct sign in their lowest-energy band, thus confirming the original assignment of Ballhausen and Gray. At low temperature the spectrum of the species $[VO(H_2O)_5]^{2+}$ is dominated by *C* terms whose signs under the lowest-energy band again support the assignment of the lowest-energy band to the transition $^2B_2 \rightarrow {}^2E$; in addition a *C* term is found under the shoulder on the higher-energy side of this band showing that the transition is $^2B_2 \rightarrow {}^2B_1$, which obtains its intensity through second-order spin–orbit coupling to the ^2E state. An estimate is made of the orbital-reduction factor in the excited ^2E state and some molecular-orbital (MO) calculations are reported in an attempt to account for the reduction. The results suggest that previous MO treatments of the vanadyl ion have overemphasized π-bonding to the axial oxygen atom and neglected π-bonding to the equatorial ligands in the antibonding orbitals. Low-temperature m.c.d. spectra of the vanadyl ion doped into $K_3TlCl_6,2H_2O$ are also reported.

ASSIGNMENT of the *d–d* spectrum of the vanadyl ion has been a source of controversy. Ballhausen and Gray[1] assigned the near i.r. band of the ion $[VO(H_2O)_5]^{2+}$ to the transitions $^2B_2 \rightarrow {}^2E$ and $^2B_1$ on the basis of molecular orbital (MO) calculations. The third transition expected, $^2B_2 \rightarrow {}^2A_1$, was predicted to occur at *ca.* 45 000 cm^{-1}. These assignments were subsequently supported by polarized crystal spectra of $VOSO_4,5H_2O$[2] and of $[VOCl_5]^{3-}$ in the host $K_3TlCl_6,2H_2O$,[3] and by natural circular dichroism (c.d.) spectra of complexes with optically active ligands.[4] However, Ortolano *et al.*[5] have postulated that all four possible *d–d* transitions occur below 20 000 cm^{-1} and that spin–orbit coupling lifts the degeneracy of the ^2E state and is primarily responsible for the structure observed in low-temperature spectra of many vanadyl complexes.

Since assignment of the spectrum by linearly polarized light is rather limited in application we have reinvestigated the assignment using magnetic circular dichroism (m.c.d.) spectroscopy. This technique provides an ideal method for assignment of the ^2E state on account of the *A* term predicted. In addition, in principle, the technique will give an estimate of the angular momentum of the state and hence a test of covalence parameters in the excited state.[6]

The transition $^2B_2 \rightarrow {}^2E$ is allowed in *xy* polarization whereas $^2B_2 \rightarrow {}^2B_1$ is forbidden in both *xy* and *z* polarizations. It is notable that in the polarized spectrum of $VOSO_4,5H_2O$ and $[VOCl_5]^{2-}$ the dipole strength in *xy* polarization is very much greater than that in *z* polarization. The dipole strength of the former also changes little with temperature, whereas the intensity of the latter band decreases appreciably as the temperature is lowered. Ballhausen and Gray[1] argue that the shoulder at 16 000 cm^{-1}, polarized *xy*, is the transition to the $^2B_1$ state allowed vibronically *via* an e_g mode. They claim support for this from its slight temperature dependence. However, it appears more probable that this shoulder is due to the transition to the $^2B_1$ state allowed in *xy* polarization by spin–orbit coupling to the ^2E state. This seems in better agreement with the relative insensitivity of the *xy* polarization to temperature. Assignment of the $^2B_1$ state in the ion $[VOCl_5]^{2-}$ is not so clear. It could be anywhere under the band envelope polarized *xy*. However, the assignment of the *z*-polarized absorption to a vibronic mechanism for both

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

[2] C. J. Ballhausen, B. F. Djurinsky, and K. J. Watson, *J. Amer. Chem. Soc.*, 1968, **90**, 3305.

[3] R. A. D. Wentworth and T. S. Piper, *J. Chem. Phys.*, 1964, **41**, 3884.

[4] K. M. Jones and E. Larsen, *Acta Chem. Scand.*, 1965, **19**, 1210.

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

[6] P. N. Schatz and A. J. McCaffery, *Quart. Rev.*, 1969, **23**, 552.

^2E and $^2B_1$ seems unequivocal on the basis of the temperature dependence.

M.c.d. spectroscopy provides a good method for determining the importance of spin–orbit interactions in the near i.r. band system.[7] The ^2E state should show C-term intensity, but to the first order the $^2B_1$ state will have no such intensity. However, if there is appreciable second-order spin–orbit coupling between these states the $^2B_1$ state will ' borrow ' C-term intensity.

The importance of covalency in vanadyl complexes has long been recognized and led to their being the subject of some early MO calculations.[8] Covalency gives rise to an orbital-reduction factor, affecting directly the orbital angular momentum observed by m.c.d. Hence m.c.d. can provide a sensitive test for MO wavefunctions. However, Ham [9] has shown that the Jahn–Teller effect in an orbitally degenerate state can also lead to effective reduction in observed orbital angular momentum. M.c.d. provides a means of separating these two factors since it has been shown that the first moment of the m.c.d. spectrum is independent of the electron–nucleus coupling giving rise to the Jahn–Teller effect.[10] A value for the orbital-reduction factor arising from covalency can therefore be obtained. We have recently used these principles to determine such factors in metal phthalocyanines.[11]

Jahn–Teller interaction in molecules with tetragonal symmetry has received considerable attention, since in this case the active vibrational modes are non-degenerate.[12,13] Although the first moment of the m.c.d. spectrum is insensitive to Jahn–Teller interaction, the fine structure in the spectrum should be profoundly affected. In view of the simplicity of the tetragonal-symmetry problem, we have extended an earlier treatment, which predicted the fine structure expected in absorption spectrum, to discover the form of the fine structure expected in the m.c.d. spectrum of a Jahn–Teller-distorted state. Although prompted by the present work on vanadyl complexes, we will report the results of this study elsewhere.[11]

THEORY

In deriving m.c.d. parameters for the vanadyl spectrum the calculation was carried out in the crystal-field approximation. Since, effectively, only symmetry properties of the wavefunctions were used, calculations at this level predict the essential physical picture. MO's could then be introduced to calculate orbital-reduction factors.

If spin–orbit coupling is neglected the ordering of the crystal-field energy levels derived from d orbitals under the C_{4v} point group is as shown in Figure 1(*a*). Magnetic-susceptibility [1] and e.p.r. measurements confirm that the ground state is orbitally non-degenerate and the small extra-hyperfine structure in the e.p.r. spectrum of vanadyl porphyrin [15] shows the orbital occupied by the single d electron to be of b_2 symmetry. In the calculation of m.c.d. parameters we first assumed that only the transition $^2B_2 \rightarrow {}^2E$ carries dipole strength, *i.e.* we neglected the small vibronic contribution to the dipole strength of the near i.r. band. In view of its small temperature dependence in xy polarization and low oscillator strength in z polarization, this is a reasonable approximation.

The ^2E and $^2B_1$ functions were then used as a basis set and thus any interaction between these states is equivalent to a unitary transformation of the basis. We note that the first moment of m.c.d. is independent of such a transformation.[10] Then if the $^2B_1$ state carries no dipole strength, the first moment of m.c.d. for the i.r. band may be predicted using only the ^2E function as basis. This simplifies the calculation.

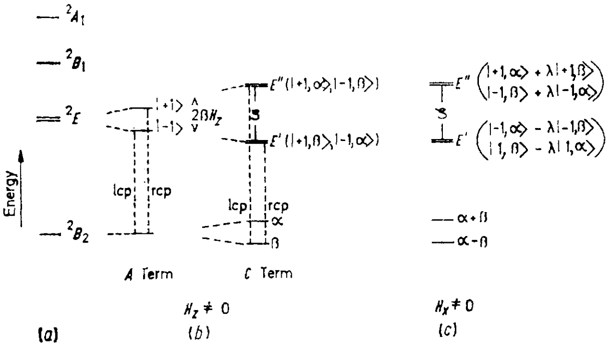

FIGURE 1 Irreducible representations of a set of d orbitals in a crystal field of C_{4v} symmetry, (*a*), the A and C terms which can arise for the transition $^2B_2 \rightarrow {}^2E$ when the magnetic field is along the four-fold axis of the system, (*b*), and the result when the magnetic field is along an axis perpendicular to the former, (*c*). l.c.p. and r.c.p. = left and right circularly polarized

The dipole strength arises from mixing of ***ungerade*** functions into the d-atomic functions by the low-symmetry field operator Y_1^0.[3] This operator will mix functions which transform as atomic $p_{\pm 1}$ functions into $d_{\pm 1}$ [although the mixed functions may be charge-transfer (c.t.) configurations transforming like p functions]. The selection rules for $^2B_2 \rightarrow {}^2E$ then reduce to the forms $\langle p_+|m_-|d_{+2}\rangle \equiv$ right cicularly polarized and $\langle p_-|m_+|d_{-2}\rangle \equiv$ left circularly polarized.[16]

When the effect of spin–orbit coupling is included the ^2E state splits into E' and E'' components: $|E'\alpha',\beta'\rangle \equiv |1,-\frac{1}{2}\rangle,|-1,+\frac{1}{2}\rangle$; and $|E''\alpha'',\beta''\rangle \equiv |1,\frac{1}{2}\rangle,|-1,-\frac{1}{2}\rangle$. The $^2B_1$ state transforms as E'', mixing with E'' (^2E). We adopted molecule fixed axes, with the Z-axis along the V–O bond. In solution, with random orientation of all molecules, half the observed dipole strength arises from molecules whose Z-axis lies parallel to the applied external magnetic field, and half from molecules whose Z-axis lies perpendicular to the field.

Considering the first category, in which the external field has symmetry H_z with respect to the molecular axes, there

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[7] M. J. Harding, S. F. Mason, D. R. Robbins, and A. J. Thomson, *J. Chem. Soc.* (*A*), 1971, 3047.

[8] L. G. Vanquickenborne and S. P. McGlynn, *Theoret. Chim. Acta*, 1968, **9**, 390.

[9] F. S. Ham, *Phys. Rev.*, 1965, **138A**, 1727.

[10] P. J. Stephens, *J. Chem. Phys.*, 1970, **52**, 3489.

[11] M. J. Stillman and A. J. Thomson, *J.C.S. Faraday II*, in the press.

[12] C. J. Ballhausen, *Theoret. Chim. Acta*, 1965, **3**, 368.

[13] M. D. Sturge, *Solid State Phys.*, 1967, **20**, 92.

[14] D. J. Robbins, *Theoret. Chim. Acta*, in the press.

[15] D. Kivelson and Sai-Kwing Lee, *J. Chem. Phys.*, 1964, **41**, 1896.

[16] J. S. Griffith, 'The Theory of Transition-metal Ions,' Cambridge, 1964.

will be two principal contributions to the first moment of m.c.d. The first arises from first-order Zeeman splitting of the ^2E state (A term) and the second from Zeeman splitting of the $^2B_2$ ground state combined with spin–orbit splitting of the ^2E excited state (a spin-dependent C term). Neglecting saturation effects, which occur at very low temperatures, the first moment of m.c.d. has form (1), where

$$\frac{\langle[\theta]_{\mathrm{M}}\rangle_1}{D} = -33{\cdot}53\left(\frac{A}{2} + \frac{C}{\boldsymbol{k}T}\right) \qquad (1)$$

D is the *total* observed dipole strength at a given temperature. The parameters A and C are given by equations (2a) and (2b), where ζ is the spin–orbit coupling constant.

$$A = \langle E_1|l_Z|E_1\rangle \qquad (2a)$$
$$(= +\beta \text{ in the atomic approximation})$$

$$C = -\frac{\beta}{4} \times \zeta \qquad (2b)$$

We note that these two contributions to the first moment are of opposite sign. This is a further example of a rather general rule which we have pointed out previously.[11] The rule may be stated as follows. If spin–orbit coupling in the excited state arises predominantly from the metal ion, A and spin-dependent C terms will have opposing signs in a metal ion with less than a half-filled shell and the same sign if the metal ion has more than a half-filled shell of d electrons. The basis of this rule is clear from the work of Henry *et al.*[17] There are no intra-state B terms since the matrix element $\langle E'|l_Z|E''\rangle$ is equal to zero.

Considering the second category of molecules, in which the external field has symmetry H_x with respect to the molecular axes, there can be no first-order splitting of the ^2E state since the matrix elements $\langle\pm 1|l\pm|\pm 1\rangle$ are zero. However the operator $2S_x = (S_+ + S_-)$ can cause mixing of the E' and E'' states through matrix elements of the type $\langle 1,\alpha|S_+|1,\beta\rangle$. Consideration of the selection rules shows that this will not give rise to m.c.d. to the first order. This results from the fact that the field H_x splits the $^2B_2$ ground state into linear combinations $\alpha \pm \beta$, where α and β are defined with respect to the molecular Z-axis, the axis of quantization.

These conclusions are illustrated in Figure 1(*b*) and (*c*). Hence in a randomly oriented sample the first moment of m.c.d. is given to a good approximation by equation (1). When all the molecules are oriented with their Z-axes parallel to the external field the parameters of equation (2) should be multiplied by a factor of two.

The final stage of the calculation is the introduction of covalence by substitution of MO's for crystal-field wavefunctions in the matrix element of l_Z (see Appendix). We considered the effect of displacement of the vanadyl ion above the plane of the four equatorial ligands since X-ray diffraction [2,18,19] data on a number of complexes reveals a small distortion of this type. The result deduced shows that $\langle e_x|l_z|e_y\rangle \approx -0{\cdot}98i\hbar\beta$ compared with the value of $-i\hbar\beta$ calculated for the ionic model. This reduction is small because, when making the conventional assumption that in the antibonding e MO's the principal covalent interaction is between vanadium and oxygen atoms of the vanadyl ion, the interacting atoms lie along the axis of quantization.

Our conclusions drawn from this theoretical analysis are summarized as follows. (*i*) At room temperature an A term, identifying the ^2E state, is expected. (*ii*) As the temperature is lowered the first moment will change sign as the spin-dependent C term begins to dominate. A plot of the first moment against $1/\boldsymbol{k}T$ yields ζ, the spin–orbit coupling constant of the excited state. (*iii*) If spin–orbit coupling between ^2E and $^2B_1$ is unimportant m.c.d. associated with the transition to the latter state should be virtually independent of temperature, since to the first order the $^2B_1$ state has no C-term intensity. However, if the $^2B_1$ state derives the majority of its intensity from mixing with ^2E, as we have assumed, it should show a similar temperature dependence to the latter. (*iv*) In principle the effect of covalence in the ^2E state can be estimated from the first moment. Thus the temperature dependence of the first moment gives the contribution from the spin-dependent C term and the intercept gives the value of the A term.

EXPERIMENTAL

The samples were prepared as follows. (*i*) $[\mathrm{VO(H_2O)_5}]^{2+}$. AnalaR grade $\mathrm{VOSO_4},x\mathrm{H_2O}$ (B.D.H.) was recrystallized from dilute $\mathrm{H_2SO_4}$ and solutions for spectroscopy were made up in 0·1M-$\mathrm{H_2SO_4}$. Absorption coefficients were taken from the literature.[20] (*ii*) $\mathrm{VO(NCS)_5(Et_4N)_3}$. A standard preparation was used [21] and the product recrystallized from alcohol. Spectra were measured in acetonitrile after ensuring that the spectra were identical in dilute and concentrated solution and hence that solvolysis is negligible. (*iii*) $[\mathrm{VOCl_5}]^{3-}$. A solution of the tetragonal host $\mathrm{K_3TlCl_6,2H_2O}$ was formed by chlorine oxidation of a suspension of TlCl in 12M-HCl followed by addition of KCl.[22] A small quantity of $\mathrm{VOSO_4},x\mathrm{H_2O}$ was added to this solution to produce a deep blue colour. Small seed crystals obtained from this solution were suspended in a saturated solution to grow a crystal of dimensions 6 × 4 × 4 mm^3. The blue crystal was dichroic and was polished on two faces normal to the unique axis. (*iv*) $\mathrm{K_2[PtCl_4]}$. The complex $\mathrm{K_2[PtCl_4]}$ was prepared from dihydrogen hexachloroplatinate(IV) by reduction with hydrazine hydrochloride.[23] The m.c.d. spectrum was measured in 0·5M-HCl. (*v*) In order to study the temperature dependence of the m.c.d. spectrum of the vanadyl ion a film of poly(vinyl acetate) (pva) containing $\mathrm{VOSO_4},x\mathrm{H_2O}$ was made by allowing a solution of the polymer in dilute sulphuric acid to evaporate on a slide. A rigid film of excellent transparency was obtained.

M.c.d. measurements were made with the apparatus previously described.[7] To study the temperature dependence of the plastic film of the vanadyl ion a small heater was wound on the sample mount between the sample and the point of contact with the helium bore of the magnet.

RESULTS AND DISCUSSION

Room-temperature solution spectra of the ions $[\mathrm{VO(H_2O)_5}]^{2+}$ and $[\mathrm{VO(NCS)_5}]^{3-}$ are given in Figures 2 and 3. The room temperature and 4 K spectra of the ion $[\mathrm{VOCl_5}]^{3-}$ in the tetragonal host $\mathrm{K_3TlCl_6,2H_2O}$ were

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[17] C. H. Henry, S. E. Schnatterley, and C. P. Slichter, *Phys. Rev.*, 1965, **A137**, 583.

[18] A. C. Hazell, *J. Chem. Soc.*, 1963, 5745.

[19] J. Selbin, G. Maus, and D. L. Johnson, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1735.

[20] C. K. Jorgensen, ' Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, 1962.

[21] J. Selbin and L. H. Holmes, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1111.

[22] B. Meyer, *Z. anorg. Chem.*, 1900, **24**, 321.

[23] G. B. Kauffnam and D. O. Cowan, *Inorg. Synth.*, 1963, **8**, 239.

measured with the light beam propagated along the unique crystal axis and are shown in Figure 4. In this system the V–O bond is oriented parallel to the fourfold crystal axis.[3] The solution spectrum of the complex $K_2[PtCl_4]$ shown in Figure 5 was remeasured because the published[24] value of A/D is greater than that predicted by the theory given above. M.c.d. parameters obtained by curve fitting and by moments analysis on these spectra are given in the Table. M.c.d. spectra of the vanadyl ion in pva between 4·2 and 300 K are shown in Figure 6.

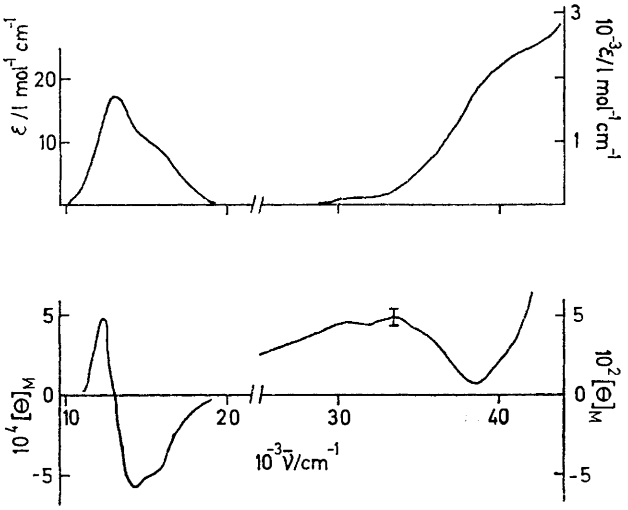

FIGURE 2 M.c.d. and absorption (upper) spectra of the species $[VO(H_2O)_5]^{2+}$ in 0·1M-H_2SO_4 at room temperature

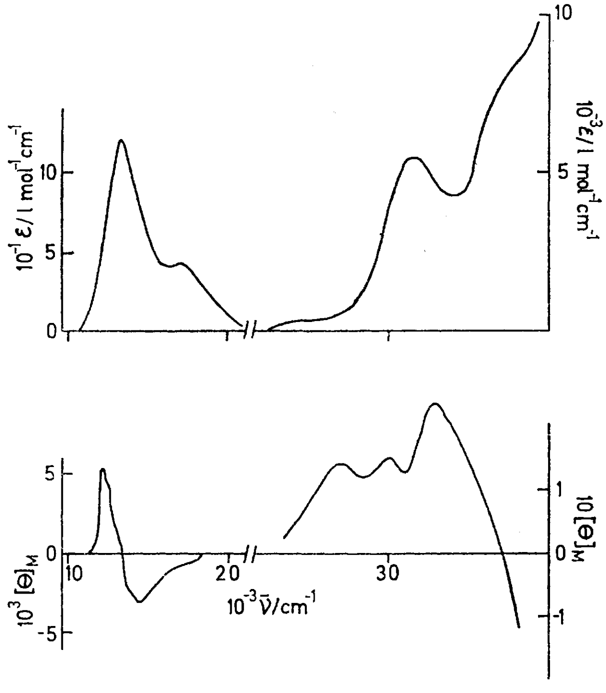

FIGURE 3 M.c.d. and absorption (upper) spectra of the ion $[VO(NCS)_5]^{3-}$ in acetonitrile at room temperature

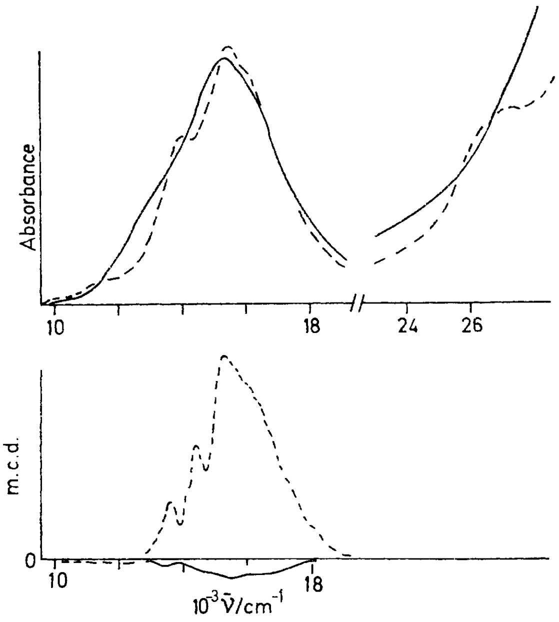

FIGURE 4 M.c.d. and absorption (upper) spectra of the ion $[VOCl_5]^{3-}$ in a single crystal of $K_3TlCl_6,2H_2O$ at 295 (——) and *ca.* 4 K (— — —)

Figure 4 shows that the first moment of m.c.d. in the lowest-energy transitions of $[VOCl_5]^{3-}$ is small, although the large increase in rotational strength at low temperature clearly demonstrates the importance of C terms. The 4 K absorption and m.c.d. spectra show a vibrational progression of *ca.* 700—800 cm⁻¹ which is assigned to the a_{1g} V–O stretching mode. The wavenumber of this vibration is characteristically 985 ± 50 cm⁻¹ for a series

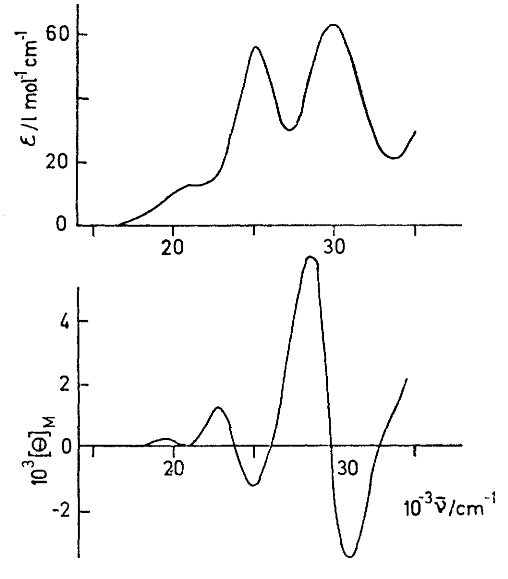

FIGURE 5 M.c.d. and absorption (upper) spectra of the complex $K_2[PtCl_4]$ in 0·5M-HCl at room temperature

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[24] A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *J. Amer. Chem. Soc.*, 1968, **90**, 5370.

of vanadyl complexes [25] and is expected to be reduced on promotion of an electron from an essentially non-bonding to an antibonding orbital. A similar progression has been observed in 90 K absorption spectrum of the complex [VO(acac)$_2$].[26a] The high-energy side of the band shows a poorly resolved progression of *ca.* 350 cm^{-1}, but since vibrational data for this system are scarce it is not possible to decide whether this is due to a second a_{1g} mode or to a non-totally symmetric mode induced by Jahn–Teller instability in the ^2E state.

Experimental m.c.d. parameters

Complex	Transition	$10^{-3}\bar{\nu}_{max.}$ cm^{-1}	$\varepsilon_{max.}$ l mol^{-1} cm^{-1}	$10^3\nu_{\frac{1}{2}}$ cm^{-1}	D Debye^2	B [a] (β/cm^{-1})	A/D β *a*	A/D β *b*
[VO(H$_2$O)$_5$]$^{2+}$	$^2B_2 \rightarrow {}^2E$	12·93	16·5	2·85	0·36 × 10^{-1} [c]	−0·12 × 10^{-5}	−0·12	−0·23
	$\rightarrow {}^2B_1$	15·63	7·5	2·57	0·12 × 10^{-1} [c]	0·34 × 10^{-5}		
[VO(NCS)$_5$]$^{3-}$	$\rightarrow {}^2E$	13·37	120	2·20	0·22 [b]	−0·4 × 10^{-5}	−0·23	−0·15
	$\rightarrow {}^2B_1$	17·36	39·6	3·05	0·73 × 10^{-1} [c]	v. small		
K$_2$[PtCl$_4$]	$^1A_{1g} \rightarrow {}^1E_g$	30·0	63·5		0·92 × 10^{-1} [d]	−0·68 × 10^{-5}	−0·38	−0·37

[a] Curve fitting. [b] Moments analysis. Integration over ^2E and $^2B_1$ bands followed by correction for dipole strength of $^2B_1$. [c] Curve-stripping program; R. E. Waddell, unpublished work. [d] Integration.

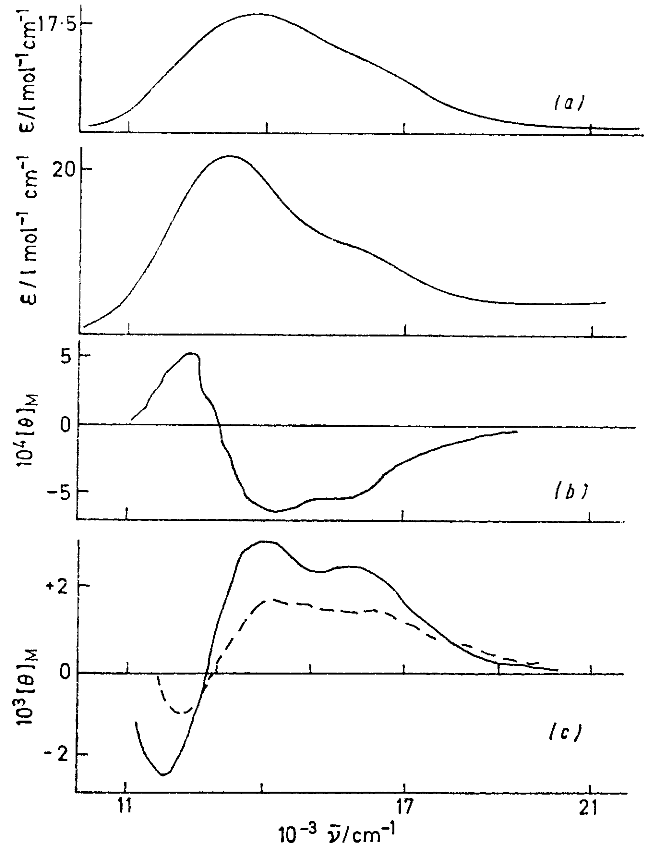

FIGURE 6 Spectra of the ion [VO(H$_2$O)$_5$]$^{2+}$: (*a*), absorption in pva film at 300 and 4·2 K; (*b*), m.c.d. in H$_2$SO$_4$; and (*c*), m.c.d. in pva film at 4·2 (——) and 18·5 K (— — —)

There are similarities in the absorption and m.c.d. spectra of the ions [VO(H$_2$O)$_5$]$^{2+}$ and [VO(NCS)$_5$]$^{3-}$ in the range 20 000—40 000 cm^{-1}. The first intense band in these systems was assigned to the c.t. transition $^2B_2 \rightarrow {}^2E$, which principally involves transfer of an electron from the axial oxygen to the metal atom. This is expected to show a negative A term, but none is evident in the spectrum. There are also rather weak bands at *ca.* 31 000 cm^{-1} in the ion [VO(H$_2$O)$_5$]$^{2+}$ and *ca.* 25 000 cm^{-1} in [VO(NCS)$_5$]$^{3-}$ which show negative B terms, and which may correspond to the band at *ca.* 27 000 cm^{-1} appearing in the 4 K absorption spectrum of [VOCl$_5$]$^{3-}$.

It can be seen that the negative first moment associated with the lowest-energy band of the ions [VO(H$_2$O)$_5$]$^{2+}$ and [VO(NCS)$_5$]$^{3-}$ confirms the original assignment [1] to the transition $^2B_2 \rightarrow {}^2E$. At low temperature the spin-dependent C term dominates in the case of the vanadyl ion in pva, the sign of the first moment now being positive. In addition the sign of the shoulder to high energy of this band has also changed sign showing that spin–orbit coupling between the ^2E and $^2B_1$ states is indeed important and therefore the source of the intensity of the $^2B_2 \rightarrow {}^2B_1$ transition. This observation also provides confirmation of the assignment.

An attempt was made to study the temperature dependence of this band accurately but, since the rotational strength is low and the low-energy edge of the band is close to the long-wavelength limit of our instrument, we were unable to obtain a series of spectra which fall to zero at low energy. Hence an accurate moments analysis was not possible. However we obtained better spectra at room temperature and, as shown in the Table, the observed magnitude of the first moment is much reduced from the value —0·5 predicted by the ionic model. Since the first moment is independent of the Jahn–Teller effect this reduction may arise from covalence effects or from partial cancellation by the positive first moment of the spin C term. As we were unable to separate these effects quantitatively by an accurate study of the temperature dependence it is only possible to estimate these factors. Typical values for ζ from e.p.r. data lie between 150 and 175 cm^{-1}.[26b] Hence the first moment of the C term is estimated to be $\langle C/D \rangle_1 = +\frac{\beta}{4} \times \frac{\zeta}{kT}$ cm^{-1} = 0·18—0·21 cm^{-1} at 300 K and the resultant first moment predicted by the ionic model is in the range —0·32 to —0·29β cm^{-1}. Comparison with the

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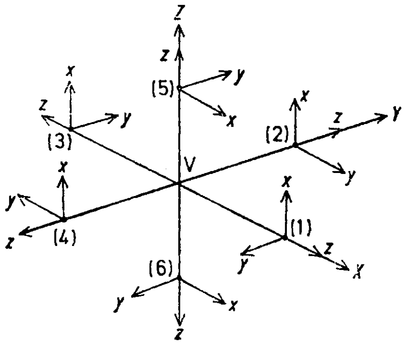
[25] J. Selbin, L. H. Holmes, and S. P. McGlynn, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1359.

[26] (*a*) G. Basu, W. Yeranos, and R. L. Belford, *Inorg. Chem.*, 1964, **3**, 929; (*b*) L. J. Boucher, E. C. Tynan, and Teh Fu Yen, 'Electron Spin Resonance of Metal Complexes,' ed. Teh Fu Yen, Adam Hilger, 1969.

observed first moments gives the following estimates for the orbital-reduction factor: $[VO(H_2O)_5]^{2+}$, 0·67—0·82; and $[VO(NCS)_5]^{3-}$, 0·47—0·52. In the case of the complex $K_2[PtCl_4]$, which has a $^1A_{1g}$ ground state, there is no spin C term and the reduction factor is found to be 0·74. The original estimate given by Martin *et al.*[27] was 0·8, and therefore the analysis of the spectrum given by McCaffery *et al.*[24] appears incorrect.

The reduction of angular momentum estimated from the data in this way is much larger than that obtained after introduction of covalence using a LCAO MO approach (see Appendix). Because the reduction factor is defined as a ratio of equations (A.2) and (A.3) it is determined largely by two-centre overlap integrals and coefficients γ and δ. Since these are the smallest terms the ratio will not be greatly affected by changes in charge distribution within the complex, by changes in the angle θ as long as this remains small (Figure 7), or by use of better functions in the evaluation of overlap integrals. In order to obtain better agreement with the observed magnitude of the orbital-reduction factor within the present LCAO approximation it would be necessary to proceed in one of two ways.

(a) V atom in-plane



(b) V atom out-of-plane

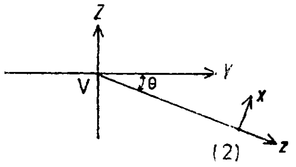


FIGURE 7

First, to increase considerably the equatorial out-of-plane π-bonding coefficient γ. This may be illustrated by consideration of bonding e orbitals which correspond to antibonding orbitals of equation (A.1), and for which the coefficients given by Vanquickenborne and McGlynn[8] are $\lambda = 0{\cdot}08$, $\alpha = 0{\cdot}37$, $\beta = -0{\cdot}48$, $\gamma/\sqrt{2} = 0{\cdot}30$, and $\delta = 0$. Substituting these values in equations (A.2) and (A.3) produces an orbital-reduction factor of 0·66. It has been pointed out already that there is no A term associated with the transition usually assigned to charge transfer from these bonding e orbitals to the metal atom, and this may be due in part to appreciable quenching of orbital angular momentum induced by covalency. Secondly, however, it is possible that some reduction occurs through admixture of metal p with d orbitals, since angular momenta associated with p and d orbitals of a single atom are opposite in sign.[16]

The degree of covalency in the ground state can be estimated from hyperfine and transferred-hyperfine interaction observed in magnetic-resonance experiments.[28] Both e.p.r. measurements on vanadium(IV) in borate glasses[29] and n.m.r. measurements on the ion $[VO(H_2O)_5]^{2+}$ [30] indicate that there is appreciable in-plane π-bonding between the vanadium d_{xy} orbital and appropriate p orbitals of the oxygen ligands. However it is much more difficult to infer similar information for excited states, but in view of these results it would seem reasonable to expect a rather larger coefficient γ in equation (A.1) than that predicted by Vanquickenborne and McGlynn.[8] Of course final judgement should await variable-temperature experiments and a more rigorous calculation, but the implication of the preliminary m.c.d. measurements is that if the simple LCAO formalism is used to describe the bonding in vanadyl complexes it can only be made consistent with experiment if out-of-plane π-bonding to the equatorial ligands is much more important in the antibonding orbitals than has so far been assumed.

APPENDIX

The Orbital-reduction Factor.—The effects of covalency may be introduced into calculation of the angular momentum of the excited state by construction of MO's.[31] X-Ray diffraction data on a number of vanadyl complexes show the vanadium atom lies above the plane of the equatorial ligands,[2,18,19] and if small deviations from C_{4v} symmetry are neglected a co-ordinate system may be constructed as in Figure 7. Here ligand (5) is the oxygen atom of the VO^{2+} ion, all localized ligand co-ordinates are right-handed systems, and metal–ligand bonds are inclined by an angle θ with respect to the principal co-ordinates X, Y, and Z. Since the metal (yz,xz) orbitals are no longer of pure π-symmetry with respect to the equatorial plane they may mix with ligand σ- and π-orbitals to give the basis functions (A.1) for the doubly degenerate state (convention as Griffith[16]), where N is a normalizing constant, $t\xi$ and $t\eta$

$$\begin{aligned} e_x &= N[\lambda t\xi + \alpha p_{y5} + \beta p_{y6} + \\ &\qquad \frac{\gamma}{\sqrt{G}}(p_{x2} - p_{x4}) + \frac{\delta}{\sqrt{F}}(p_{z2} - p_{z4})] \\ e_y &= -N[\lambda t\eta + \alpha p_{x5} - \beta p_{x6} + \\ &\qquad \frac{\gamma}{\sqrt{G}}(p_{x1} - p_{x3}) + \frac{\delta}{\sqrt{F}}(p_{x1} - p_{x3})] \end{aligned} \tag{A.1}$$

are metal orbitals derived from the t_{2g} set in O_h symmetry,[16]

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[27] D. S. Martin, J. G. Foss, M. E. McCarville, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 1966, **5**, 491.

[28] J. Owen and J. H. M. Thornley, *Rep. Progr. Phys.*, 1966, **29**, 673.

[29] H. G. Hecht and T. S. Johnson, *J. Chem. Phys.*, 1967, **46**, 23.

[30] G. Vigee and J. Selbin, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2273.

[31] C. J. Ballhausen, ' Introduction to Ligand Field Theory,' McGraw–Hill, 1962.

λ, α, β, γ, and δ are mixing coefficients, and F and G are group-overlap integrals.[31]

Normalization followed by substitution in the orbital angular-momentum matrix element gives equations (A.2) and (A.3). Here standard theory has been used [32] and the Hermitian property of the operator l_z is involved to simplify some of the matrix elements.[28]

$$\begin{aligned}\frac{1}{N^2} = (\lambda^2 + \alpha^2 + \beta^2 + \gamma^2 + \delta^2 +\\ 2\alpha\lambda \langle t\xi|p_{y5}\rangle + 2\beta\gamma \langle t\xi|p_{y6}\rangle + 2\alpha\beta \langle p_{y5}|p_{y6}\rangle +\\ \frac{4\alpha\lambda}{\sqrt{G}} \langle t\xi|p_{x2}\rangle + \frac{4\alpha\gamma}{\sqrt{G}} \langle p_{y5}|p_{x2}\rangle + \frac{4\beta\gamma}{\sqrt{G}} \langle p_{y6}|p_{x2}\rangle +\\ \frac{4\lambda\delta}{\sqrt{F}} \langle t\xi|p_{z2}\rangle + \frac{4\alpha\delta}{\sqrt{F}} \langle p_{y5}|p_{z2}\rangle + \frac{4\beta\delta}{\sqrt{F}} \langle p_{y6}|p_{z2}\rangle -\\ \frac{4\gamma\delta}{\sqrt{FG}} \langle p_{x2}|p_{z4}\rangle) \quad \text{(A.2)}\end{aligned}$$

$$\begin{aligned}\langle e_x|l_z|e_y\rangle = -N^2 i\hbar (\lambda^2 + \alpha^2 + \beta^2 +\\ 2\alpha\lambda \langle t\xi|p_{y5}\rangle + 2\beta\lambda \langle t\eta|p_{y6}\rangle + 2\alpha\beta \langle p_{y5}|p_{y6}\rangle +\\ \frac{4\gamma\lambda}{\sqrt{G}} \langle t\xi|p_{x2}\rangle + \frac{4\alpha\gamma}{\sqrt{G}} \langle p_{y5}|p_{x2}\rangle + \frac{4\beta\gamma}{\sqrt{G}} \langle p_{x6}|p_{y2}\rangle +\\ \frac{4\lambda\delta}{\sqrt{F}} \langle t\xi|p_{z2}\rangle + \frac{4\alpha\delta}{\sqrt{F}} \langle p_{y5}|p_{z2}\rangle + \frac{4\beta\delta}{\sqrt{F}} \langle p_{y6}|p_{z2}\rangle) -\\ N^2 \left(\frac{\gamma^2}{G} \langle p_{x2} - p_{x4}|l_z|p_{x1} - p_{x3}\rangle + \frac{2\gamma\delta}{\sqrt{FG}} \langle p_{z2} -\right.\\ \left. p_{z4}|l_z|p_{x1} - p_{x3}\rangle + \frac{\delta^2}{F} \langle p_{z2} - p_{z4}|l_z|p_{z1} - p_{z3}\rangle\right) \quad \text{(A.3)}\end{aligned}$$

In order to calculate the off-axis angular-momentum matrix elements when the metal atom in a complex lies out-of-plane, that is, when the angle θ is non-zero, it is necessary to proceed in two stages. (*i*) The metal co-ordinate system is rotated through an angle θ about the X or Y axes to be parallel with the co-ordinate system of a particular equatorial ligand (see Figure 7). (*ii*) The ligand co-ordinates are related to the new metal co-ordinates, and hence back to the original set X, Y, and Z. Applying this procedure to Figure 7 one finds equation (A.4). The

$$\begin{aligned}l_Z^{(M)} = l_z^{(5)} = -l_z^{(6)} = \cos\theta \left(l_x^{(1)} + i\hbar a \frac{d}{dy_1}\right) -\\ \sin\theta\, l_z^{(1)} = \cos\theta \left(l_x^{(3)} + i\hbar a \frac{d}{dy_3}\right) - \sin\theta\, l_z^{(3)} \quad \text{(A.4)}\end{aligned}$$

necessary matrix elements are then easily evaluated. For $\langle p_{x2} - p_{x4}|l_Z^{(M)}|p_{x1} - p_{x3}\rangle$ equation (A.5) is applicable,

$$\begin{aligned}l_z^{(M)}|p_{x1}\rangle = [\cos\theta \left(l_x^{(1)} + i\hbar a \frac{d}{dy_1}\right) - \sin\theta\, l_x^{(1)}]|p_{x1}\rangle\\ = \cos\theta\, (0 + i\hbar a|\delta_{xy1}\rangle) - \sin\theta\, i\hbar|p_{y1}\rangle \quad \text{(A.5)}\end{aligned}$$

where $|\delta_{xy1}\rangle$ is a function with the angular dependence of a d_{xy} orbital resulting from the operation $\frac{d}{dy}|p_x\rangle$. Repeating this process for $|p_{x3}\rangle$ gives (A.6). Similarly one finds equations (A.7) and (A.8).

$$\begin{aligned}\langle p_{x2} - p_{x4}|l_Z^{(M)}|p_{x1} - p_{x3}\rangle =\\ 4i\hbar[\cos\theta\, a\langle p_{x2}|\delta_{xy1}\rangle - \sin\theta \langle p_{x2}|p_{y1}\rangle] \quad \text{(A.6)}\end{aligned}$$

$$\begin{aligned}\langle p_{z2} - p_{z4}|l_Z^{(M)}|p_{x1} - p_{x3}\rangle =\\ 4i\hbar[\cos\theta\, a \langle p_{z2}|\delta_{xy1}\rangle - \sin\theta \langle p_{z2}|p_{y1}\rangle] \quad \text{(A.7)}\end{aligned}$$

$$\begin{aligned}\langle p_{z2} - p_{z4}|l_Z^{(M)}|p_{z1} - p_{z3}\rangle =\\ 4i\hbar \cos\theta\, [-\langle p_{z2}|p_{y1}\rangle + a\langle p_{z2}|\delta_{yz1}\rangle] \quad \text{(A.8)}\end{aligned}$$

To a very good approximation these overlap integrals are given by equations (A.9) and (A.10) (assuming that the

$$\langle p_{x2}|p_{y1}\rangle \approx 0\ (= 0 \text{ if } \theta = 0) \quad \text{(A.9)}$$

$$\langle p_{x2}|\delta_{xy1}\rangle \approx \langle p_{y6}|\delta_{xy1}\rangle \quad \text{(A.10)}$$

bond lengths d_{12} and d_{16} are approximately equal in Figure 7). Therefore, using the Hermitian property of l_Z, equation (A.11) is obtained. Expressions (A.12) and (A.13) are also applicable. The matrix element $\langle p_{z2}|\delta_{yz1}\rangle$ cannot be simplified using the Hermitian property of l_Z, and must be obtained numerically.[33] If the vanadium atom is in-plane ($\theta = \delta = 0$) and all ligands are made equivalent equations (A.2) and (A.3) should reduce to that for an octahedral complex given by Gerloch and Miller.[32]

$$\begin{aligned}\langle p_{x2}|l_Z^{(M)}|p_{x1}\rangle \approx \langle p_{y6}|l_Z^{(M)}|p_{x1}\rangle =\\ -\langle p_{x1}|l_Z^{(M)}|p_{y6}\rangle = \langle p_{x1}|l_z^{(6)} l p_{y6}\rangle =\\ -i\hbar \langle p_{x1}|p_{x6}\rangle = +i\hbar\tfrac{1}{2}[S_{26}^{\text{II}}(p,p) + S_{26}^{\sigma}(p,p)] \quad \text{(A.11)}\end{aligned}$$

$$\langle p_{z2}|\delta_{xy1}\rangle \approx 0\ (= 0 \text{ if } \theta = 0) \quad \text{(A.12)}$$

$$\langle p_{x2}|p_{y1}\rangle \approx \langle p_{z2}|p_{y6}\rangle \quad \text{(A.13)}$$

To convert the nomenclature of this work to that of Gerloch and Miller [32] set $\lambda = 1$, $\alpha = \beta = \lambda/2$, and $\gamma = \lambda/\sqrt{2}$. Then, using their nomenclature, our results reduce to the form (A.14) which is the formula given by Gerloch and Miller.[32] However, the angular momentum matrix element reduces to (A.15). This is not the result given by Gerloch and Miller. There is a mistake of sign in going from the first to the second equation on page 43 of their review.[32] The best published eigenfunctions have been calculated for the ion $[VO(H_2O)_5]^{2+}$ assuming the metal atom to lie in-plane.[8] Using these functions for the anti-bonding *e* orbitals we have as a first approximation for the ion $[VO(H_2O)_5]^{2+}$: $\lambda = 0{\cdot}86$; $\alpha = = 0{\cdot}67$; $\beta = -0{\cdot}11$; $\gamma/\sqrt{G} = -0{\cdot}09$; and $\delta = \theta = 0$. It should be noted that the differences between equations (A.2) and (A.3) occur only in the smallest terms.

$$\frac{1}{N^2} = [1 + 4\lambda S(m,p) + \lambda^2(1 - S_{12} + 2S_{13})] \quad \text{(A.14)}$$

$$\begin{aligned}\langle E_x|l_Z|E_y\rangle = -i\hbar N^2 [1 + \frac{\lambda^2}{4} + \frac{\lambda^2}{4} + \lambda S(m,p) +\\ \lambda S(m,p) - \frac{\lambda^2}{2} S_{12} + 2\lambda S(m,p) + \lambda^2 S_{13} + \lambda^2 S_{13} + \lambda^2 S_{13}] =\\ -i\hbar N^2 [1 + 4\lambda S(m,p) + \frac{\lambda^2}{2} (1 - S_{12} + 6S_{13})] \quad \text{(A.15)}\end{aligned}$$

Making the additional assumption that the ligand orbitals involved in bonding are pure p orbitals the angular-momentum matrix elements may be calculated from overlap integrals (A.16)—(A.21), and using equations (A.5), (A.8), and (A.13) one obtains (A.22). Here the M and numerical

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[32] M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, 1968, **10**, 1.

[33] D. J. Robbins, Ph.D. Thesis, University of East Anglia, 1971.

subscripts indicate metal and ligand atoms respectively, and it is implicit that the orbitals involved are vanadium $3d$

$$\langle t\xi|p_{y5}\rangle = S_{\mathrm{M5}}{}^{\Pi}(d,p) \quad (\mathrm{A}.16)$$

$$\langle t\xi|p_{y6}\rangle = S_{\mathrm{M6}}{}^{\Pi}(d,p) \quad (\mathrm{A}.17)$$

$$\langle t\xi|p_{x2}\rangle = S_{\mathrm{M2}}{}^{\Pi}(d,p) \quad (\mathrm{A}.18)$$

$$\langle p_{y5}|p_{y6}\rangle = S_{56}{}^{\Pi}(p,p) \quad (\mathrm{A}.19)$$

$$\langle p_{y5}|p_{x2}\rangle = \tfrac{1}{2}[S_{25}{}^{\Pi}(p,p) + S_{25}{}^{\sigma}(p,p)] \quad (\mathrm{A}.20)$$

$$\langle p_{x6}|p_{x2}\rangle = \tfrac{1}{2}[S_{26}{}^{\Pi}(p,p) + S_{26}{}^{\sigma}(p,p)] \quad (\mathrm{A}.21)$$

$$\langle p_{x2} - p_{x4}|l_z|p_{x1} - p_{x3}\rangle \approx 4\mathrm{i}\hbar\beta\,\langle p_{y6}|p_{x2}\rangle \quad (\mathrm{A}.22)$$

and oxygen $2p$ orbitals. These overlap integrals were obtained from tables based on simple Slater functions[34,35] with internuclear distances derived from X-ray data given by Ballhausen *et al.*[2] and the following values for the orbital exponents μ:[34] ligand (5), 2·2 (−0·5); all other ligands, 2·3 (+0·3); and vanadium, 1·0 (+1·0). The values in parentheses are approximate effective nuclear charges to which the exponents correspond. Substitution of the numerical values of (A.16) to (A.22) in equations (A.2) and (A.3) gives (A.23), which is to be compared with the value $-\mathrm{i}\hbar\beta$ calculated for the ionic model.

$$\langle e_x|l_z|l_y\rangle \approx -0{\cdot}98\,\mathrm{i}\hbar\beta \quad (\mathrm{A}.23)$$

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[34] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

[35] H. H. Jaffé, *J. Chem. Phys.*, 1953, **21**, 258.