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Crystal Field Interpretation of the Electronic Spectrum of the Pentachlorovanadate(IV) Ion

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The electronic spectrum of the pentachlorovanadate(IV) ion is discussed in terms of a crystal field model. It is difficult to interpret in terms of a C_{4v} model, but a satisfactory result is obtained if C_{2v} symmetry is assumed.

Introduction

In our original report[1] of the pentachlorovanadate(IV) ion, present in the compound $[PCl_4][VCl_5]$, we suggested that it may have C_{2v} (i.e. distorted trigonal bipyramidal) symmetry, based upon a vibrational analysis and by analogy with other d^1 systems. A recent critical review of five coordinate complexes[2] confirms our suggestion that d^1 (and d^9) complexes of stoicheiometry ML_5 would be expected to have structures based upon the trigonal bipyramid. We also stated that we were unable to assign a stereochemistry for the ion purely on the basis of its electronic spectrum, as arguments could be made for both C_{4v} (i.e. square pyramidal) or C_{2v} structures (*N.B.*, both of these models predict three d↔d bands). Recently, Russell and Smith,[3] using our spectral data, have published an interpretation of the electronic spectrum of $[VCl_5]^-$ based upon an angular overlap model. They report the data is best interpreted in terms of C_{4v} symmetry, and argue an analogy with the d^4 ion, $[MnCl_5]^{2-}$.[4,5]

The aim of this work is to support our original claim that the electronic spectrum of $[VCl_5]^-$ is a poor criterion for establishing its structure. A crystal field interpretation of the spectrum will be shown to favour C_{2v} symmetry. Although the crystal field model is undoubtedly open to criticism, it has been extensively used to interpret the electronic spectra of five coordinate complexes,[6–10] and has been more widely applied than the angular overlap model.[11,12]

Results and Discussion

Electronic Properties of $[PCl_4][VCl_5]$

As reported previously, the three d↔d transitions for $[VCl_5]^-$ occur at

$$\nu_1 = 6.2\ \text{kK}$$
$$\nu_2 = 8.1\ \text{kK}$$
$$\nu_3 = 16.0\ \text{kK}$$

Although the complex gives no e.s.r. spectrum at room temperature, a signal is obtained at −196° C at $g = 1.84$. This may be taken to indicate two ground state energy levels split by approximately thermal energy (ca. 200 cm^{-1}).

The Crystal Field

Griffith's[13] notation will be employed, unless otherwise stated. The potential at a point (r, Θ, Φ) due to a single ligand on the z-axis is given[13] by

$$V_A = \sum_{k=0}^{\infty} \gamma_{k0}{}^{A} r^k Z_{k0}(\Theta, \Phi)$$

For a set of ligands i, at the points (R_i, Θ_i, Φ_i), the potential at (r, Θ, Φ) is given[13] by

$$V_E = \sum_{k,\alpha} \beta_{k\alpha} r^k Z_{k\alpha}(\Theta, \Phi)$$

where,

$$\beta_{k\alpha} = \left(\frac{4\pi}{2k+1}\right)^{1/2} \gamma_{k0}{}^{E} \sum_{i} Z_{k\alpha}(\Theta_i, \Phi_i).$$

V, the total potential due to the ligand field, is given by $V = V_A + V_E$. For the square pyramid (C_{4v}) with Θ defined as in Fig. 1,

$$V_A = \gamma_{00}{}^{A} + \gamma_{20}{}^{A} r^2 Z_{20} + \gamma_{40}{}^{A} r^4 Z_{40},$$
$$V_E = 4\gamma_{00}{}^{E} + 2\gamma_{20}{}^{E}(3\cos^2\Theta - 1) r^2 Z_{20} + {}^1\!/_2\gamma_{40}{}^{E}(35\cos^4\Theta - 30\cos^2\Theta + 3) r^4 Z_{40} + (\sqrt{35}/2)\gamma_{40}{}^{E}(\sin^4\Theta) r^4 Z_{44}{}^{c}.$$

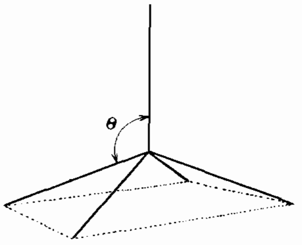

Figure 1. Square pyramid (C_{4v}).

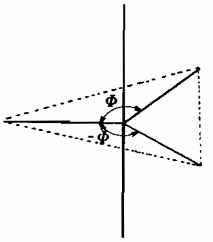

Figure 2. Distorted trigonal bipyramid (C_{2v}).

For the distorted trigonal bipyramid (C_{2v}), with Φ defined as in Fig. 2,

$$
\begin{aligned}
V_A &= 2\gamma_{00}{}^{A} + 2\gamma_{20}{}^{A}r^2Z_{20} + 2\gamma_{40}{}^{A}r^4Z_{40},\\
V_E &= 3\gamma_{00}{}^{E} - {}^{3}/_{2}\gamma_{20}{}^{E}r^2Z_{20} + {}^{1}/_{2}\sqrt{3}(1 + 2\cos2\Phi)\gamma_{20}{}^{E}r^2\\
&\quad Z_{22}{}^{c} + {}^{9}/_{8}\gamma_{40}{}^{E}r^4Z_{40} - {}^{1}/_{4}\sqrt{5}(1 + 2\cos2\Phi)\gamma_{40}{}^{E}r^4\\
&\quad Z_{42}{}^{c} + {}^{1}/_{8}\sqrt{35}(1 + 2\cos4\Phi)\gamma_{40}{}^{E}r^4Z_{44}{}^{c}.
\end{aligned}
$$

The Potential Energy Matrix

For C_{4v} symmetry, the potential energy matrix is diagonal over the manifold of real d orbitals. The diagonal elements may be evaluated for a point charge model. using the formula[13]

$$\gamma_{ko} = \frac{z}{R^{k+1}}\left(\frac{4\pi}{2k+1}\right)^{1/2}$$

where z is the charge on the ligand.

Ignoring all terms in γ_{00} (these raise all orbitals equally in energy), the energies of the d-orbitals in the field of C_{4v} symmetry are given by

$$
\begin{aligned}
E_{3z^2-r^2} &= 2Ds + 6Dt\\
E_{x^2-y^2} &= -2Ds + Dt + 5(\sin^4\Theta)Dq\\
E_{xy} &= -2Ds + Dt - 5(\sin^4\Theta)Dq\\
E_{xz} = E_{yz} &= Ds - 4Dt
\end{aligned}
$$

where

$$Dq = \frac{1}{6}\left(\frac{z_E}{R^5{}_E}\right)\overline{r^4}$$

$$Ds = \frac{1}{7}\left[\frac{z_A}{R^3{}_A} + \frac{2z_E}{R^3{}_E}(3\cos^2\Theta - 1)\right]\overline{r^2}$$

$$Dt = \frac{1}{21}\left[\frac{z_A}{R^5{}_A} + \frac{z_E}{2R^5{}_E}(35\cos^4\Theta - 30\cos^2\Theta + 3)\right]\overline{r^4}$$

For a d^1 system, the possible electronic transitions are represented in Fig. 3, their magnitudes being given by

$$
\begin{aligned}
h\nu_1 &= -3Ds + 5Dt - 5(\sin^4\Theta)Dq\\
h\nu_2 &= Ds + 10Dt\\
h\nu_3 &= -3Ds + 5Dt + 5(\sin^4\Theta)Dq\\
h(\nu_3 - \nu_1) &= 10Dq(\sin^4\Theta)
\end{aligned}
$$

However, for C_{2v} symmetry, the potential energy matrix is not diagonal over the manifold of real d orbitals; there is an interaction between the two orbitals belonging to the a_1 representation, resulting in a 2 × 2 secular determinant. Calculation has shown that this interaction is very small (i.e. less than the experimental error involved in measuring electronic spectra), and it has therefore been neglected. The energies of the d-orbitals in the field of C_{2v} symmetry are now given by

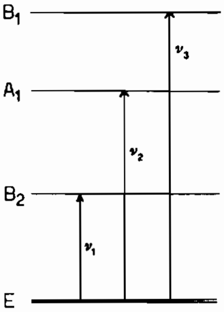

Figure 3. Energy level diagram for square pyramidal (C_{4v}) d^1 complexes.

$$
\begin{aligned}
E_{3z^2-r^2} &= 2Ds + 6Dt\\
E_{x^2-y^2} &= -2Ds + Dt + {}^{5}/_{4}(1 + 2\cos4\Phi)Dq\\
E_{xy} &= -2Ds + Dt - {}^{5}/_{4}(1 + 2\cos4\Phi)Dq\\
E_{yz} &= Ds - 4Dt + \delta\\
E_{xz} &= Ds - 4Dt - \delta
\end{aligned}
$$

where

$$Dq = \frac{1}{6}\left(\frac{z_E}{R_E{}^5}\right)\overline{r^4}$$

$$Ds = \frac{1}{7}\left(\frac{2z_A}{R_A{}^3} - \frac{3z_E}{2R_E{}^3}\right)\overline{r^2}$$

$$Dt = \frac{1}{21}\left(\frac{2z_A}{R_A{}^5} + \frac{9z_E}{8R_E{}^5}\right)\overline{r^4}$$

$$Du = \frac{3}{14}(1 + 2\cos2\Phi)\left(\frac{z_E}{R_E{}^3}\right)\overline{r^2}$$

$$\delta = \frac{5}{7}(1 + 2\cos2\Phi)Dq - Du \simeq -{}^{4}/_{7}(1 + 2\cos2\Phi)Dq$$

For a d^1 system, the possible electronic transitions are represented in Fig. 4, their magnitudes being given by

$$
\begin{aligned}
h\nu_1 &= -3Ds + 5Dt - {}^{5}/_{4}(1 + 2\cos4\Phi)Dq + \delta\\
h\nu_2 &= -3Ds + 5Dt + {}^{5}/_{4}(1 + 2\cos4\Phi)Dq + \delta\\
h\nu_3 &= Ds + 10Dt + \delta\\
h(\nu_2 - \nu_1) &= {}^{5}/_{2}(1 + 2\cos4\Phi)Dq
\end{aligned}
$$

It should be noted that the definition of Dt for the square pyramid (C_{4v}) is of a different form from that for a tetragonally distorted octahedron (C_{4v}), as defined by Piper and Carlin.[14] The present definition is more general.

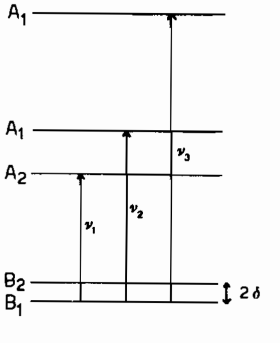

Figure 4. Energy level diagram for distorted trigonal bipyramidal (C_{2v}) d^1 complexes.

Interpretation of the Electronic Spectrum of $[VCl_5]^-$

Dq for $[VCl_6]^{2-}$ is known to be 1540 cm^{-1}.[15,16] It will be assumed that this is also the value for $[VCl_5]^-$, as very little difference in metal–ligand distance is anticipated.[3] The parameters calculated from the observed magnitudes of ν_1, ν_2 and ν_3 are given in Table I, for both C_{4v} and C_{2v} symmetry.

If the molecule had C_{4v} symmetry, then it would be expected that Θ would be between 95° and 105°.[2] The calculated value of Θ corresponds to a physically unrealistic situation (*N.B.* If it were assumed that $E(B_2) > E(A_1)$, then Θ is even larger). If the molecule had C_{2v} symmetry, then it would be expected that Φ would be between 115° and 125°.[2] Thus, the calculated value of Φ is within the acceptable range. Also, the e.s.r. spectrum was consistent with a value of $[E(B_2)–E(B_1)]$ of about 200 cm^{-1}. Finally, Table II shows that the calculated values of Ds and Dt are comparable with those for complexes of known structures. Thus, interpretation upon a crystal field model undoubtedly favours a C_{2v} structure.

In summary, it is believed that this interpretation is as valid as the interpretation based upon the angular overlap model,[3] and thus it is felt inadvisable to predict the structure of $[VCl_5]^-$ purely on the basis of its electronic spectrum. Only a full X-ray determination will finally prove its structure. However, a polarized crystal spectrum or a magnetic circular dichroism study would yield information about the symmetry of the excited state, which would distinguish between the two possible geometries.

TABLE I. Calculated Parameters for $[VCl_5]^-$.

	C_{4v}[a]	C_{2v}
Ds, cm^{-1}	–2014	271
Dt, cm^{-1}	1011	1553
Θ	116° 40′	–
Φ	–	116° 10′
δ, cm^{-1}	–	200

[a] Calculated assuming $E(A_1) > E(B_2)$.

TABLE II. Spectral Parameters for Trigonal Bipyramidal Complexes.

	Ds, cm^{-1}	Dt, cm^{-1}	Ref.
$VCl_3(Me_2S)_2$	–100	1260	6
$VBr_3(Me_2S)_2$	150	1285	6
$[VCl_5]^-$	271	1553	
$TiCl_3(NMe_3)_2$	414	1469	7
$VCl_3(NMe_3)_2$	440	1450	7
$VBr_3(NMe_3)_2$	520	1340	7
$TiBr_3(NMe_3)_2$	557	1354	7

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