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Electronic Spectrum and Stereochemistry of the Pentachlorovanadate(IV) Ion

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The electronic spectrum and stereochemistry of the pentachlorovanadate(IV) ion are discussed in terms of the angular overlap model. It is shown that the spectrum is difficult to interpret if trigonal bipyramidal geometry is assumed, but the three d-d *transitions can be adequately accounted for by a square pyramidal configuration, with the metal atom lying slightly above the centre of the equatorial plane.*

Introduction

The preparation and properties of the pentachlorovanadate(IV) ion, as found in the ionic compound $PCl_4^+VCl_5^-$, have recently been reported.[1] The electronic properties of such a simple d^1 complex halide are clearly of much interest, since they should be amenable to detailed theoretical analysis. The coordination geometry about the metal atom has not been definitely established, although a trigonal bipyramidal ion was suggested[1] on the basis of the infra-red spectrum and by analogy with other V(IV) compounds. However, it could equally well be argued that square pyramidal geometry was more probable, by analogy with the pentachloromanganate(III) ion[2] and the well-known oxovanadium(IV) systems. The *d-d* spectrum of VCl_5^- has been reported,[1] but the bands have not yet been assigned in detail.

The aim of this work was to interpret the *d-d* spectrum of VCl_5^- in terms of the angular overlap model[3-5], by finding a plausible geometry in which the spectrum could be assigned with sensible values of the angular overlap parameters. It was hoped that the results might stimulate further structural studies of this interesting system, and exemplify the utility of the angular overlap model in calculations of ligand field splittings (and perphaps predictions of molecular geometry) in non-cubic systems.

It seems reasonable to assume that the most probable structures for VCl_5^- are either trigonal bipyramidal (D_{3h}) or square pyramidal (C_{4v}). It is possible that the actual structure lies somewhere between these two extremes, but it seems unlikely that it should deviate far from either of these relatively regular shapes; in either case, simple ligand field arguments suggest that the ground state should be orbitallv degenerate but spin-orbit coupling can remove this degeneracy and there is unlikely to be any severe Jahn-Teller distortion.

We shall discuss the assignment of the *d-d* spectrum for each of these geometries in turn. First, we shall describe the electronic properties of VCl_5^- and then discuss the salient features of the theory we use to calculate the splitting of the orbitals of the partly-filled shell, with particular reference to the constraints we must place on the values of the angular overlap parameters such that they may be regarded as reasonable.

Electronic Properties of $PCl_4^+VCl_5^-$

The electronic spectrum of $PCl_4^+VCl_5^-$, has been reported[1]. Peak are observed at 8.1 kK and 16.0kK, with a shoulder at 6.2kK.

An attempt was made to measure the room temperature e.s.r. spectrum[6] at 9.4 GHz, but no signal could be seen in the range $g = 1.3 \rightarrow \infty$. This can be taken to indicate an orbitally degenerate ground state; in contrast, e.s.r. signals at $g \approx 2$ are easily observed in oxovanadium(IV) systems where the ground state is nondegenerate.

Theory: Overlap integrals and Internuclear Distances

In an angular overlap[3-5] treatment of an MX_n chromophore, the ligand field splitting is deemed to arise from the effects of covalent bonding, in contrast to the electrostatic crystal field model. If a metal *d*-orbital is allowed to overlap with a ligand group orbital, the antibonding M.O. arising from the combination, which may be regarded as still essentially a metal d-orbital with some small admixture of ligand character, lies higher in energy than the pure d-orbital by an energy which is proportional to the square of the appropriate group overlap integral G_{mx}. We can write:

$$G_{mx} = k \,.\, S_{mx}^{\lambda} \qquad (1)$$

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(1) I.M. Griffiths, D. Nicholls and K.R. Seddon, *J. Chem. Soc.* (A), 2513 (1971).
(2) I. Bernal, « Progress in Inorganic Chemistry », Proc. XI I.C.C.C., Haifa 1968, ed. M. Cais, Elsevier, 1968, p. 518.
(3) C.E. Schäffer, *Structure and Bonding*, 5, 68 (1968).
(5) C.K. Jørgensen, « Modern Aspects of Ligand Field Theory », North Holland, Amsterdam, 1971.
(6) J.H.J. Dawson and D.W. Smith, unpublished work.

where S^{λ}_{mx} is the diatomic overlap integral $S[nd_{\lambda}, \Phi(x)]$ and indicates the type of overlap ($\lambda = \sigma,\pi,\delta$, etc). If all the metal-ligand distances are the same, so that only one value of each of the S^{λ}_{mx} need be considered, we can write the destabilization δ of an antibonding MO relative to the pure metal orbital as:

$$\delta = \sum_{i} k_i^2 e_{\lambda} \tag{2}$$

where the summation is performed over the all ligand group orbitals having the same symmetry as the metal orbital. The e_{λ} are parameters depending on the identity of the metal and the ligand orbitals, and on the metal-ligand distances:

$$e_{\lambda} \propto (S^{\lambda}_{mx})^2 \tag{3}$$

For a chromophore wehere the ligands are simple monatomic ions such as halide, it seems reasonable to suppose that the atomic orbitals used for σ-bonding are not appreciably different from those used for π-bonding; thus we may consider that chloride uses only its 3p-orbitals for bonding to a metal. This assumption introduces some simplification, since we can now write:

$$e_{\pi}/e_{\sigma} = (S^{\pi}{}_{mx}/S^{\sigma}{}_{mx})^2 \tag{4}$$

This assumption has led to good results in the interpretation of ligand field splittings in a number of halide chromophores.[7-10] e_{δ} can presumably be neglected for halide complexes.

We can now formulate our strategy for the interpretation of the *d-d* spectrum of VCl_5^-. e_{σ} and e_{π} will be regarded as freely-chosen parameters, to be fitted to the experimental data; the transition energies can be written as simple multiples of these, for any assumed geometry. Our criteria for deciding upon the most probable geometry are as follows:

1. The geometry must be physically plausible.

2. The value of the ratio e_{π}/e_{σ} should be close to the value predicted by the relation $e_{\pi}/e_{\sigma} = (S^{\pi}_{mx}/S^{\sigma}_{mx})^2$ for a reasonable metal-ligand distance.

3. The absolute values of e_{π} and e_{σ} required to fit the d-d transition energies should be reasonably consistent with experimental data for other V(IV) - Cl systems, such as VCl_6^{2-}.

We now consider the question of what range of internuclear distances might be considered reasonable in VCl_5^-, and what values of the ratio e_{π}/e_{σ} would be appropriate over this range. In gaseous VCl_4, the V-Cl distance has been determined[11] as 2.14 Å. No data are available for VCl_6^{2-}; but the Ti-Cl distance in $TiCl_6^{2-}$ is[12] 2.35 Å, and the Mn-Cl distance in $MnCl_6^{2-}$ 2.28 Å[13]. In $VOCl_2(NMe_3)_2$, the V-Cl distance is reported to be 2.25 Å.[14] Thus it seems probable that the metal-ligand distance in VCl_5^- is in the range 2.2 – 2.3 Å, and most likely not far off 2.25 Å.

We have calculated the diatomic overlap integrals $S(3d_{\sigma},3p_{\sigma})$ and $S(3d_{\pi},3p_{\pi})$ between vanadium and chlorine in the range of internuclear distances from 2.10 – 2.40 Å. The radial wave functions of Richardson et al.[15] for V^+ and of Clementi[16] for Cl were used. Assuming the relation (4) the predicted ratio e_{π}/e_{σ} can be calculated over this range. This is shown in the Table. Thus in the range 2.2 – 2.3Å we expect e_{π}/e_{σ} to be about 0.43 – 0.53.

Table I. Overlap integrals $S(3d_{\lambda},3p_{\lambda})$ between V and Cl in the range 2.1-2.4 Å.

R(Å)	S_{π}	S_{σ}	$(S_{\pi}/S_{\sigma})^2$
2.10	0.145	0.175	0.687
2.15	0.133	0.173	0.592
2.20	0.123	0.169	0.530
2.25	0.114	0.165	0.478
2.30	0.106	0.161	0.434
2.35	0.097	0.155	0.391
2.40	0.089	0.149	0.356

Trigonal Bipyramidal Geometry

With the assumption of trigonal bipyramidal geometry for VCl_5^-, the polar coordinates θ and Φ for the ligand positions are fixed by symmetry, although the axial and equatorial distances need not be the same. If we calculate the group overlap integral coefficients k by means of the tables published by Kettle[17], the angular overlap model leads to the following relative energies of the orbitals of the partly-filled shell:

$$E(a_1') = 2e_{\sigma}(a) + (3/4)e_{\sigma}(e)$$

$$E(e'') = (3/2)e_{\pi}(e) + 2e_{\pi}(a)$$

$$E(e') = (9/8)e_{\sigma}(e) + (3/2)e_{\pi}(e)$$

The labels in brackets indicate values appropriate to axial (a) and equatorial (e) ligands; if the axial and equatorial distances are different, we can say that $e_{\lambda}(e)/e_{\lambda}(a) = [S^{\lambda}_{mx}(e)/S^{\lambda}_{mx}(a)]^2$.

If the axial and equatorial bond lengths are the same, so that $e_{\lambda}(e) = e_{\lambda}(a)$, then e″ will lie lower in energy than e′ if $e_{\pi}/e_{\sigma} < 0.563$. Thus we expect the ground state to be $^2E''$, although the possibility of a $^2E'$ ground state ougth to be considered.

Assuming a $^2E''$ ground state, the d-d transition energies are:

$$^2E'' \rightarrow {}^2E': (9/8)e_{\sigma} - 2e_{\pi}$$

$$^2E'' \rightarrow {}^2A_1': (11/4)e_{\sigma} - (7/2)e_{\pi}$$

In these expressions, all metal-ligand bonds are assumed to be equal in length.

The bands observed at 6.2 kK and 8.1 kK would

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[7] D.W. Smith, *J. Chem. Soc.* (A), 2529 (1969).
[8] D.W. Smith, *Chem. Phys. Letters*, 6, 83 (1970).
[9] D.W. Smith, *J. Chem. Soc.* (A), 2900 (1970).
[10] D.W. Smith, *Inorg. Chim. Acta*, 5, 231 (1971).
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[13] P.C. Moews, *Inorg. Chem.*, 5, 5 (1966).
[14] J.E. Drake, J. Vekris and J.S. Wood, *J. Chem. Soc.* (A), 1000 (1968).
[15] J.W. Richardson, R.R. Powell, W.C. Nieupoort and W.F. Edgell, *J. Chem. Phys.*, 36, 1057 (1962).
[16] E. Clementi, Supplment to IBM Journal of Research and Development 9, 2 (1965).
[17] S.F.A. Kettle, *Inorg. Chem.*, 4, 1821 (1965).

be assigned to the $^2E'' \rightarrow {}^2E'$ transition, with the excited state split by a dynamic Jahn-Teller effect; spin-orbit coupling alone can split the excited state by only 2λ, and this cannot be greater than 0.5 kK. We may therefore take the energy of the $^2E'$ state as the mean of the two transition energies, i.e. 7.2 kK. The $^2A_1'$ state can be placed 16.0 kK above the ground state. We can then find values of e_σ and e_π which, when substituted into the expressions for the transition energies, give the observed values. These turn out to be $e_\sigma = 4.38$ kK and $e_\pi = -1.16$ kK. This result makes little sense, since a negative value of e_π implies that the ligands are behaving as π-acceptors, which seems absurd for VCl_5^-. Relatively small distortions involving displacements of the axial ligands along the z-axis and of the equatorial ligands in the equatorial plane, while retaining D_{3h} symmetry, are unlikely to lead to any significant improvement in this result.

We now consider the possibility of a $^2E'$ ground state. The d-d transition energies are now given by:

$$^2E' \rightarrow {}^2E'' : 2e_\pi - (9/8)e_\sigma$$

$$^2E' \rightarrow {}^2A_1' : (13/8)e_\sigma - (3/2)e_\pi$$

The experimental d-d transition energies can be fitted with $e_\pi/e_\sigma = 0.70$, which seems to be unreasonably high; moreover, the absolute values of e_σ and e_π (27.3 kK and 19.0 kK respectively) seem also to be unreasonably high, and they predict that an octahedral VCl_6^{2-} ion with the same V-Cl bond lengths as VCl_5^- would have $\Delta_o = 6$ kK, which is far too small.

We are therefore forced to conclude that the electronic spectrum of VCl_5^- cannot be adequately assigned in D_{3h} symmetry since unreasonable values of the angular overlap parameters are required to fit the observed transition energies.

Square Pyramidal Geometry

We suppose that the four equatorial ligands lie in a square plane parallel to the xy-plane, while the one axial ligand lies on the z-axis. The ligand positions are not determined by symmetry alone since the angle θ between the metal-(axial ligand) bond and each metal-(equatorial ligand) bond may take any value. Of course, only values of θ which do not involve excessive ligand-ligand interaction need be considered; we might consider values of θ in the range 80-110° as reasonable, on the basis of the known structures of square pyramidal molecules. The angular overlap model leads to:

$$E(a_1) = 4(\cos^2\theta - \tfrac{1}{2}\sin^2\theta)^2 e_\sigma(e) + 3\sin^2\theta e_\pi(e) + e_\sigma(a)$$

$$E(b_1) = 3\sin^4\theta e_\sigma(e) + \sin^2 2\theta e_\pi(e)$$

$$E(b_2) = 4\sin^2\theta e_\pi(e)$$

$$E(e) = (3/2)\sin^2 2\theta e_\sigma(e) + 2\cos^2\theta e_\pi(e) + 2\cos^2 2\theta e_\pi(e) + e_\pi(a)$$

These expressions indicate that for reasonable values of θ, the ground state of VCl_5^- should be ^2E, i.e. with the odd electron in (formally) the $d_{xz,yz}$ orbitals. The only reasonable alternative would be a $^2B_2$ ground state, but the e.s.r. data (or rather lack of e.s.r. data!) mentioned above suggest that the ground state is orbitally degenerate, split to some small extent by spin-orbit coupling and (perhaps) a low symmetry component in the ligand field.

If we accept that a ^2E ground state is most probable for C_{4v} symmetry, we can write down the d-d transition energies in terms of three parameters: e $(=e_\sigma)$, c $(=e_\pi/e_\sigma)$ and s $(=\sin\theta)$. The three predicted d-d transitions are calculated to be

$$E_1(^2E \rightarrow {}^2B_2) = (14sc - 6s + 6s^2 - 8s^2c - 5c)e$$

$$E_2(^2E \rightarrow {}^2A_1) = (5 - 18s + 15s^2 + 22sc - 20s^2c - 5c)e$$

$$E_3(^2E \rightarrow {}^2B_1) = (9s^2 - 6s + 14sc - 12s^2c - 5c)e$$

A least-squares fitting procedure was used to find the values of s,c and e which led to calculated transition energies closest to the observed values. The best values turned out to be s = 0.99, c = 0.49 and e = 12.0 kK, which led to $E_1 = 5.3$ kK, $E_2 = 7.0$ kK and $E_3 = 17.5$ kK. These are in good agreement with the observed transition energies at 6.2 kK, 8.1 kK and 16.0 kK. Moreover, the values of s,c and e are eminently acceptable ones; s = 0.99 corresponds to θ = 95.8° (or 84.2°) which is perfectly reasonable for a square pyramidal complex. c = 0.49 corresponds (see Table) to a V-Cl bond length of 2.24 Å which is as expected. The absolute values of the parameters e_σ and e_π are also quite acceptable; if we assume that octahedral VCl_6^{2-} should have a V-Cl bond length in the range 2.30 – 2.35 Å, we can calculate its Δ_o from the values of e_σ and e_π deduced for VCl_5^-, which we believe to be appropriate to a V-Cl distance of about 2.24 Å, by assuming the proportionality of e_λ to (S^λ_{mx}).[2] In this way we predict Δ_o for VCl_6^{2-} to be about 14.5 kK, in excellent agreement with the experimental value[18] of 15.4 kK.

Thus the *d-d* spectrum of VCl_5^- can be most satisfactorily interpreted on the assumption of square pyramidal (C_{4v}) symmetry, and the angular overlap parameters required to fit the spectrum take values which are theoretically sound and are consistent with other data for V(IV) systms. This does not, of course, prove anything about the structure of VCl_5^-; only a full X-ray determination will do that. We hope that our predictions will help to stimulate further investigation of this anion, and a final solution to the problem should provide a rather crucial test of the utility of the angular overlap method as a means of predicting molecular geometry in the absence of full structural data.

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(18) P.A. Kitly and D. Nicholls, *J. Chem. Soc.*, 4915 (1965).