

A Unified Ligand Field Model Interpretation of the Electronic Spectrum of the Pentachlorovanadate (IV) Ion

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The Application of a Unified Ligand Field Model, comprising the effects of covalence as well as ionicity, to the d–d transitions observed for the pentachlorovanadate (IV) ion, having C_{2v} symmetry, is illustrated. The charges on the equatorial and axial chlorines are the only two parameters obtained from the data; all others are calculated ab initio. The effect of covalence and ionicity is discussed; the latter dominates. The spectrum is adequately accounted for in terms of this model.

Introduction: The Model

In recent papers the relevance of models describing molecular electronic energies in terms of electrostatic as well as covalence effects was pointed out and a Unified Ligand Field Model (ULFM) developed [1–4]. In this ULFM the influence of covalence is expressed in terms of parameters reminiscent of the angular overlap model (AOM) whereas the ionic contributions are described by means of a reparameterization of the point charge electrostatic model (PCEM).

The simplicity of the model was seen to be due to the introduction of this symmetry orientated reparameterization of the PCEM, which clarifies the parametric equivalence between the PCEM and AOM [1], and the utilization of the additivity postulate [3] for ligand contributions to the one-electron energies. Hence, in the case of d-orbitals, the destabilization energy of orbital |M_i⟩ due to N identical ligands becomes [1–3]

$$E_{m_i} = \sum_L \sum_m^5 (A_{im}^L)^2 e_m + \sum_L \sum_m^5 (A_{im}^L)^2 U_m \quad (1)$$

The A_{im}^L are elements of the unitary matrix which defines the transformation of the central ion orbitals |M_i⟩, expressed in the molecular coordinate system XYZ, to those expressed relative to a diatomic

coordinate system X'Y'Z' defined such that ligand L is on the positive Z'-axis [3]. Hence A_{im}^L is a function of the angular position of ligand L [1, 5].

The AOM parameters e_m are given by [3]

$$e_m = [(\frac{1}{4} H_1^2 + \frac{1}{2} H_m H_1 - \frac{3}{4} H_m^2) / (H_m - H_1)] S_{ml}^2$$

where $H_m = \langle M_i | H | M_i \rangle$ and $H_1 = \langle X_j | H | X_j \rangle$ are often associated with the VOIE's of the relevant metal and ligand orbitals |M_j⟩ and |X_j⟩ [5]. S_{ml} is the appropriate diatomic overlap.

The symmetry orientated electrostatic parameters U_m can be expressed in terms of the radial parameters

$$\alpha_k^L = Z_L e^2 \int_{r=0}^{\infty} (R_{nl})^2 \frac{r^k}{r^{k+1}} r^2 dr$$

and for d-orbitals one has [1, 3]

$$\begin{aligned} d_{z^2} & \quad U_1 = \alpha_0 + \frac{2}{7} \alpha_2 + \frac{2}{7} \alpha_4 \\ d_{yz}, d_{zx} & \quad U_2 = U_3 = \alpha_0 + \frac{1}{7} \alpha_2 - \frac{4}{21} \alpha_4 \\ d_{xy}, d_{x^2-y^2} & \quad U_4 = U_5 = \alpha_0 - \frac{2}{7} \alpha_2 + \frac{1}{21} \alpha_4 \end{aligned}$$

Systems with different ligands and/or metal-ligand distances would obviously involve the introduction of additional parameters e'_m , U'_m etc., as will be illustrated in the following application of the ULFM.

Application: Pentachlorovanadate (IV) Ion

The three observed d–d transitions [6] for the [VCl₅][−] present in the compound [PCl₄] [VCl₅] occur at

$$\begin{aligned} E_1 &= 6.2 \text{ kK} \\ E_2 &= 8.1 \text{ kK} \\ E_3 &= 16.0 \text{ kK.} \end{aligned}$$

In an attempt to interpret the spectrum of this d¹ system in terms of the effects of covalence Russell and Smith [7] could achieve satisfactory results only if a square pyramidal symmetry was assumed, in contrast to a trigonal bipyramidal geometry.

Seddon, on the other hand, adopted an ionic description of the ligand effects and showed that the

*This work was done while on leave at the University of Colorado during 1982.

parameter values implied by a C_{4v} symmetry were unacceptable [8]. He could, however, simulate the observed spectrum with reasonable values for his ionic parameters when a C_{2v} symmetry (distorted trigonal bipyramid) was assumed.

Ultimately an X-ray determination by Ziegler *et al.* [9] revealed an almost ideal C_{2v} symmetry. The three angles spanned by a vanadium IV ion between the equatorial chlorines are 116.3° , 127.4° and 116.3° whereas the V–Cl distances are 2.166 Å, 2.166 Å and 2.185 Å. Finally, the axial metal-ligand distances are 2.288 Å and 2.311 Å.

In view of the covalency implied by Russell and Smith and the ionicity assumed by Seddon, an application to this complex of the ULFM, comprizing both effects, is appropriate.

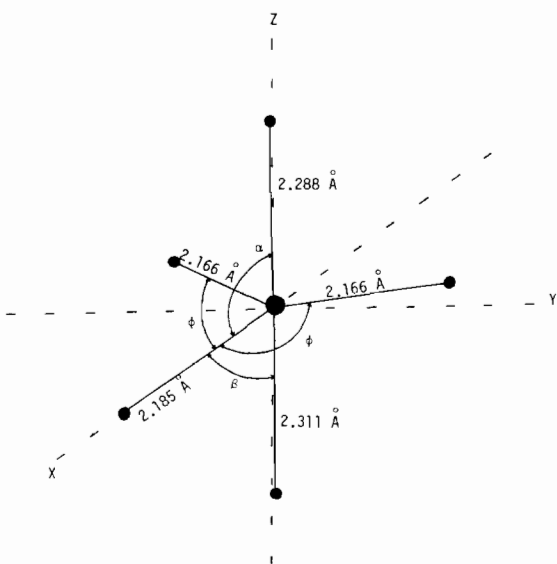


Fig. 1. $[VCl_5]^-$ (ref. [9]): Distorted D_{3h} ; $\phi = 116.3^\circ$, $\alpha = 89.05^\circ$, $\beta = 91.6^\circ$. V–Cl distances are indicated. Co-ordinate system centred at V.

With this in mind a coordinate system centred on V (see Fig. 1) is chosen such that the three equatorial ligands are in the xy plane; one chlorine being on the x axis so that the azimuthal angles of the other two are $\phi_1 = 116.3^\circ$ and $\phi_2 = 243.7^\circ = (2\pi - \phi_1)$. (It is remarkable that Seddon's analysis predicted $\phi_1 = 116.17^\circ$!).

A straightforward application of eq. (1) where—due to the reparameterization of the PCEM—the coefficients of U_m and e_m are the same, gives the d-orbital destabilization energies. The primed parameters refer to the axial ligands and since $\sin^2 \phi_1 = \sin^2 \phi_2$ and $\cos^2 \phi_1 = \cos^2 \phi_2$ the single angle $\phi = 116.3$ is sufficient. The energies appear in descending order [8].

$$E_{z^2} = \frac{3}{4} (U_1 + e_1) + 2(U'_1 + e'_1) + \frac{9}{5} (U_5 + e_5)$$

$$E_{x^2-y^2} = \frac{3}{4} [1 + 2 \cos^2 2\phi] (U_1 + e_1) + 2 \sin^2 2\phi (U_3 + e_3) + \frac{1}{4} [1 + 2 \cos^2 2\phi] (U_5 + e_5) + 2(U'_5 + e'_5)$$

$$E_{xy} = \frac{3}{2} \sin^2 2\phi (U_1 + e_1) + [1 + 2 \cos^2 2\phi] (U_3 + e_3) + \frac{1}{2} \sin^2 2\phi (U_5 + e_5) + 2(U'_5 + e'_5)$$

$$E_{yz} = 2 \sin^2 \phi (U_3 + e_3) + 2(U'_3 + e'_3) + [1 + 2 \cos^2 \phi] (U_5 + e_5)$$

$$E_{xz} = [1 + 2 \cos^2 \phi] (U_3 + e_3) + 2(U'_3 + e'_3) + 2 \sin^2 \phi (U_5 + e_5)$$

These expressions are easily checked by means of the sum rule resulting from the unitarity of the transformation matrices [2, 4]:

$$\sum_L^N \sum_m^5 (A_{im}^L)^2 = N; i = 1, \dots, 5.$$

The assignment of the observed transitions are [8] $E_1(d_{xy} \rightarrow d_{xz})$, $E_2(d_{x^2-y^2} \rightarrow d_{xz})$, $E_3(d_{z^2} \rightarrow d_{xz})$. Expressing the U_m in terms of the α_k and neglecting δ -bonding [7] results in

$$E_1 = 6 \sin^2 \phi \cos^2 \phi e_1 + 2 \sin^2 \phi [1 - 4 \cos^2 \phi] e_3 - 2e'_3 + \frac{6}{7} \sin^2 \phi \alpha_2 - \frac{6}{7} \alpha'_2 + \frac{10}{21} \sin^2 \phi [7 \cos^2 \phi - 1] \alpha_4 + \frac{10}{21} \alpha'_4.$$

$$E_2 = \frac{3}{4} [3 - 8 \cos^2 \phi \sin^2 \phi] e_1 + [2 \cos^2 \phi (4 \sin^2 \phi - 1) - 1] e_3 - 2e'_3 + \frac{6}{7} \sin^2 \phi \alpha_2 - \frac{6}{7} \alpha'_2 + \frac{1}{84} [65 + 40 \cos^2 \phi (1 - 7 \sin^2 \phi)] \alpha_4 + \frac{10}{21} \alpha'_4$$

$$E_3 = \frac{3}{4} e_1 + 2e'_1 - [1 + 2 \cos^2 \phi] e_3 - 2e'_3 - \frac{6}{7} \cos^2 \phi \alpha_2 + \frac{2}{7} \alpha'_2 + \frac{1}{84} [75 - 40 \sin^2 \phi] \alpha_4 + \frac{20}{21} \alpha'_4.$$

In evaluating the e_m , H_m and H_1 are taken as the negative of the ground state ionization potentials of V and Cl, *i.e.* -54.4 kK and -105 kK respectively. The V–Cl diatomic overlaps are obtained from the values tabled by Smith and Russell: taking the equatorial V–Cl distances as $R_E = 2.17$ Å the tabled σ and π overlaps were used in a graph from which the overlaps at 2.17 Å were obtained as $S_\sigma = 0.172$ and $S_\pi = 0.129$. At an axial V–Cl distance of $R_A = 2.3$ Å the tables give $S'_\sigma = 0.161$ and $S'_\pi = 0.106$. The e_m 's are then calculated as

$$e_1 = 1.98 \text{ kK} \quad e_3 = 1.1 \text{ kK}$$

$$e'_1 = 1.74 \text{ kK} \quad e'_3 = 0.75 \text{ kK}.$$

The α_k 's could be calculated from the tables of Ballhausen and Ancmon [10] for

$$\int (R_{nl})^2 \frac{r_{<}^k}{r_{>}^{k+1}} r^2 dr$$

if the charges on the equatorial and axial ligands, Z_E and Z_A , were known. Here Z_E and Z_A will serve as parameters to be determined from the observed d-d transitions.

Hence, from the tables,

$$\alpha_2 = Z_E e^2 \int (R_{nl})^2 \frac{r_{<}^2}{r_{>}^3} r^2 dr$$

$$= 22.1 Z_E; \text{ for } R_E = 4.1 a_0$$

Similarly $\alpha_4 = 12.5 Z_E$. Furthermore, graphs were constructed from the tables from which the values of the integrals for the axial parameters α'_2 and α'_4 corresponding to $R_A = 4.3 a_0$ could be deduced as $\alpha'_2 = 19.83 Z_A$ and $\alpha'_4 = 10.85 Z_A$.

The parameters Z_A and Z_E were used in a least squares procedure to obtain a best fit between the calculated and observed energies. The resulting parameters and corresponding energies are

$$Z_A = 0.74 \quad E_1 = 6 \text{ kK}$$

$$Z_E = 0.83 \quad E_2 = 8.3 \text{ kK}$$

$$E_3 = 16 \text{ kK}$$

The agreement is most satisfactory.

Discussion

The ionic parameters Dq, Ds and Dt considered by Seddon can be expressed in terms of the present α_k 's as

$$Dq = \frac{\alpha_4}{6}$$

$$Ds = \frac{2}{7} \alpha'_2 - \frac{3}{14} \alpha_2$$

$$Dt = \frac{3}{56} \alpha_4 + \frac{2}{21} \alpha'_4$$

Hence the present calculation implies $Ds = 0.26 \text{ kK}$ and $Dt = 1.3 \text{ kK}$, which still fall within the acceptable range $-0.1 \rightarrow 0.56 \text{ kK}$ for Ds and $1.26 \rightarrow 1.55 \text{ kK}$ for Dt tabled by Seddon.

The values $Ds = 0.271 \text{ kK}$ and $Dt = 1.553 \text{ kK}$ obtained in the ionic model [8] imply $Z_E = 0.98$ and $Z_A = 0.86$, hence $Z_E > Z_A$, as is the case in our analysis. Seddon's assumed value of 1.54 kK for Dq,

however, corresponds to $Z_E = 0.74$, representing a slight inconsistency in his method.

In order to investigate the sensitivity of the present analysis to varying values of H_m these calculations based on the actual symmetry were repeated with $H_m = -81 \text{ kK}$ (10 eV). The results are:

$$Z_A = 0.71 \quad E_1 = 5.9 \text{ kK}$$

$$E_2 = 8.2 \text{ kK}$$

$$Z_E = 0.79 \quad E_3 = 15.9 \text{ kK}$$

The fit is slightly worse than before.

In an effort to reduce the experimental parameters to one, instead of two, the above procedure was repeated assuming all V-Cl distances as $R = 2.25 \text{ \AA}$ and $Z_A = Z_E = Z_L$.

This resulted in

$$Z_L = 0.81 \quad E_1 = 3.1 \text{ kK}$$

$$E_2 = 5.2 \text{ kK}$$

$$E_3 = 17.5 \text{ kK}$$

which is much worse than the results based on the actual symmetry.

In order to investigate the suitability of the ULFM for structure predictions a distorted D_{3h} symmetry was assumed; firstly with $\phi = 100^\circ$ and then with $\phi = 118^\circ$, corresponding to approximate C_{4v} and C_{2v} symmetries respectively (see Seddon). The number of parameters were reduced to three by using for the complex concerned the plausible approximations $\alpha'_2 \approx 1.8\alpha'_4$ and $e'_1 \approx 2e'_3$, and similarly for the e's and α 's, as well as the value $Dq = 1.54 \text{ kK}$, i.e. $\alpha_4 = 9.24 \text{ kK}$, valid for $[VCl_6]^{2-}$ [8]. The parameter values which reproduce the observed energies are:

$$\phi = 100^\circ \quad e_1 = -12.1 \text{ kK}$$

$$e'_1 = -70.3 \text{ kK}$$

$$\alpha'_2 = 104.6 \text{ kK}$$

$$\phi = 118^\circ \quad e_1 = 0.46 \text{ kK}$$

$$e'_1 = -12.28 \text{ kK}$$

$$\alpha'_2 = 32.2 \text{ kK}$$

Apart from the negative values for the covalence parameters when $\phi = 100^\circ$ the electrostatic parameters imply $Ds = 26.3 \text{ kK}$ and $Dt = 6.0 \text{ kK}$, which is well outside the acceptable range. For $\phi = 118^\circ$ $Ds = 5.6 \text{ kK}$ and $Dt = 2.2 \text{ kK}$ which represent some improvement. The value for e_1 is, in contrast to that for e'_1 , acceptable. Hence, although these calculations can be interpreted to favour a C_{2v} more than a C_{4v} symmetry, they are not beyond criticism.

Finally, Seddon reported that, in spite of the absence of an e.s.r. spectrum at room temperature, a signal was observed at -196°C at $g = 1.84$, suggesting two close lying ground state levels. His assumption of $Dq = 1.54 \text{ kK}$ predicted a split of $2\delta = 0.38 \text{ kK}$. Assuming $Z_E = 0.98$ as implied by Seddon's parameter values

$$Dq = \frac{12.5Z_E}{6} = 2.04 \text{ kK} \text{ and } \alpha_2 = 21.66 \text{ kK} \text{ and hence}$$

$$\delta = \frac{5}{7}(1 + 2 \cos 2\phi)Dq - \frac{3}{14}(1 + 2 \cos 2\phi)\alpha_2 = 0.68 \text{ kK}$$

actually giving $2\delta = 1.37 \text{ kK}$ in his case.

In the present calculation, including the effect of covalence, one gets

$$\begin{aligned} 2\delta = E_{yz} - E_{xz} = & [2(\sin^2 \phi - \cos^2 \phi) - 1] e_3 \\ & + \frac{3}{7} [1 - 4 \cos^2 \phi] \alpha_2 + \\ & + \frac{5}{21} [4 \cos^2 \phi - 1] \alpha_4 = 1.4 \text{ kK}. \end{aligned}$$

These values differ appreciably from the speculative 0.2 kK (see ref. [8]) and further investigations based on better experimental evidence might be worthwhile.

Conclusion

This particular application of the ULFM, involving only two parameters, was remarkably successful in explaining the observed spectrum of $[\text{VCl}_5]^-$. The fact that $Z_A = 0.74 < Z_E = 0.83 < 1$ indeed suggest that the Cl orbitals are involved in covalent bonding, the axial ones more so than the equatorial ones. Seddon's results implying $Z_A = 0.86 < Z_E = 0.98 < 1$ point to the same phenomenon, although less so as no covalency is provided for in his model. This interpretation is corroborated by the fact that an increase in $|H_m|$, causing an increase in the covalence parameters and hence in the covalent contribution to the one-electron energies (as is obvious for the expressions for these), resulted in a decreased Z_A and Z_E .

From the parameter values obtained in this model it is obvious that for $[\text{VCl}_5]^-$ the main contribution to the one-electron energies derives from the electrostatic effect, covalence playing only a secondary rôle. This may, in part, be the reason why the CF was more successful in predicting the structure than the AOM which ignores crystal field effects.

Although it was shown that the ULFM may be taken to at least favour a C_{2v} symmetry as opposed to a C_{4v} one, the large number of parameters (in this case eight) tend to complicate such predictions. In order to find reliable relationships between the covalence as well as the ionic parameters spectroscopic data for a range of chlorovanadate (IV) systems would be required, a requirement characteristic of such predictions [11].

The unsatisfactory results obtained when all V-Cl distances were assumed equal gives an indication of the influence that metal-ligand distances can have on the calculations. Rough estimates for these could be risky.

The extension and application of this ULFM to d^9 , d^n and f systems might be worthwhile. Such investigations are underway.

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References

- 1 P. J. Steenkamp and J. W. Gonsalves, *Aust. J. Chem.*, **33**, 1705 (1980).
- 2 P. J. Steenkamp and J. W. Gonsalves, *J. Chem. Educ.*, **58**, 380 (1981).
- 3 P. J. Steenkamp, to be published.
- 4 P. J. Steenkamp, to be published.
- 5 M. Gerloch and R. C. Slade. 'Ligand-Field Parameters', New York, Cambridge University Press, 1973.
- 6 I. M. Griffiths, D. Nicholls and K. R. Seddon, *J. Chem. Soc. (A)*, 2513 (1971).
- 7 C. W. G. Russell and D. W. Smith, *Inorg. Chim. Acta*, **6**, 677 (1972).
- 8 K. R. Seddon, *Inorg. Chim. Acta*, **9**, 123 (1974).
- 9 M. L. Ziegler, B. Nuber, K. Weidenhammer and G. Hoch, *Z. Naturforsch.*, **32B**, 18 (1977).
- 10 C. J. Ballhausen and E. M. Ancmon, *Kgl. Danske Vidensk. Matt. Fys. Medd.*, **31**, no. 9 (1958).
- 11 D. W. Smith, *Structure and Bonding*, **35**, 87 (1978) p. 95.