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The Visible and Ultraviolet Spectrum of a Distorted Trigonal Bipyramidal Complex of Cobalt(II)

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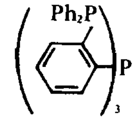
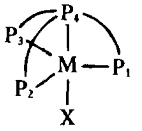
Ligand field calculations using the "Angular Overlap" model, developed to allow the use of tensor operator theory, have been performed in order to analyse the visible and ultraviolet spectrum of the complex ion $[CoCl(QP)]^+$ *(QP = tris-(o-diphenylphosphinophenyl)-phosphine) which has recently been shown to possess a distorted trigonal bipyramidal structure.*

Introduction

Norgett *et al.*,[1] have recently described two-parameter ligand field calculations for trigonal bipyramidal complexes of nickel(II), cobalt(II), and iron(II) and have discussed the interpretation of spectra of complexes of tris-(*o*-diphenylphosphinophenyl)phosphine, (I), of the type $[MX(QP)]^+$, (II).



(I)



(II)

Subsequent determination of the structure of $[CoCl(QP)][BPh_4]$ by X-ray diffraction[2] has shown that the co-ordination of the metal ion in this complex departs significantly from the C_{3v} symmetry assumed in the earlier calculations, *e.g.*, the equatorial angles are P(1)–Co–P(2) = 108.7°, P(1)–Co–P(3) = 112.7°, and P(2)–Co–P(3) = 137.6°. As these results cast some doubt on this interpretation of the visible and ultraviolet spectra of complexes $[CoX(QP)]^+$, new calculations were performed taking into account this major distortion from regular structure.

This distortion could arise from the operation of the Jahn-Teller effect as d^7 ions in C_{3v} or D_{3h} symmetry would give rise to orbitally degenerate ground states. The existence of such distortion had been postulated[3] in order to explain the observed magnetic properties of complexes $[CoX(QP)]^+$. Qualitatively it would be expected that the Jahn-Teller distortion should be large as the odd electron is in the antibonding levels d_{xy} and $d_{x^2-y^2}$ and that the splitting of these antibonding levels will be greater than that of the non-bonding pair d_{xz} and d_{yz}.

Theoretical Section

For the purpose of the improved calculation the following approximate geometry for $[CoCl(QP)]^+$ has been assumed: P(1)–Co–P(2) and P(1)–Co–P(3) = 110° and P(2)–Co–P(3) = 140°. It has also been assumed that, although the three equatorial ligands are not identical by symmetry requirement, they are equivalent from the point of view of bonding to the central atom. The Hamiltonian employed utilises two independent parameters subsequently fitted from the experimental spectrum. In this case, however, as the symmetry is much lower than C_{3v}, it is necessary to introduce some approximation, in addition to the strict requirements of symmetry, in order to reduce the Hamiltonian to the two-parameter form. For this purpose the "Angular Overlap" model of Schäffer and Jørgensen[4] has been used as it is particularly suitable for semi-quantitative calculations. As previously,[1] only σ-bonding has been considered.

The Ligand-field Hamiltonian. The effect of placing a metal ion in an enviroment of any general form can always be represented by a Hamiltonian which involves a limited sum of terms each of which consists of a numerical factor multiplying a spherical harmonic or, more conveniently, a spherical tensor $C_q^{(k)}$ where

$$C_q^{(k)} = 4\pi/(2k+1)^{\frac{1}{2}} Y_{kq}(\theta,\varphi).$$

The methods used to calculate the matrix elements of these tensors between free-ion states have been briefly summarized elsewhere.[1]

In the case of a regular trigonal bipyramid, the symmetry limits the form of the Hamiltonian which can contain only the spherical tensors $C_0^{(2)}$ and $C_0^{(4)}$. The problem then requires two parameters which determine the magnitude of the independent coefficients multiplying these operators. The set of five *d*-states are split into three levels (labelled *e″*, *e′*, and a_1' in D_{3h} symmetry) and the parameters determine the

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(1) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc.*, (A), 540 (1967); *Coord. Chem. Revs.*, 2, 99 (1967).

(2) T. L. Blundell, H. M. Powell, and L. M. Venanzi, *Chem. Comm.*, 763 (1967).

(3) J. G. Hartley, D. G. E. Kerfoot, and L. M. Venanzi, *Inorg. Chim. Acta*, *1*, 145 (1967).

(4) C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, *9*, 401 (1965).

values of the two independent splittings. The previous treatment of regular trigonal bipyramidal complexes used such a Hamiltonian and fitted the parameters from the experimental spectra. No physical significance was attached to their numerical values.

Consideration of the distorted complex shows that the most general Hamiltonian requires, by symmetry, five independent parameters, *i.e.*, the coefficients of the operators $C_0^{(2)}$, $\{C_2^{(2)}+C_{-2}^{(2)}\}$, $C_0^{(4)}$, $\{C_2^{(4)}+C_{-2}^{(4)}\}$, and $\{C_4^{(4)}+C_{-4}^{(4)}\}$. This general Hamiltonian, however, cannot be used as such. One possible way of reducing it to a more tractable form would be by the use of a point charge model, which allows factorisation of the general parameters into a part determined by the geometry and a part dependent on the ligand. It is useful, for the purpose of comparison with some formulations used later, to give the expression for any Hamiltonian in that form which acts between the angular part of the free ion wave functions for the most general case of N ligands with co-ordinates θ_μ and φ_μ:

$$\mathcal{H} = \sum_{\mu} \sum_{k=0}^{\infty} Q_\mu^k \{4\pi/(2k+1)\}^{1/2} \sum_{q=-k}^{k} Y^*_{kq}(\theta_\mu \varphi_\mu) C_q^{(k)}$$

where $Q_\mu^k \{g_\mu e^2/R^{(n+1)}\} \langle r^n \rangle$. The letter μ denotes the individual ligands, $g_\mu e$ is the effective ligand charge, R is the metal ion-ligand separation, and $\langle r^n \rangle$ is the expectation value of r^n taken over the *d*-wave function of the metal ion. In the case of a regular trigonal bipyramid this takes the form

$$\mathcal{H}_0 = \frac{1}{2} Q^2 C_0^{(2)} + \frac{25}{8} Q^4 C_0^{(4)}$$

with

$$Q^2 = 4Q^2_{\text{ax.}} - 3Q^2_{\text{eq.}}$$

and

$$Q^4 = \frac{16}{25} Q^4_{\text{ax.}} + \frac{9}{25} Q^4_{\text{eq.}}$$

This factorization, which at first sight appears to be peculiar to the point charge model, and is not necessarily applicable to a ligand field approach, has been shown by Bradbury and Newman to be of much wider validity.[5] The chief requirement for such a simplification is that the effect of ligands should be additive. If this requirement is assumed to apply to the complexes discussed here, one can perform the factorization employing the point charge model and, subsequently, utilise the radial integrals as the new set of parameters. The Hamiltonian obtained contains four independent parameters which correspond in number to the four energy gaps needed to describe the splitting of the five *d*-orbitals when the degeneracy is completely removed.

It is convenient to factorize the Hamiltonian into:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{pert.}}$$

where $\mathcal{H}_0$ is the Hamiltonian for the regular trigonal bipyramid and $\mathcal{H}_{\text{pert.}}$ is the perturbation caused by the distortion.

Then, in the case of a distorted trigonal bipyramid, the Hamiltonian can be reduced to the following form:

$$\begin{aligned}\mathcal{H}_{\text{pert.}} = & -0.326\, Q^2_{\text{eq.}} (C_2^{(2)}+C_{-2}^{(2)}) \\ & +0.210\, Q^4_{\text{eq.}} (C_2^{(4)}+C_{-2}^{(4)}) \\ & +0.704\, Q^4_{\text{eq.}} (C_4^{(4)}+C_{-4}^{(4)}).\end{aligned}$$

This form of the Hamiltonian is not readily adaptable to calculation because it contains four unknowns. As it is very difficult to propose any suitable approximation which might give some insight into the relative strength of the binding of axial and equatorial ligands, calculations have been performed starting from a molecular orbital standpoint. Schäffer and Jørgensen have described[4] a generalised model which allows the estimation of all the matrix elements within a manifold of one electron states in terms of a limited number of parameters, one for each inequivalent ligand, which describe the bonding to the metal ion. The basis of the method is that the matrix elements are set proportional to the square of the overlap integrals which are themselves calculated by evaluating the angular part of the *d*-function at the various ligand positions. These authors have proposed methods which allow the calculation of both diagonal and off-diagonal matrix elements.

This approach, however, is of no direct help in the calculation of matrix elements of the "ligand field" between several electron states. To this end, it is convenient to use some equivalent Hamiltonian which gives the same matrix elements when diagonalised within a manifold of one electron states, but may also be used more generally. This is easily done as Schäffer and Jørgensen have shown the equivalence of their angular overlap model to a scheme which employs a singular δ-function potential which acts between normalised *d*-states. They write

$$V_\sigma = \sum_{\mu=1}^{N} \sigma_\mu^* \delta(\theta - \theta'_\mu) \delta(\varphi - \varphi'_\mu)$$

where σ^*_μ is the usual angular overlap parameter developed by Jørgensen *et al.*[6] As mentioned earlier, only the effect of σ-bonding will be considered here.

A number of comments are necessary at this point. To avoid confusion, it is necessary to point out that by $\delta(\theta - \theta')\delta(\varphi - \varphi')$, Schäffer and Jørgensen mean the singular δ-type function which is normalised over the surface of a sphere; this is usually written $\delta(\Omega - \Omega')$ and has the required property

$$\int f(\theta, \varphi) \delta(\Omega - \Omega') d\Omega = f(\Omega').$$

Because of the normalisation, this is correctly written

$$\delta(\Omega - \Omega') = \{\delta(\theta - \theta')\delta(\varphi - \varphi')\}/\sin\theta'.$$

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[5] M. I. Bradbury and D. J. Newman, *Chem. Phys. Letters, 1*, 44 (1967).

[6] C. K. Jørgensen, R. Pappalardo, and H. H. Schmidtke, *J. Chem. Phys., 39*, 1422 (1963).

Schäffer and Jørgensen themselves define the new parameter e which, in the case of d-electrons, is related to σ^* by the expression

$$e = 5\sigma^*.$$

In Table IV of their paper, these authors give a very useful table of matrix elements in terms of this parameter for various symmetries but they utilise orbitals normalised to 4π. Throughout this paper orbitals normalised to unity will be used and for this reason, new parameters e' have been defined which are equal to $e/4\pi$. The advantage of this substitution is that one can calculate matrix elements using spherical tensors acting between states normalised to unity and one obtains answers in the same arithmetic form as those of Schäffer and Jørgensen.

$$V_\sigma = \sum_\mu \frac{4\pi e'_\mu}{5} \delta(\Omega-\Omega_\mu).$$

Employing the normal expansion of the δ-function in terms of a complete set of states,

$$V_\sigma(\theta,\varphi) = \sum_{\mu=1}^{N} \sum_{k=0}^{\infty} \frac{4\pi e'_\mu}{5} \sum_{q=-k}^{k} Y^*_{kq}(\theta_\mu,\varphi_\mu) Y_{kq}(\theta,\varphi) =$$

$$\sum_{\mu=1}^{N} \sum_{k=0}^{\infty} (4\pi)^{1/2} e'_\mu \frac{(2k+1)^{1/2}}{5} \sum Y^*_{kq}(\theta_\mu,\varphi_\mu) C_q^{(k)}$$

The above form of Hamiltonian can now be conveniently employed to calculate all required matrix elements both for one and many electron systems. Indeed, in view of the simple methods available for the calculation of matrix elements of $C_q^{(k)}$, it is likely that this provides the easiest method of use of the angular overlap model.

However, it also allows a deeper insight on the applicability of the point charge model. Comparison of the above Hamiltonian with that for the point charge model shows that they are equivalent if the respective parameters obey the following relationship:

$$Q_\mu^k = e'_\mu \frac{2k+1}{5}.$$

In particular, $Q^2_\mu = e'_\mu$ and $Q^4_\mu = \frac{9}{5} e'_\mu$

Using these relations, it is possible to write down the equivalent Hamiltonians in the angular overlap formalism which correspond to those previously obtained for the point charge model.

For the regular trigonal bipyramid

$$\mathcal{H}_0 = (2.0\, e'_{ax.} - 1.5\, e'_{eq.}) C_0^{(2)} + (3.6\, e'_{ax.} + 2.025\, e'_{eq.}) C_0^{(4)}$$

and for the distorted system

$$\begin{aligned} \mathcal{H} = \mathcal{H}_0 &- 0.326\, e'_{eq} (C_2^{(2)} + C_{-2}^{(2)}) \\ &+ 0.379\, e'_{eq.} (C_2^{(4)} + C_{-2}^{(4)}) \\ &+ 1.269\, e'_{eq.} (C_4^{(4)} + C_{-4}^{(4)}). \end{aligned}$$

In the case of the regular system, when any parameterisation involves only two independent functions, it is possible to express the factors Q^2 and Q^4 uniquely in terms of e'_{eq} and $e'_{ax.}$. This provides a useful comparison between the new results for cobalt(II) with the calculations reported previously for the regular trigonal complexes of nickel(II) and iron(II) with similar ligands. In the latter cases

$$Q^2/Q^4 = \frac{4Q^2_{ax.} - 3Q^2_{eq.}}{1/25\,(16Q^4_{ax.} + 9Q^4_{eq.})} = \frac{125}{9} \frac{(4e'_{ax.} - 3e'_{eq.})}{(16e'_{ax.} + 9e'_{eq.})}$$

The angular overlap Hamiltonian for the distorted system has a number of features of interest. In particular, when diagonalised within a manifold of one electron d-orbitals, it causes no splitting of the (d_{xz}, d_{yz}) doublet since these are not involved in σ-bonding. Although this degeneracy is not required by symmetry, it was noted earlier that this splitting should be small.

A programme which will diagonalise a Hamiltonian of this form involving spherical tensor operators has been described elsewhere.[1] This programme was slightly developed to allow for the different parameterisation required by the angular overlap approach but it was otherwise unchanged. Following standard practice, the angular overlap Hamiltonian for the distorted system was calculated neglecting the term in Y_{00} as it does not affect the splitting of the d-orbitals. The energy level diagram included in this paper was obtained in this way.

The results were interpreted in terms of the magnitude of $e'_{ax.}$ and the ration $e'_{eq.}/e'_{ax.}$ The graphs are plotted as energy against $e'_{ax.}$ at constant $e'_{eq.}/e'_{ax.}$, the Racah parameter B again being employed as the unit of energy.

Results

The main features of the spectrum of [CoCl(QP)][BPh$_4$] are bands at 9,600 cm^{-1}, 16,500 cm^{-1}, and 19,600 cm^{-1}. The energy-level diagram for the distorted complex is given in Figure 1. The ratio $e'_{eq.}/e'_{ax.}$, which gives the best fit with experiment, is 0.8. The spin-allowed transitions, in the one-electron limit, in order of increasing energy are listed below. (See also Figure 2):

(1) $(e'')^4(e'_a)^2(e'_b)^1 \rightarrow (e'')^4(e'_a)^1(e'_b)^2$

(2) $(e'')^4(e'_a)^2(e'_b)^1 \rightarrow (e'')^4(e'_a)^2(a'_1)^1$

(3) $(e'')^4(e'_a)^2(e'_b)^1 \rightarrow (e'')^3(e'_a)^2(e'_b)^2$

(4) $(e'')^4(e'_a)^2(e'_b)^1 \rightarrow (e'')^3(e'_a)^2(e'_b)^2$ or $(e'')^4(e'_a)^2(e'_b)^1(a'_1)^1$.

Thus if the band at 9,600 cm^{-1} is assigned to the lowest energy transition, (1), higher energy bands should occur at 16,100 and 21,000 cm^{-1} and correspond to transitions (2) and (3) respectively, in good agreement with the experimental values observed.

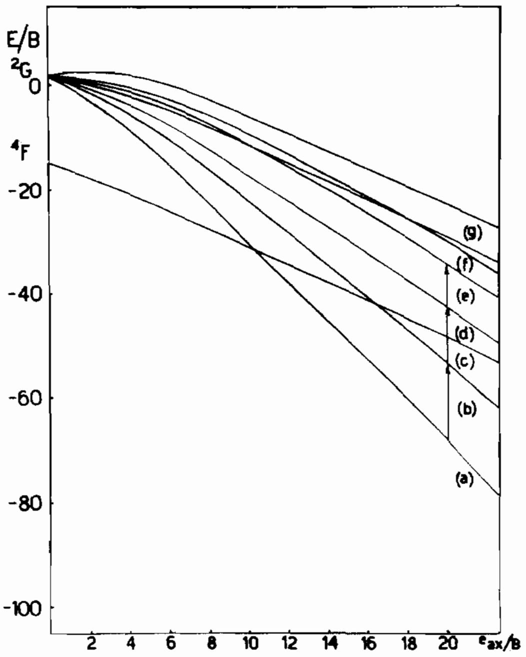

Figure 1. Energy level diagram for distorted trigonal bipyramidal complexes of d^7-metal ions calculated using the angular overlap model, for $e_{eq}/e_{ax.}=0.8$. (a) = $(e'')^4(e'_a)^2(e'_b)^1$; (b) = $(e'')^4(e'_a)^1(e'_b)^2$; (c) = $(e'')^4(e'_a)^1(e'_b)^1(a'_1)^1$ lowest quartet state); (d) = $(e'')^4(e'_a)^2(a'_1)^1$; (e) and (f) = $(e'')^3(e'_a)^2(e'_b)^2$; (g) = $(e'')^4(e'_a)^1(e'_b)^1(a'_1)^1$.

This assignment of absorption bands is signficantly different from that given previously[1] using an energy level diagram calculated for a complex with regular geometry.

The value of the parameter $e_{eq.}/e_{ax.}$, (0.8) which gives the best spectral fit requires comment on two counts. Its values indicates that the axial phosphorus ligand is more strongly bound than the equatorial ligands. The X-ray diffraction study of $[CoCl(QP)]^+$ shows[2] that the P(4)—Co bond-length is 2.02Å while those to equatorial donor atoms range from 2.26 to 2.32 Å. This effect is likely to be caused by the rigid geometric requirements of the organic ligand as the distances between phosphorus atoms are expected to be shorter than those required to obtain angles $P_{eq.}$—Co—$P_{ax.}$ of 90°.[7] Thus, as a compromise solution, a short P(4)—Co bond will result together with $P_{eq.}$—Co—$P_{ax.}$ angles of less than 90°, as experimentally found.[2]

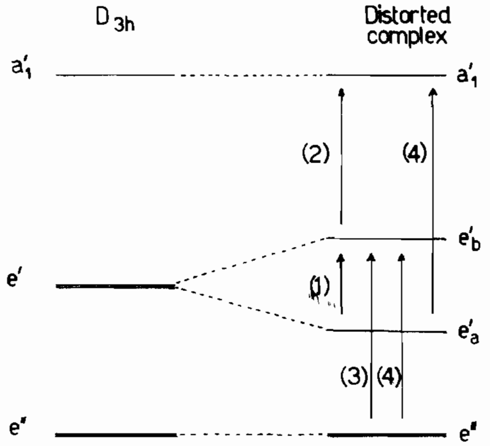

Figure 2. Schematic representation of the spin-allowed transitions, in the one-electron limit.

It is also interest to compare the values of $e'_{eq.}/e'_{ax.}$ which can be calculated for complexes $[MCl(QP)]^+$ (M=Fe and Ni). The best spectral fit was obtained[1] for values of Q^2/Q^4 of 1.3 and 2.0 respectively which correspond to values of $e'_{eq.}/e'_{ax.}$ of 0.65 and 0.4 respectively. Little reliance can be placed on the value obtained for the nickel complexes as the higher energy band was obtained only as a shoulder on the side of strong adsorption and its position determined from Gaussian analysis of the overlapping bands.[1] Furthermore, as the calculated absorption maxima, in all cases examined, are fairly insensitive to changes in $e'_{eq.}/e'_{ax.}$, it is reasonable to suppose that all the spectra could be adequately described by a single value of this parameter. In effect the accuracy of the experimental data and of the calculations is not sufficient to allow any comparison of the bonding in complexes $[MCl(QP)]^+$ (M=Fe, Co, and Ni).

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(7) C. A. McAuliffe, D. Phil. Thesis, Oxford (1967)