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# Theoretical Analysis of the Electronic Transitions of Pentacoordinated $CoBr_2 \cdot TPDA$

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*The observed electronic spectrum of the high-spin penta-coordinated Dibromo(N, N, N′, N′-tetramethylpyridine dicarboxamide)cobalt(II) was refined by means of a gaussian analysis. The resulting peaks are interpreted in terms of a LCAO MO theory where interelectronic repulsion and configuration interaction effects are included. The results obtained for relevant symmetries are compared. Conclusions regarding the influence of covalence and configuration interaction are presented.*

## Introduction

In recent years experimental data on the physical properties of a large number of penta-coordinated complexes of divalent cobalt, nickel and copper became available. In any theoretical interpretation of such data various aspects such as symmetry, bond lengths, ligand nature and $d^n$ electron configuration have to be incorporated as accurately as possible – within the limitations of the particular model.

The present study accesses the applicability of a LCAO MO theory [1] to the observed electronic spectrum of penta-coordinated Dibromo(N, N, N′, N′-tetramethylpyridine dicarboxamide)cobalt(II) [2].

Two forms of $CoBr_2 \cdot tpda$ with similar physical properties exist. Their spectra correspond to those of other distorted square pyramidal $CoBr_2$ complexes [2]. The actual stereochemistry of the $\beta$ form of $CoBr_2 \cdot tpda$ was determined by X-ray analysis [3], providing us with the information needed in our theoretical discussion.

Firstly the theory was applied to an assumed square pyramidal symmetry and the results compared with those obtained when the actual symmetry of the molecule was considered.

We first give an outline of the theoretical model. This is followed by its application to the complex concerned and an interpretation of the results obtained.

## Theoretical Section

For the purpose of this study we confine ourselves to a consideration of 3d electrons since these are assumed to participate in the observed electronic transitions. The Hamiltonian operator for such a system can be written as

$$H = \sum_{i} (H_i^M + V_i) + \sum_{i<j} V_{ij}$$

$H_i^M$ is the energy operator for an electron under the influence of the central ion core whereas $V_i$ represents its potential energy in the ligand field and

$$\sum_{i<j} V_{ij}$$

is the potential energy arising from inter-electronic repulsion.

An expression for the energy of such an electron can be obtained in the context of the LCAO MO theory. The molecular orbital for an outer electron in the complex may be approximated as

$$d_i = a_i d_i^o + b_i \phi_i^o$$

where $\phi_i^o$ is the group orbital of the ligands belonging to the same representation as the atomic 3d orbital $d_i^o$ whereas $a_i$ and $b_i$ are appropriate constants. The energy of such an orbital is then, in the absence of interelectronic repulsion, approximated as

$$\epsilon_i = \int d_i^o H_i^M d_i^o d\tau + \int d_i^o V_i d_i^o d\tau + \frac{\{H(d_i^o, \phi_i^o) - S(d_i^o, \phi_i^o)\epsilon(d_i^o)\}^2}{\epsilon(d_i^o) - \epsilon(\phi_i^o)}$$

$$\equiv \epsilon^o + U_i + \epsilon_i'$$

where

$$\epsilon(d_i^o) = \int d_i^o (H_i^M + V_i) d_i^o d\tau,$$

$$\epsilon(\phi_i^o) = \int \phi_i^o (H_i^M + V_i) \phi_i^o d\tau,$$

$$H(d_i^o, \phi_i^o) = \int d_i^o (H_i^M + V_i) \phi_i^o d\tau, \text{ and}$$

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$$S(d_i^o, \phi_i^o) = \int d_i^o \phi_i^o d\tau$$

$\epsilon^o$ is obviously the degenerate energy of the 3d orbitals in the absence of the ligands while $U_i$ represents the electrostatic energy of the electron in the ligand field and $\epsilon_i'$ results from the antibonding with the ligand orbitals, *i.e.* covalence.

If $d_i$ corresponds to the irreducible representation $\gamma$, it is convenient to write $d_\gamma$ and $\epsilon_\gamma$ instead of $d_i$ and $\epsilon_i$ respectively.

The effect of the mutual interaction of the outer electrons on the energy can be calculated in terms of the Racah parameters, under the assumption that the deformation of the orbitals can be neglected for this purpose. Finally the picture is completed by including the effect of configuration interaction.

## Interpretation of the $CoBr_2$·tpda Spectrum

We now turn to the application of the above theory to the experimentally observed electronic spectrum of the penta-coordinated high-spin complex $\beta$ $CoBr_2$·tpda [2].

The solid reflectance spectrum of this $d^7$ system exhibits broad peaks at about 5kk and 15kk and another peak at 17.75kk whereas a further peak at 20.1kk was associated with charge transfer.

In order to interpret the braod peaks observed at 5kk and 15kk a computer programme was developed to resolve these into a number of gaussian peaks. The peak at 5kk was found to represent two transitions with energies 4.886kk and 5.602kk whereas the other peak was resolved into two peaks at 13.948kk and 15.277kk – as illustated in Fig. 1.

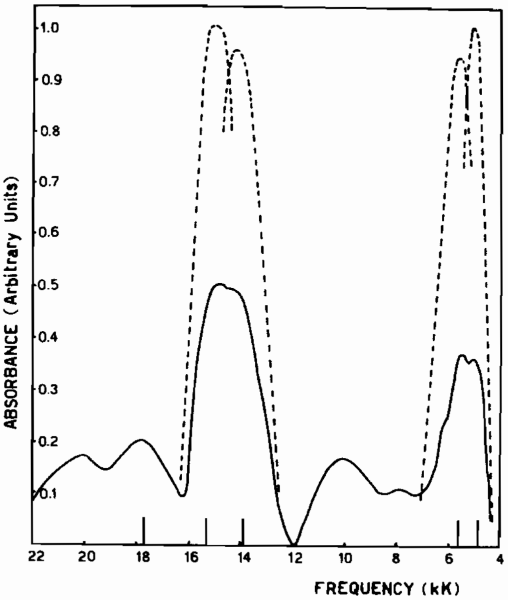

Figure 1. Absorbance spectrum of $\beta$ $CoBr_2$·tpda with normalized gaussian curves superimposed in order to resolve the peaks at 5kk and 15kk, the resulting RMSE being 0.07 and 0.02 respectively (the atypical low-intensity effect at 10kk is absent in the $\alpha$ species of this complex and in other penta-coordinated $Co^{II}$ chromophores [4]).

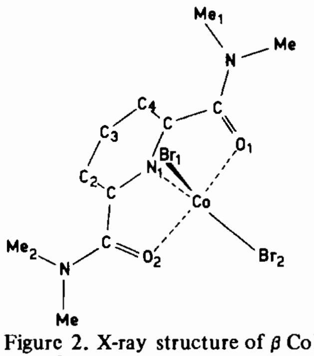

Figure 2. X-ray structure of $\beta$ $CoBr_2$·tpda: Br(1)–Co–Br(2) = 111.7°; Br(1)–Co–N(1) = 94; Br(2)–Co–N(1) = 154; O(1)–Co–O(2) = 140.

The five electronic transition energies thus determined are now interpreted in terms of the theory.

A full X-ray structure determination revealed the complex to be approximately square pyramidal with an axial bromine (Fig. 2). The second bromine, the two carbonyl oxygen atoms and the pyridine nitrogen form the base of the pyramid in such a way that the complex has a $C_s$ macrosymmetry [3].

In order to obtain an assignment of the observed levels it is noted that ordinary crystal field calculations, when applied to this particular high-spin complex, give the energy level scheme in Fig. 3 for the splitting of the one-electron energy levels in fields of $C_{4v}$ and $C_s$ symmetry.

Assuming the chromophore to have $C_{4v}$ symmetry we use Ciampolini's assignment [4] for the electronic configurations of high-spin $Co^{II}$ chromophores of $C_{4v}$ symmetry and obtain the ground state as $^4A_2$

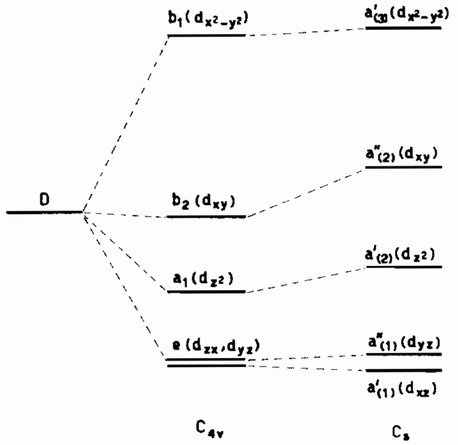

Figure 3. Single electron energy levels in crystal fields of $C_{4v}$ and $C_s$ symmetries for five-coordinated chromophores with reference to $CoBr_2$·tpda.

state with electronic configuration $(e)^4(b_1)^1(a_1)^1$-$(b_2)^1$ whereas for the excited states;

$$^4B_2 \rightarrow (e)^2(b_1)^1(a_1)^2(b_2)^2;\ ^4E \rightarrow (e)^3(a_1)^2(b_1)^1(b_2)^1$$

$$^4B_1 \rightarrow (e)^2(b_1)^2(a_1)^2(b_2)^1;\ ^4E \rightarrow (e)^3(a_1)^1(b_1)^2(b_2)^1$$

$$^4A_2 \rightarrow (e_1)^2(a_1)^1(b_2)^2(b_1)^2$$

By using the hole formulation one can write the wave functions for these states simbolically in terms of Slater determinants as follows.

$$|^4A_2> = |d_{x^2-y^2}\, d_{z^2}\, d_{xy}|;\quad |^4B_2> = |d_{xy}d_{yz}d_{x^2-y^2}|$$

$$|^4E> = |d_{yz}d_{xy}d_{x^2-y^2}|;\ |^4B_1> = |d_{yz}d_{xz}d_{xy}|$$

$$|^4E> = |d_{yz}d_{z^2}d_{xy}|;\quad |^4A_2> = |d_{yz}d_{xz}d_{z^2}|$$

Here spin is not considered more explicitly since it is not needed in calculating interelectronic repulsion and configuration interactions.

By considering these configurations and wave functions the energy levels for a $d^7$ system of $C_{4v}$ symmetry are found in the context of the present theory to be given – apart from a common additive constant f(A, B, C) – by

$$E(^4A_2) = 4\epsilon_e + \epsilon_{a_1} + \epsilon_{b_1} + \epsilon_{b_2} + 3A - \left(\frac{13}{2} + \frac{\sqrt{191}}{2}\right) B$$

$$E(^4B_2) = 2\epsilon_e + 2\epsilon_{a_1} + \epsilon_{b_1} + 2\epsilon_{b_2} + 3A - 15B$$

$$E(^4E) = 3\epsilon_e + 2\epsilon_{a_1} + \epsilon_{b_1} + \epsilon_{b_2} + 3A - \left(9 + \frac{\sqrt{84}}{2}\right) B$$

$$E(^4B_1) = 2\epsilon_e + 2\epsilon_{a_1} + 2\epsilon_{b_1} + \epsilon_{b_2} + 3A - 15B$$

$$E(^4E) = 3\epsilon_e + \epsilon_{a_1} + 2\epsilon_{b_1} + \epsilon_{b_2} + 3A - \left(9 - \frac{\sqrt{84}}{2}\right) B$$

$$E(^4A_2) = 2\epsilon_e + \epsilon_{a_1} + 2\epsilon_{b_1} + 2\epsilon_{b_2} + 3A - \left(\frac{13}{2} - \frac{\sqrt{191}}{2}\right) B$$

Following Ciampolini the observed electronic transitions are assigned as

$^4A_2 \rightarrow {^4B_2}$ (4.886kk)
$\rightarrow {^4E}$ (5.602kk)
$\rightarrow {^4B_1}$ (13.948kk)
$\rightarrow {^4E}$ (15.276kk)
$\rightarrow {^4A_2}$ (17.75kk).

Using these assignments values for the single electron energy levels as well as the Racah parameter B can be obtained. B was found as 665,7 $cm^{-1}$. The single electron energy levels were expressed relative to the degenerate $\epsilon_e$ as groundstate and found to be $\epsilon_{b_2} = 0.23$kk, $\epsilon_{a_1} = 5.72$kk and $\epsilon_{b_1} = 9.29$kk. This indicates that the level corresponding to $d_{z_2}$ lies higher in energy than that corresponding to $d_{xy}$ whereas in the pure crystal field case the opposite was true.

Since crystallographic data indicated that $CoBr_2 \cdot$-tpda has $C_s$ macrosymmetry it is of interest to repeat the above calculations for this case.

In the absence of proper assignments for the electronic transitions of a high-spin $d^7$ complex of this symmetry the wave functions for all possible high-spin configurations were constructed. Various sets of five transtions at a time were considered and the theoretical expressions for the transition energies were then associated with the five experimental values. In each case the parameter values were evaluated. In this way sets of completely unrealistic values were obtained except for the case where the $^4A''$ state with configuration $(a'_{(1)})^2(a''_{(1)})^2(a'_{(2)})^1$ $(a''_{(2)})^1(a'_{(3)})^1$ was taken as ground state with the excited states (in the order given) as:

$$^4A' \rightarrow (a'_{(1)})^2(a''_{(1)})^1(a'_{(2)})^1(a''_{(2)})^1(a'_{(3)})^2;$$

$$^4A'' \rightarrow (a'_{(1)})^1(a''_{(1)})^2(a'_{(2)})^1(a''_{(2)})^1(a'_{(3)})^2;$$

$$^4A'' \rightarrow (a'_{(1)})^1(a''_{(1)})^1(a'_{(2)})^2(a''_{(2)})^2(a'_{(3)})^1;$$

$$^4A' \rightarrow (a'_{(1)})^1(a''_{(1)})^1(a'_{(2)})^2(a''_{(2)})^1(a'_{(3)})^2;$$

$$^4A'' \rightarrow (a'_{(1)})^1(a''_{(1)})^1(a'_{(2)})^1(a''_{(2)})^2(a'_{(3)})^1$$

In the light of the foregoing results the observed transitions are then assumed to be between the states

$^4A'' \rightarrow {^4A'}$ (4.886kk)
$^4A''$ (5.602kk)
$^4A''$ (13.948kk)
$^4A'$ (15.276kk)
$^4A''$ (17.75 kk)

In this case the evaluation of the configuration interaction was more complicated than for the $C_{4v}$ symmetry because of the number of levels (several $^4A'$ levels and several $^4A''$ levels) contributing to this effect. A matrix diagonalizing procedure was used to include the effect of configuration interaction in a computarized calculation of the interelectronic repulsion. The resulting expressions for the energy levels are (ignoring the common additive constant)

$$E(^4A'') = 2\epsilon_{a_{(1)}} + 2\epsilon_{a''_{(1)}} + \epsilon_{a'_{(2)}} + \epsilon_{a''_{(2)}} + \epsilon_{a'_{(3)}} + 3A - 12.08\ B\ (-12B)$$

$$E(^4A') = 2\epsilon_{a'_{(1)}} + \epsilon_{a''_{(1)}} + \epsilon_{a'_{(2)}} + \epsilon_{a''_{(2)}} + 2\epsilon_{a'_{(3)}} + 3A - 11.6B\quad (-12B)$$

$$E(^4A'') = \epsilon_{a'_{(1)}} + 2\epsilon_{a''_{(1)}} + \epsilon_{a'_{(2)}} + \epsilon_{a''_{(2)}} + 2\epsilon_{a'_{(3)}} + 3A - 12B\qquad (-12B)$$

$$E(^4A'') = \epsilon_{a'_{(1)}} + \epsilon_{a''_{(1)}} + 2\epsilon_{a'_{(2)}} + 2\epsilon_{a''_{(2)}} + \epsilon_{a'_{(3)}} + 3A - 15.02\,B \quad (-15B)$$

$$E(^4A') = \epsilon_{a'_{(1)}} + \epsilon_{a''_{(1)}} + 2\epsilon_{a'_{(2)}} + \epsilon_{a''_{(2)}} + 2\epsilon_{a'_{(3)}} + 3A - 14.57\,B \quad (-15B)$$

$$E(^4A'') = \epsilon_{a'_{(1)}} + \epsilon_{a''_{(1)}} + \epsilon_{a'_{(2)}} + 2\epsilon_{a''_{(2)}} + 2\epsilon_{a'_{(3)}} + 3A - 2.89B \quad (-3B)$$

The terms in brackets indicate what the term involving B would be in the absence of configuration interaction.

Using the above assignment and theoretical energy expressions B was found to be 937.5 $cm^{-1}$ whereas (relative to $\epsilon_{a'_{(1)}}$) $\epsilon_{a''_{(1)}} = 1.02$kk; $\epsilon_{a''_{(2)}} = 4.62$kk; $\epsilon_{a'_{(3)}} = 5.53$kk and $\epsilon_{a'_{(2)}} = 13.1$kk.

This suggests that the one-electron levels corresponding to $d_{z^2}$, $d_{xy}$ and $d_{x^2-y^2}$ have changed their relative positions as compared to the pure crystal field case; the level $d_{z^2}$ has again been raised considerably.

## Discussion

A comparison between the results obtained when $C_{4v}$ symmetry was assumed and those referring to $C_s$ is of some interest.

It is noted that the calculated single-electron energies imply in both cases a considerable increase in energy for the $d_{z^2}$ level when compared with the pure crystal field predictions (Fig. 1); in the case of $C_s$ symmetry it has been raised above the $d_{xy}$ and $d_{x^2-y^2}$ levels to occupy the highest position. It seems reasonable to interpret this as due to the antibonding effect of covalence between the $d_{z^2}$ orbital and ligand orbitals. This interpretation seems to be supported by the fact that all five ligands may contribute to the overlap with the $d_{z^2}$ orbital while for the other d orbitals at most four are found to contribute [5].

The value of 937.5 $cm^{-1}$ obtained for B when the correct macrosymmetry, *i.e.* $C_s$, was considered compares favourably with that of 971 $cm^{-1}$ suggested by Sugano and Tanabe [6] in the case of $Co^{II}$. The B value of 665.7 $cm^{-1}$ obtained when $C_{4v}$ symmetry was assumed is regarded as unsatisfactory.

It can be concluded that a consideration taking account of the correct macrosymmetry in this case represents a definite improvement when compared to the assumption of a $C_{4v}$ symmetry – although the calculations in the former case were complicated due to the presence of configuration interaction.

The theoretical expressions for the $C_s$ energy levels, as given previously, suggest that the effect of configuration interaction in this case is probably small. When the calculations are repeated in the absence of configuration interaction, one obtains $\epsilon_{a''_{(1)}} = 0.72$kk; $\epsilon_{a''_{(2)}} = 4.27$kk; $\epsilon_{a'_{(3)}} = 5.6$kk and $\epsilon_{a'_{(2)}} = 13.25$kk while $B = 954\ cm^{-1}$.

These results indeed do not differ drastically from those obtained in the presence of configuration interaction. For $C_{4v}$ symmetry, however, it was found that negligence of this effect caused considerable changes in parameter values. Only in some cases, therefore, would it be realistic to ignore configuration interaction.

As a final point it is to be noted that the above theoretical interpretation gave reasonable results although spin–orbit coupling has been neglected.

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