*Inorganica Chimica Acta*, *72* (1983) 95–101

# Electronic Spectra of Planar Bis-acetylacetonato Copper(II) Complexes

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Received October 12, 1982

*The electronic spectra of $CuL_2$ (L = acetylacetonato, benzoyl-acetylacetonato, 3-phenyl-acetylacetonato, dipivaloylmethane) have been treated by the Angular Overlap Method (AOM) and the Crystal Field Theory (CFT). The experimental values of the ligand bite angle (α) and the spin orbit coupling constant (ζ) have been used to solve the 5 X 5 secular determinants for $d^9$ in the double group $D_{2h}'$, and to find the transition energies. The inclusion of α explicitly in the transition energy expressions brings about a small, non-negligible correction to the calculated spectral parameters, while ζ is important in explaining the observed band intensities and polarizations. The failure of the CFT to explain the electronic spectra of some of the studied complexes is attributed to the need for different CFT parameters for the different type of orbitals involved in the transitions.*

## Introduction

There has been a long-standing dispute over the d-AO ordering in planar bis-acetylacetonate (acac) complexes of Cu(II) of $D_{2h}$ symmetry (Fig. 1). Several schemes have been proposed and tested on the basis of MO calculations [1–3] and spectral shifts, occurring on adduct-formation [4–8]. At present it seems that this dispute is solved in favour of the Belford-Hitchman d-ordering [6, 7, 9–11], namely $xy \gg z^2 > x^2 - y^2 > xz > yz$. This d-orbital ordering is strongly supported by the spectral shifts occurring upon adduct formation [6], and recently by EPR spectra and by the intensity of electronic transitions versus the ligand pK correlation [12].

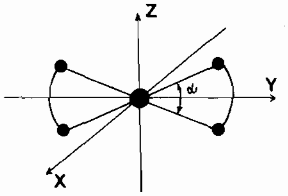

Fig. 1. Illustration of the Cu(bidentate)$_2$ complexes and choice of the coordinate axes.

The electronic spectra of Cu(II) acetylacetonates have been thus far treated by the Crystal Field Theory (CFT) and the Angular Overlap Method (AOM) (see [6, 11, 13] and refs. therein). In these treatments, however, with the exception of Cu(acac)$_2$ [13], the effect of the ligand bite angle (α) (as found from X-ray diffraction measurements) and spin-orbit coupling have been neglected. Such omissions were thought to be unimportant because α was close to 90° and the complexes were assumed to be square planar, $D_{4h}$, or $D_{2h}$ with $\alpha = 90°$.

We report here our theoretical interpretation of the electronic spectra of a number of Cu(II) complexes of acac derivatives. We have treated these spectra by the CFT and the AOM in the full $D_{2h}'$, double group. The study is intended to display the effect of the ligand bite angle and the spin-orbit coupling on the transition energies and the band intensities and polarizations.

## Results and Discussion

The relevant spectral and structural data, obtained from literature sources, are collected in Table I.

### *Crystal Field Treatment*

The transition energies for $d^9$ in $D_{2h}$ symmetry are [13, 19]:

$$E[{}^2B_{1g} \rightarrow {}^2A_g^-(z^2 \rightarrow xy)] = 4Cp + (20/7)Dq - 10Dq \cos^2 \alpha \quad (1)$$

$$E[{}^2B_{1g} \rightarrow {}^2A_g^+(x^2 - y^2 \rightarrow xy)] = 10Dq - 20Dq \cos^2 \alpha; \quad (2)$$

$$E[{}^2B_{1g} \rightarrow {}^2B_{3g}(yz \rightarrow xy)] = 2Cp(1 - \cos \alpha) + (1/7)Dq(50 + 20 \cos \alpha - 70 \cos^2 \alpha) \quad (3)$$

$$E[{}^2B_{1g} \rightarrow {}^2B_{2g}(xz \rightarrow xy)] = 2Cp(1 + \cos \alpha) + (1/7)Dq(50 - 20 \cos \alpha - 70 \cos^2 \alpha) \quad (4)$$

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0020-1693/83/$03.00

TABLE I. Electronic Spectral Band Positions, Band Polarizations and Structural Data on the $CuL_2$ Complexes of $D_{2h}$ Symmetry.

| Complex | Bite angle (°) | Cu–O dist. (Å) | Observed band positions (kK = $10^3$ $cm^{-1}$)[i] | | | |
|---|---|---|---|---|---|---|
| | | | I | II | III | IV |
| $Cu(Phacac)_2$ | 91.4 | 1.91[e] | 15.4(y > x,z) | 16.9(y > x,z) | 19.0(y > x) | 20.6(y)[a] |
| $Cu(Bzacac)_2$ | 93.0 | 1.93[f] | 14.2(y > x,z) | 15.6(y > x,z) | 18.1(y,x,z)[b] | |
| $Cu(acac)_2$ | 93.5 | 1.92[g] | 14.5(x + z) | 15.6(y;x + z)[c] | 18.0(x + z)[c] | |
| $Cu(dpm)_2$ | 94.6 | [h] | 15.6(y) | 16.4(x) | 18.2(y) | 20.0(y > x)[d] |

[a] Ref. [10]. [b] Ref. [9]. [c] Refs. [16–18]. [d] Ref. [18]. [e] Ref. [14]. [f] Ref. [15]. [g] Ref. [16]. [h] Ref. [18]. [i] Polarizations given in parenthesis.

$$\langle {}^2A_g^+(x^2-y^2)|V(D_{2h})|{}^2A_g^-(z^2)\rangle = 2\sqrt{3}\,(Cp + 5/7Dq)\cos\alpha \qquad (5)$$

where [20]

$$Dq = \frac{1}{6}\cdot\frac{Ze^2}{a^5}\cdot\langle r^4\rangle \qquad Cp = \frac{2}{7}\cdot\frac{Ze^2}{a^3}\cdot\langle r^2\rangle$$

and $\alpha$ is the ligand bite angle. The relation between Wasson's parameters ($\alpha_2$, $\alpha_4$) [19], and the K parameter used previously [13] with the Dq and Cp parameters defined above [20] is:

$$\alpha_4 = 6Dq \qquad \alpha_2 = (7/2)Cp \qquad K = (1/2)Cp \qquad (6)$$

Using these expressions and the experimental $\alpha$ values we have calculated the 'd–d' transition energies for a wide range of parameter values: Cp/Dq = –5 to +5. Figure 2 illustrates the results for 91.4°. In this Figure $\Delta E_i/\Delta E_1$ represents the transition energies divided by the lowest (first) transition energy. The horizontal dashed lines give the experimental ratios for the complex under consideration, $Cu(Ph\text{-}acac)_2$. It is seen from this Figure that the theoretical transition energy ratios cannot cross the experimental lines at a single Cp/Dq value. The same holds for all complexes listed in Table I (see Figs. 2–5) with a possible exception of $Cu(acac)_2$. The spectrum of $Cu(acac)_2$ was fitted upon inclusion of the spin–orbit coupling in a double CFT treatment [13]. When trying to extend such spin-orbit treatments to the other complexes, spectral fits were found lacking: in the entire range of positive Cp/Dq ratios the transitions to $B_{2g}$ and $B_{3g}$ remain the highest and closely spaced near the minimum of the functions

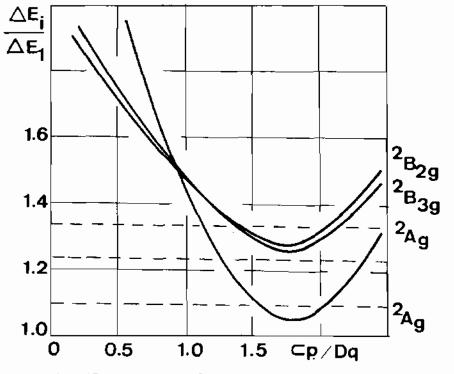

Fig. 2. Variation of the transition energies, relative to the first transition ($\Delta E_1$) as a function of the Cp/Dq ratio. The bite angle is 91.4° and the experimental transition energy ratios for $Cu(Ph\text{-}acac)_2$ are given by dashed lines.

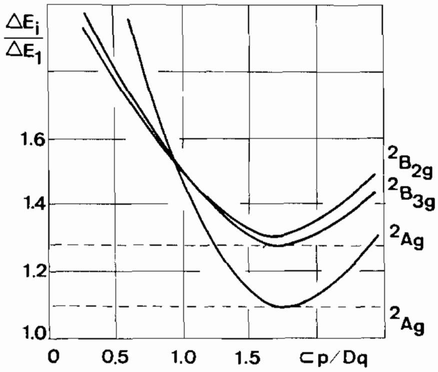

Fig. 3. Variation of the transition energies, relative to the first transition ($\Delta E_1$) as a function of the Cp/Dq ratio. The bite angle is 93° and the experimental transition energy ratios for $Cu(Bz\text{-}acac)_2$ are given by dashed lines.

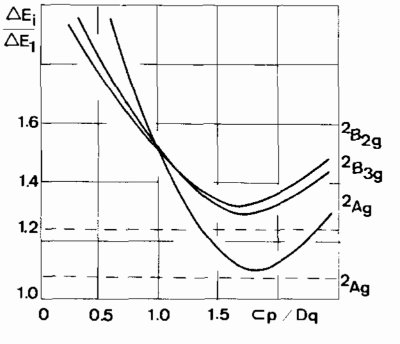

Fig. 4. Variation of the transition energies, relative to the first transition ($\Delta E_1$) as a function of the Cp/Dq ratio. The bite angle is 93.5° and the experimental transition energy ratios for $Cu(H\text{-}acac)_2$ are given by dashed lines.

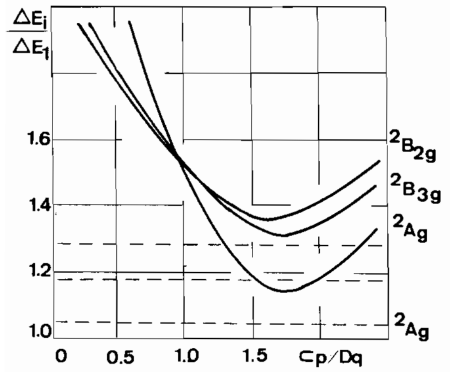

Fig. 5. Variation of the transition energies, relative to the first transition ($\Delta E_1$) as a function of the Cp/Dq ratio. The bite angle is 94.6° and the experimental transition energy ratios for $Cu(dpm)_2$ are given by dashed lines.

$$\Delta E_i/\Delta E_1 = f(W), \quad W = Cp/Dq.$$

*Angular Overlap Treatment*

The transition energies for $d^9$ in $D_{2h}$ in terms of AOM [20–22] have been calculated before [13]:

$$E[{}^2B_{1g} \rightarrow {}^2A_g^-(z^2 \rightarrow xy)] = e\sigma(3 \sin^2 \alpha - 1) + e\pi(\parallel)\cdot\cos^2 \alpha, \quad (8)$$

$$E[{}^2B_{1g} \rightarrow {}^2A_g^+(x^2 - y^2 \rightarrow xy)] = 3e\sigma \cos 2\alpha + 4e\pi(\parallel)\cdot\cos 2\alpha, \quad (9)$$

$$E[{}^2B_{1g} \rightarrow {}^2B_{3g}(yz \rightarrow xy)] = 3e\sigma \sin^2 \alpha + 4e\pi(\parallel)\cdot\cos^2 \alpha - 2e\pi(\perp)\cdot(1 + \cos \alpha), \quad (10)$$

$$E[{}^2B_{1g} \rightarrow {}^2B_{2g}(xz \rightarrow xy)] = 3e\sigma\cdot\sin^2 \alpha + 4e\pi(\parallel)\cdot\cos^2 \alpha - 2e\pi(\perp)\cdot(1 - \cos \alpha), \quad (11)$$

$$\langle {}^2A_g^+(x^2 - y^2)|A(D_{2h})|{}^2A_g^-(z^2)\rangle = \sqrt{3}\cdot e\sigma\cdot\cos \alpha, \quad (12)$$

where ∥ and ⊥ refer to the molecular plane (not the principal axis, as in ref. [6]).

Using these expressions and the experimental $\alpha$ values, we have calculated the transition energies for $e\sigma = 0$–$15$, $e\pi(\parallel) = 0$–$10$ and $e\pi(\perp) = 0$–$10$ kK. The same expressions, together with the non-zero spin-orbit matrix elements [13] were used to find the transition energies in the $D'_{2h}$ (double group) treatment within the same parameter ranges by taking the value of the spin–orbit coupling constant $\zeta = 0.829$ kK and decreasing it to zero in a stepwise procedure solving simultaneously the full $5 \times 5$ secular matrix. The upper limit of $\zeta$ is the free-ion value of Cu(II) [23].

If the Belford-Hitchman d-ordering is imposed in advance, the problem of finding a unique fit to the spectra of the studied compounds is easily solved. The results are given in Table II.

Only one of the two components of each E′ state is given in Table II. The other component may be found by changing the spin-notation above each AO function and the sign in front of the xz and xy orbitals. Both components contain imaginary terms (due to the spin–orbit coupling operator). The AOM operator can mix only $z^2$ and $x^2 - y^2$; the mixing between the other d-AO's results from the spin-orbit coupling operator. This mixing increases with increasing $\alpha$ and $\zeta$ values.

Since the best fits were obtained for $\zeta = 0.83$ kK (the free ion value) the results with this $\zeta$ value are given in Table II and discussed further. With the exception of the ground state, all excited states show extensive mixing between the d-orbitals. The ground state is predominantly a hole in xy with a small admixture of $x^2 - y^2$.

With the exception of $Cu(dpm)_2$, for all the other complexes the ordering of the d orbitals is that of Belford and Hitchman. This is readily seen for $Cu(Ph\text{-}acac)_2$ and $Cu(Bz\text{-}acac)_2$, but the mixing of d-AO's is large for $Cu(acac)_2$ and it blurs out the differences between the first and second transitions with respect to the orbitals $z^2$ and $x^2 - y^2$ and the third transition with respect to the orbitals xz and yz.

It is also seen from Table II that the mixing between $x^2 - y^2$ and $z^2$ increases with increasing $\alpha$; while the first transition in the $Cu(Bz\text{-}acac)_2$ spectrum is predominantly $xy \rightarrow z^2$, it is $xy \rightarrow x^2 - y^2, z^2$ in the $Cu(acac)_2$ spectrum.

The d-orbital ordering for $Cu(dpm)_2$ is $xy \gg xz > z^2 > yz > x^2 - y^2$. No solution giving the Belford-Hitchman assignment is possible for $Cu(dpm)_2$ in the studied parameter ranges.

*Intensities and Polarizations*

The treatment that follows is intended to show that spin-orbit coupling in $Cu^{II}$ complexes, where $\zeta_{Cu}$ has a relatively large value, plays a major role in determining the polarizations by mixing the d-orbitals and changing the selection rules.

All transitions of d–d nature are $E'_g \rightarrow E'_g$ in the $D'_{2h}$ double group, implying that both the ground and the excited state are spin-degenerate. Any odd-parity vibration ($\alpha_u$) can change the parity of either the ground state or the excited state but not their spin-degeneracy. Thus, if the $\alpha_u$ operative in lifting the parity rule is not degenerate (as is the case in $D_{2h}$, where all vibrations are not degenerate), then

$$\alpha_u \times E'_g = E'_u$$

and the transitions $E'_g \rightarrow E'_u$ are symmetry-allowed in all three polarizations (x, y, z). Hence, to deduce the intensity ratios between the d–d bands in the experimental spectrum of a given complex one has to consider simply the eigenvectors in Table II and their products. The selection rules in $D'_2$ (the g subscript has been dropped on the assumption that *some* odd-parity vibration is operative) are given in Table III.

TABLE II. Calculated Eigenvalues and Eigenvectors of the Full 5 × 5 Energy Matrix with AOM Parameters which Fit the Experimental Transition Energies. $d^9$ in $D_{2h}'$, Hole Formalism.

| Eigenvalue | Eigenvectors | | | | |
|---|---|---|---|---|---|
| kK | $i\overset{+}{y}z$ | $\overset{+}{x}z$ | $i\bar{x}y$ | $\bar{z}^2$ | $x^2 \overset{-}{-} y^2$ |
| $\alpha = 91.4°$ | $e\sigma = 7.8$ kK | $e\pi(\parallel) = 1.60$ kK | $e\pi(\perp) = 2.00$ kK | | |
| −23.446 | −0.021 | −0.021 | +0.998 | +0.001 | −0.048 |
| −8.097 | −0.126 | +0.180 | −0.009 | +0.956 | −0.195 |
| −6.482 | −0.235 | −0.153 | +0.037 | +0.191 | +0.940 |
| −4.236 | +0.584 | +0.763 | +0.041 | −0.011 | +0.271 |
| −3.339 | +0.766 | −0.601 | +0.005 | +0.223 | +0.048 |
| $\alpha = 93.0°$ | $e\sigma = 7.4$ kK | $e\pi(\parallel) = 1.60$ kK | $e\pi(\perp) = 2.40$ kK | | |
| −22.218 | −0.023 | −0.023 | +0.998 | +0.002 | −0.051 |
| −8.006 | −0.099 | +0.257 | −0.019 | +0.871 | −0.406 |
| −6.378 | −0.384 | −0.174 | +0.028 | +0.389 | +0.819 |
| −5.018 | +0.401 | +0.834 | +0.048 | −0.025 | +0.375 |
| −3.979 | +0.826 | −0.456 | +0.015 | +0.298 | +0.148 |
| $\alpha = 93.5°$ | $e\sigma = 7.8$ kK | $e\pi(\parallel) = 2.00$ kK | $e\pi(\perp) = 3.20$ kK | | |
| −23.406 | −0.023 | −0.024 | +0.998 | +0.003 | −0.053 |
| −9.027 | −0.014 | +0.339 | −0.030 | +0.657 | −0.672 |
| −7.521 | −0.476 | −0.014 | +0.019 | +0.628 | +0.616 |
| −6.704 | +0.346 | +0.863 | +0.048 | −0.070 | +0.357 |
| −5.342 | +0.808 | −0.373 | +0.019 | +0.411 | +0.197 |
| $\alpha = 94.6°$ | $e\sigma = 8.59$ kK | $e\pi(\parallel) = 1.58$ kK | $e\pi(\perp) = 4.47$ kK | | |
| −25.694 | −0.023 | −0.025 | +0.999 | +0.003 | −0.042 |
| −10.258 | +0.033 | +0.814 | +0.009 | +0.520 | −0.258 |
| −9.078 | −0.656 | −0.406 | −0.032 | +0.626 | −0.107 |
| −7.833 | +0.703 | −0.414 | −0.013 | +0.394 | −0.423 |
| −5.708 | +0.273 | −0.012 | +0.041 | +0.427 | +0.861 |

TABLE III. Selection Rules between the Different Components Forming the Spin-Degenerate E′ States in the Double Group $D_2'$.

| | yz | xz | xy | $x^2 - y^2$ | $z^2$ |
|---|---|---|---|---|---|
| yz | – | z | y | x | x |
| xz | z | – | x | y | y |
| xy | y | x | – | z | z |
| $x^2 - y^2$ | x | y | z | – | – |
| $z^2$ | x | y | z | – | – |

In Table III, the symbols x, y and z denote the directions of the electric dipole in the allowed band polarizations and – denotes a symmetry-forbidden transition.

Writing down the ground state and the excited states, *e.g.* for Cu(3-Ph-acac)$_2$, the first transition (*ca.* 15 kK) is between:

$$E'(I) \quad a\begin{cases} -0.021(i\overset{+}{y}z) - 0.021(\overset{+}{x}z) + 0.998(i\bar{x}y) - \\ -0.001(\bar{z}^2) - 0.048(x^2 \overset{-}{-} y^2) \end{cases}$$

$$b\begin{cases} -0.021(i\bar{y}z) + 0.021(\bar{x}z) - 0.998(i\overset{+}{x}y) - \\ -0.001(\overset{+}{z}^2) - 0.048(x^2 \overset{+}{-} y^2) \end{cases}$$

$$E'(II) \quad a\begin{cases} -0.126(i\overset{+}{y}z) + 0.180(\overset{+}{x}z) - 0.009(i\bar{x}y) + \\ +0.956(\bar{z}^2) - 0.195(x^2 \overset{-}{-} y^2) \end{cases}$$

$$b\begin{cases} -0.126(i\bar{y}z) - 0.180(\bar{x}z) + 0.009(i\overset{+}{x}y) + \\ +0.956(\overset{+}{z}^2) - 0.195(x^2 \overset{+}{-} y^2) \end{cases}$$

and seeking the matrix elements $\langle E'(I)|Q|E'(II)\rangle$, where Q is the electric-dipole transition-moment operator, we can estimate these elements as products of eigenvectors if we set the non-zero (by symmetry) integrals $\langle d|Q|d\rangle$ to unity and thus get rough estimates of the transition moments.

Using this procedure in a consistent manner for all the transitions of the studied complexes it is readily seen that all these transitions are y-polarized, the bulk of intensity coming from the xy → yz components. This result is in fact in agreement with the experimental polarizations in the Cu(Ph-acac)$_2$ and Cu(Bz-acac)$_2$ spectra. It is, however, at variance with the polarization data on the Cu(acac)$_2$ and Cu(dpm)$_2$ spectra. The lack of agreement for Cu(acac)$_2$ may be attributed to the peculiar orientation of the molecules in the crystal [16], giving rise to several polarization components.

Since the incorporation of the experimental bite angle value into the expressions for the transition energies constitutes a minor energy correction ($\alpha$ deviates slightly from $\alpha = 90°$), it may be expected that the orbital energies should be approximately the same for all four complexes. In fact, the structure of $Cu(dpm)_2$ has not been determined and the value of 94.6° has been taken from the X-ray analysis of the structure of $Ni(dpm)_2$ during Cotton-Wise's MO calculations [18]. A reduction of $\alpha$ for $Cu(dpm)_2$ by several tenths of a degree is sufficient to restore the d-orbital ordering as observed for the other complexes, as well as the predominant y-polarization nature of the bands. The large separation of the $z^2 \rightarrow xy$ and $x^2 - y^2 \rightarrow xy$ transitions in the $Cu(dpm)_2$ spectrum, which brings about the deviation from the Belford-Hitchman assignment, is a result of the high bite angle value which yields a high value for the off-diagonal element and thus pushes apart the two $A_g$ states. Actually, the spectrum of $Cu(dpm)_2$ is closer to that of $Cu(Ph\text{-}acac)_2$ than to that of $Cu(acac)_2$, so that one might expect an $\alpha$ value of about 91–92° for $Cu(dpm)_2$. On adopting an uncertain value of $\alpha$ for $Cu(dpm)_2$, our results as to this complex are unreliable and could not serve to cast doubt on the general validity of the Belford-Hitchman d-orbital ordering.

### *Interpretation of the AOM Parameter Values*

When comparing the $e\sigma$ values (Table II) with the R(Cu–O) values (Table I), it is seen that the variation of $e\sigma$ reflects in general the changes in R (see also Table IV). On the other hand $e\pi(\parallel)$ is almost constant and $e\pi(\perp)$ increases with increasing $\alpha$. This trend in the $e\pi(\perp)$ values, however, is not related to variations of the bite angle; it reflects the effect of the substituents. The $\pi$-acceptor ability of the ligands is expected to increase in the series acac < Bz-acac < Ph-acac. The reverse trend is observed for the $e\pi(\perp)$ values, and to a lesser extent for the $e\pi(\parallel)$ values.

The comparison of the $e_i$ values ($i = \sigma, \pi$) from Table IV with those obtained by neglecting the real bite angle values and assuming $\alpha = 90°$ [11] shows that this refinement brings about a small yet non-negligible correction. The $e_i$ values obtained with real bite angles are equal or higher than those obtained with the general assumption $\alpha = 90°$, and the divergence between the two sets increases with increasing $\alpha$ values. The off-diagonal elements amount to 0.3–1 kK with the parameter values listed in Table IV.

TABLE IV. AOM Parameter Values Obtained from the Spectral Fits (kK).

| Complex | $\alpha$ | R(Cu–O) | $e\sigma$ | $e\pi(\parallel)$ | $e\pi(\perp)$ |
|---|---|---|---|---|---|
| $Cu(Ph\text{-}acac)_2$ | 91.4 | 1.91 | 7.8 | 1.60 | 2.00 |
| $Cu(Bz\text{-}acac)_2$ | 93.0 | 1.93 | 7.4 | 1.60 | 2.40 |
| $Cu(H\text{-}acac)_2$ | 93.5 | 1.92 | 7.8 | 2.00 | 3.20 |
| $Cu(dpm)_2$ | 94.6 | | 8.59 | 1.58 | 4.47 |

If the bite angle is kept equal to 90° in a double group treatment, one can account for the appearance of four d–d bands (see Fig. 6).

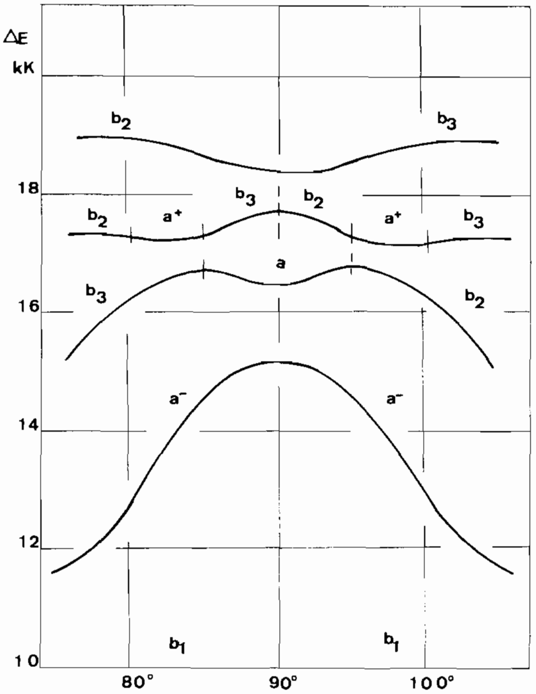

Fig. 6. Variation of the transition energies (in kK) as a function of the bite angle ($\alpha$) for $e\sigma = 7.8$ kK, $e\pi(\parallel) = 1.65$ kK, $e\pi(\perp) = 2.9$ kK and $\zeta = 0.829$ kK. The AOM parameter values are averages for the $d^9$ Cu(II) complexes $D'_{2h}$ double group. The leading orbital in the combinations is denoted. The curves are symmetric about $\alpha = 90°$ as to energy but differ as to eigenvectors. The g's are omitted.

Distortions away from the exact $D_{2h}$ symmetry could possibly lead to changes in the transition energies, intensities and polarizations. There are many possible ways of distorting a planar complex; we shall consider for the sake of illustration one only, distortion to a pseudotetrahedral structure. The AOM expressions including the bite angle and the dihedral angle as variables have been obtained previously [25] and are used here to plot the transition energies as a function of the dihedral angle (see Fig. 7).

It is readily seen from this Figure that the transition energies are pushed to lower values and the separation between them becomes larger with increasing dihedral angle. In fact the minimum in $\Delta E_i$ vs. $2\omega$ follows the minimum in the energy of xy and this minimum is shifted to lower $2\omega$ values with increasing $\alpha$.

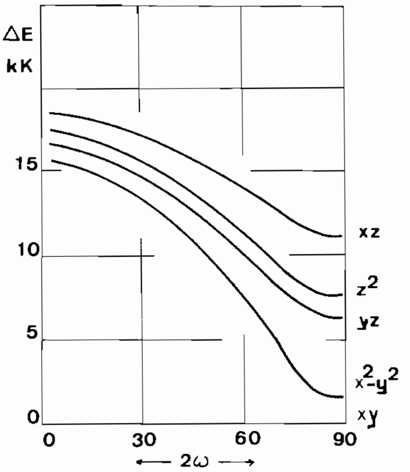

Fig. 7. Variation of the transition energies (in kK) as a function of the dihedral angle giving the transition from planar (0°) to pseudotetrahedral (90°) structure. $\alpha = 94°$, $e\sigma = 7.8$ kK, $e\pi(\perp) = 2.9$ kK, $e\pi(\parallel) = 1.65$ kK, $\zeta = 0.829$ kK. The eigenvectors are also functions of the dihedral angle; the orbital designation at the right hand side of the Figure is valid for $2\omega = 90°$.

The variations of ΔE at low 2ω values (0–10°) are very small and it thus follows that for a structure which is close to planar, the angle 2ω is a minor factor as to the exact value of the transition energy. It is evident from the comparison of Figs. 6 and 7 that the bite angle is much more effective than 2ω in causing changes of the transition energies.

## Comparison between the AOM and CFT Treatments

With the AOM parameters obtained from the spectral fits (Table IV), we have calculated (eqns. (8–12), see also [13]) the d-orbital energies of the studied complexes. The baricentre rule was further imposed and the resulting orbital energies have been equated to the CFT expression (eqns. (1–6), see also [13]) for the same orbitals where the experimental α-values have been substituted and Cp and Dq have been retained as variables. The resulting 5 equations form three distinct (for the planar complex) orbital sets: (1) σ-set ($xy, z^2$); (2) $\pi(\perp)$ set ($xz, yz$); (3) $\pi(\parallel)$ set ($x^2 - y^2$). The first two sets have been solved separately to find Cp and Dq and the results are collected in Table V.

It is seen that both Cp and Dq differ in the two sets. Thus, if we want to reproduce the results provided by AOM we have to use different Cp and Dq values in the CFT treatment for the σ and π orbitals.

Bearing in mind that the Cu–O bond lengths are almost constant throughout the series, several features emerge from Table V:

TABLE V. Crystal Field Parameters (in kK) Obtained from the AOM Parameters and the CFT Transition Energies for $d^9$ in $D_{2h}$ Symmetry.

| Ligand | α | σ-set | | | $\pi(\perp)$-set | | |
|---|---|---|---|---|---|---|---|
| | | Cp | Dq | Cp/Dq | Cp | Dq | Cp/Dq |
| 3-Ph-acac | 91.4 | 2.80 | 1.53 | 1.83 | 3.07 | 1.82 | 1.69 |
| Bz-acac | 93.0 | 2.68 | 1.42 | 1.89 | 2.57 | 1.02 | 2.52 |
| H-acac | 93.5 | 2.97 | 1.30 | 2.29 | 2.80 | 0.70 | 4.00 |
| dpm | 94.6 | 3.31 | 1.36 | 2.43 | 2.90 | 0.00 | |

(1) The difference between the two sets is especially great for the Dq values.

(2) $Dq_\pi$ is the only parameter which exhibits large variations and thus determines the increase of $Cp_\pi/Dq_\pi$ down the series.

(3) The $(Cp/Dq)_\pi$ value for $Cu(dpm)_2$ in Table V would be unrealistically high (see for comparisons ref. [26]) supporting our claim that the α value used in the spectral fit is incorrect.

From the expressions for the xz and yz orbital energies in the two approximations (AOM and CFT), by equating and taking the difference we obtain

$$20Dq_\pi = 21Cp_\pi - 14e\pi(\perp)$$

Since $Cp_\pi$ is almost constant throughout the series (2.6–3.1 kK) it is evident that the variations of $Dq_\pi$ arise from $e\pi(\perp)$; $Dq_\pi$ decreases with increasing $e\pi(\perp)$, as might be expected for a complex with metal–ligand π-bonds when the antibonding π-MOs are raised in energy [26].

With increasing α-values (>90°) the π-overlap conditions between AO's of Cu and π-MO's of the ligands would deteriorate since the bonding atoms are displaced from their most favourable positions (at $\alpha = 90°$). The effect of the bite angle, however, has been already taken explicitly in the transition energy

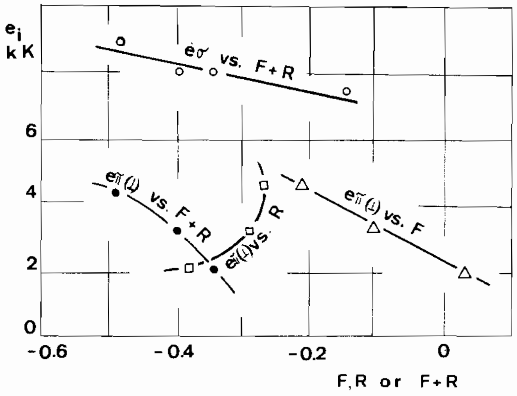

Fig. 8. Variation of the angular overlap parameters (eσ and eπ) as a function of the Swain's substituent parameters F (field), R (resonance) and the sum of them (F + R).

expressions (eqns. (1–6) and 8–12)), hence the values of $Dq_\pi$ and $e\pi(\perp)$ must reflect the effect of substituents. In fact, both $e\sigma(Dq_\sigma)$ and $e\pi(\perp)$ have been found to increase parallel to the change of the field and resonance substituent constants (taken from ref. [27]) towards the more negative values, while $e\pi(\parallel)$ is almost constant (Fig. 8). This is consistent with correlations between spectroscopic properties and ligand pK values (providing the σ-inductive effect of the substituents) for a series of bis(β-diketonato)-copper(II) complexes, found recently by Yokoi [12].

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