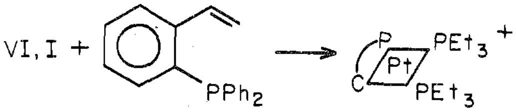
but changes in ionic strength can affect k_{obsd} of both Schemes I and II.

Neither Scheme I nor Scheme II detracts from the proposal that insertion follows coordination of olefin in the apical position on square-planar d^8 complexes which do not contain a good leaving group.[5,6] In fact, the results observed by Brookes[29] are compatible with just such a scheme.

Thus VI or I reacts very rapidly with diphenylstyrylphosphine to give inserted products. The mechanism probably proceeds *via* initial displacement of NO_3^- or Cl^- to give a P-bonded diphenylstyrylphosphine. Insertion can then proceed from a five-coordinate intermediate stabilized by a chelate effect. An alternative mechanism involving displacement of PEt_3 by olefin is possible but less likely in view of the bascity of tertiary alkylphosphines.



It is, however, clear from the results observed in this study that the square-planar hydrido(olefin) complex formed by initial substitution provides a lower energy pathway leading to insertion. As the leaving group trans to hydride becomes poorer, direct insertion from a five-coordinate intermediate formed by initial interaction with the olefin is expected to become competitive. In some cases, however, the rate of insertion from an initially formed five-coordinate intermediate approaches that of insertion from the reactive square-planar hydrido(olefin) intermediates of the types IV and XIII.[30]

Acknowledgments. We are grateful for the financial support of this work by the National Research Council of Canada and for the award (to C. R. J.) of a National Research Council postdoctoral fellowship.

Registry No. C_2H_4, 74-85-1; *trans*-PtH(acetone)$(PEt_3)_2{}^+PF_6{}^-$, 51716-77-9; *trans*-PtH$(C_2H_4)(PEt_3)_2{}^+PF_6{}^-$, 51794-48-0; *trans*-Pt-C_2H_5(acetone)$(PEt_3)_2{}^+$, 51716-78-0.

Supplementary Material Available. The Appendix will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2213.

[29] P. R. Brookes, *J. Organometal. Chem.*, 47, 179 (1973).

[30] This appears to be the case with the reaction of ethylene with *trans*-$PtHSnCl_3(PEt_3)_2$ in methanol or ethanol: H. C. Clark, C. R. Jablonski, J. Halpern, T. A. Weil, and A. Mantovani, *Inorg. Chem.*, in press.

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Single-Crystal Electronic Spectrum of Quinolinebis(acetylacetonato)copper(II) and Its Implications on the d Orbital Energies of Planar β-Ketoenolate–Copper(II) Complexes

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The single-crystal polarized electronic spectrum of the square-pyramidal complex quinolinebis(acetylacetonato)copper(II) is reported and the d-orbital energy sequence is deduced to be $d_{xy} >> d_{z^2} > d_{x^2-y^2} > d_{yz} \approx d_{xz}$. The angular overlap model is used to estimate the variation in the d-orbital energies accompanying the distortion of a planar bis(acetylacetonato)copper(II) complex to a square-pyramidal geometry. The transition energies observed for quinolinebis(acetylacetonato)copper(II) are in good agreement with the calculated values if the d-orbital energy sequence in planar bis(acetylacetonato)copper(II) is the same as that in the quinoline adduct. The intensities of the "d–d" transitions in quinolinebis(acetylacetonato)copper(II) substantiate the hypothesis that the bulk of the intensity in the "d–d" spectra of β-ketoenolate–copper(II) complexes is borrowed from charge-transfer transitions in which an electron is transferred from combinations of the essentially nonbonding lone pair electrons of the oxygen atoms to the central metal ion.

Introduction

The "d–d" electronic spectra of bis(acetylacetonato)copper(II) ($Cu(acac)_2$) and similar complexes with substituted β-diketones have been the subject of numerous studies.[1] The close similarity of the spectra suggests that the metal-ligand bonding remains quite similar throughout this series of compounds. Despite the fact that many of the spectra have been measured using single crystals at low temperatures, the energy sequence of the d orbitals in the complexes has remained uncertain. A major reason for this ambiguity has been the fact that the selection rules for the optical transitions of a centrosymmetric complex such as $Cu(acac)_2$ provide little information which can be used to assign the spectrum.

It is known that five-coordinate adducts are formed on the addition of bases such as pyridine to solutions of copper-acetylacetonate complexes in inert solvents.[2] Several attempts have been made to use the intensity changes and energy shifts which occur on adduct formation to deduce the d-orbital energies in the complexes.[2-4] However, the ambiguity of the analysis of the broad bands into their component peaks combined with the uncertainty of the precise geometry of the species present in solution has prevented general agreement on the interpretation of the results.

The present study describes the "d–d" electronic spectrum of a single crystal of the square-pyramidal adduct bis(acetyl-

[1] For a recent review of some of the work in this area see D. W. Smith, *Struct. Bonding (Berlin)*, 12, 50 (1972).

[2] R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, 26, 1165 (1957).

[3] R. L. Belford and W. A. Yeranos, *Mol. Phys.*, 6, 121 (1965).

[4] L. L. Funck and T. R. Ortolano, *Inorg. Chem.*, 7, 567 (1968).

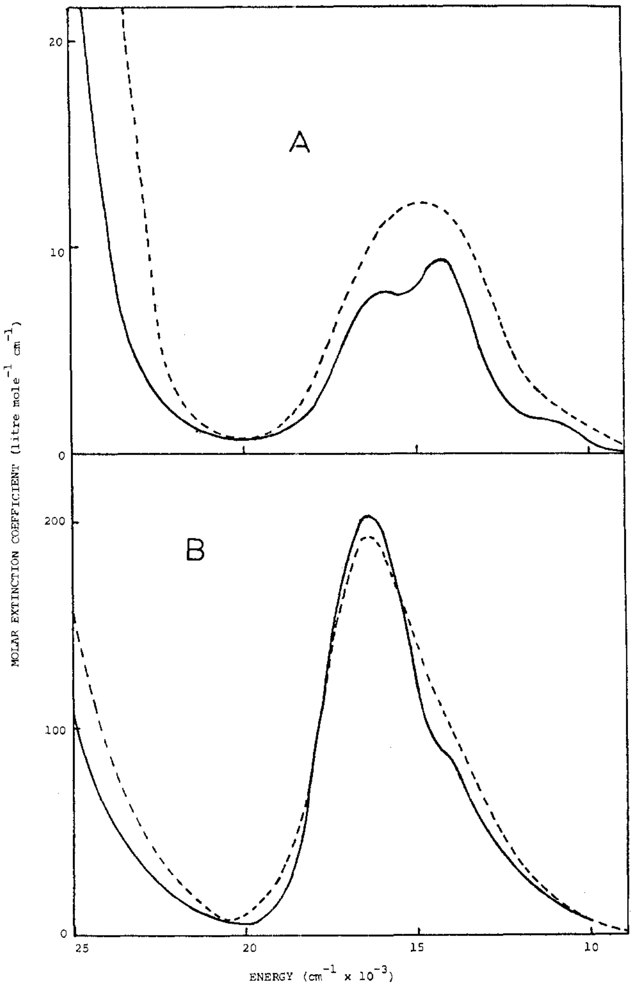

Figure 1. The spectrum of the (100) crystal face of Cu(acac)$_2$·quin with the electric vector (A) 4° from the *b* axis and (B) −86° from the *b* axis. The solid line shows the spectrum at 80°K; the broken line, that at 265°K.

acetonato)quinolinecopper(II) (Cu(acac)$_2$·quin). The static selection rules operating in this noncentrosymmetric complex greatly facilitate the assignment of its optical spectrum. By correlating the structural changes which occur on adduct formation with the shifts in the energies of the "d-d" transitions the probable d-orbital sequence in Cu(acac)$_2$ itself can be deduced. Moreover, the intensities of the optical transitions in Cu(acac)$_2$·quin provide useful information on the mechanism which induces the intensity in the "d-d" transitions of copper-acetylacetonato complexes in general.

Experimental Section

Single crystals of Cu(acac)$_2$·quin were prepared by the method of Jose, *et al.*,[5] and the complex was found to have a satisfactory analysis. The crystals belong to the triclinic space group $P\bar{1}$ with unit cell dimensions a = 14.23 Å, b = 8.66 Å, c = 8.02 Å, α = 94.0°, β = 89.4°, and γ = 110.8°. The morphology of the crystals was deduced by measuring interfacial angles using an optical goniometer and the well-developed faces were found to be (100) and (001). Sharp extinction directions were observed at 4 and −86° from the *b* axis in the *bc* plane and at 20 and −70° from the *b* axis in the *ab* plane (a positive sign indicates rotation into a quadrant containing an obtuse angle). The extinction directions were not found to alter significantly as a function of either wavelength or temperature. Spectra of several crystal faces of each type were measured using a Beckman DK2A spectrophotometer with the electric vector of polarized light along each extinction direction. Typical spectra are

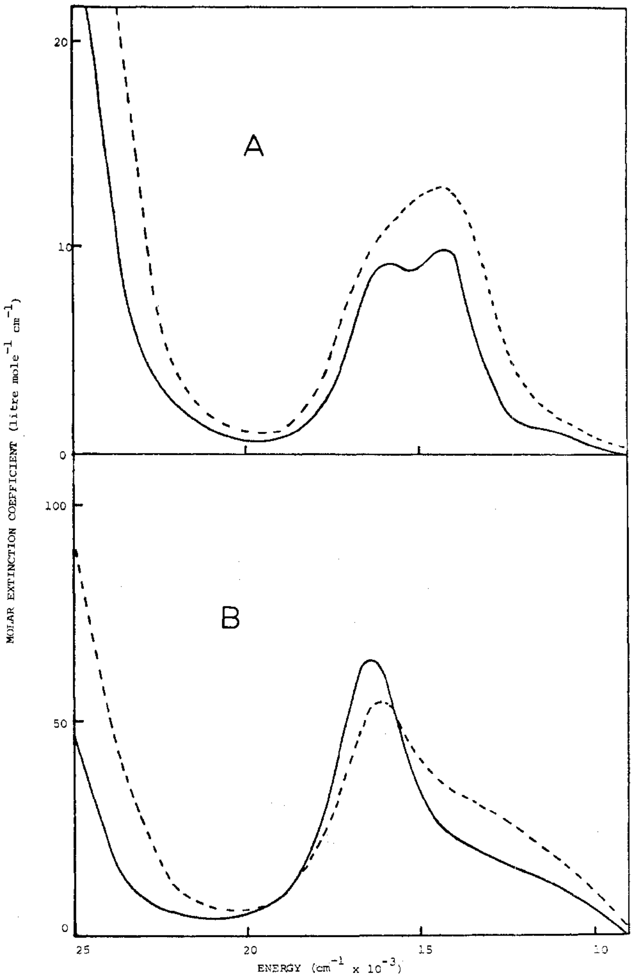

Figure 2. The spectrum of the (001) crystal face of Cu(acac)$_2$·quin with the electric vector (A) 20° from the *b* axis and (B) −70° from the *b* axis. The solid line shows the spectrum at 80°K; the broken line, that at 265°K.

shown in Figures 1 and 2. The molar extinction coefficients were obtained by measuring crystal thickness using a graduated eyepiece and are estimated to be accurate to within 10% except for the more intense spectrum of the (100) face which is accurate to within 25%. Typical crystal thicknesses ranged from 0.01 to 0.17 mm, the thicker crystals being used to investigate the less intense regions of the spectra. A Glan–Thomson prism was used to polarize the radiation. The crystals were masked with aluminum foil and cooled using an Andonian Associates dewar. As the crystals quickly lost quinoline when exposed to the atmosphere, they were cooled rapidly to ~260°K and measurements were made between this temperature and 80°K. The temperature was measured using two Fe–Au–chromel thermocouples placed above and below the crystals.

Results and Discussion

The molecular geometry of Cu(acac)$_2$·quin is illustrated schematically in Figure 3, together with the coordinate system used in the interpretation of the spectrum. The four Cu-O bond lengths are not considered to differ significantly,[5] the mean distance being 1.95 Å. The Cu-N bond length is 2.36 Å, and the Cu is raised out of the plane of the four oxygen atoms by 0.2 Å, toward the quinoline group. Although crystallographically the point group of the molecule is C_1, the molecular symmetry closely approximates C_{2v}. The coordinate system used to discuss the spectra was defined with y lying along the vector from the midpoint of the two oxygen atoms of one chelate ring to the midpoint of the oxygen atoms of the second chelate ring, with x orthogonal to y and lying in the plane of the four oxygen atoms and with z orthogonal to x and y. The matrix which trans-

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(5) P. Jose, S. Ooi, and Q. Fernando, *J. Inorg. Nucl. Chem.*, 31, 1971 (1969).

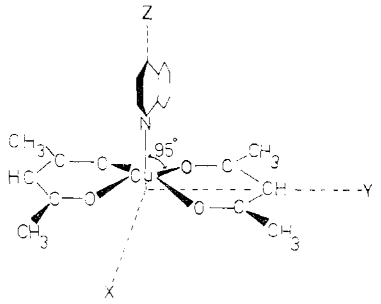

Figure 3. The molecular geometry and coordinate system of Cu(acac)$_2$·quin.

Table I. Projections Made by the Electric Vector of Polarized Light for the Extinction Directions of the (001) and (100) Crystal Faces of Cu(acac)$_2$·quin

Crystal face	Angle,[a] deg	(Molecular projections)^2		
		x	y	z
(100)	+4 (A)	0.8562	0.0047	0.1392
	−86 (B)	0.0156	0.7788	0.2057
(001)	+20 (A)	0.9635	0.0286	0.0083
	−70 (B)	0.0001	0.1955	0.8044

[a] Angle made with the *b* axis; a positive sign indicates rotation into the quadrant containing an obtuse angle.

forms a vector expressed in crystal coordinates into molecular coordinates is

$$\begin{array}{c} x \\ y \\ z \end{array} = \begin{bmatrix} -0.0070 & -0.9149 & -0.1247 \\ 0.4422 & 0.0010 & -0.8825 \\ 0.8969 & -0.4036 & 0.4535 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}$$

The molecular projections made by an electric vector along the extinction directions of each crystal face are given in Table I. The crystal spectra at 80°K were transformed into molecular spectra by a procedure which has been described in detail elsewhere[6] and the resulting spectra are shown in Figure 4. The molecular spectra of a typical copper–acetylacetonato complex, bis(benzoylacetonato)copper(II) [Cu($C_6H_5COCHCOCH_3$)$_2$ or Cu(benzac)$_2$], are also shown for comparison.[7] The molecular spectra were obtained by carrying out transformations on the crystal spectra at particular wavelengths, and the actual results are shown in the figure. It is to be noted that the x and y spectra are likely to be quite accurately defined, as the former occurs fairly "pure" in the A spectrum of the (001) face, while the latter dominates the B spectrum of the (100) face. The comparatively weak z spectrum is likely to be less accurately represented, as in effect this is obtained by subtracting the y contribution from the B spectrum of the (001) face.

Assignment of the Spectrum of Cu(acac)$_2$·quin. If the fact that the quinoline molecule (which lies approximately in the xz plane) does not conform to the twofold rotation about the z axis is ignored, the complex Cu(acac)$_2$·quin has approximate C_{2v} (z) symmetry (Figure 3). The ground state in this point group is $A_2(d_{xy})$. The only "d–d" transitions which can have nonzero intensity by a static electric dipole mechanism are $A_2(d_{xy}) \leftarrow B_1(d_{xz})$ in y polarization and $A_2(d_{xy}) \leftarrow B_2(d_{yz})$ in x polarization (the d orbitals comprising the major component of each molecular orbital are shown in parentheses). Using vibronic selection rules, all the transitions are formally allowed in each polarization.

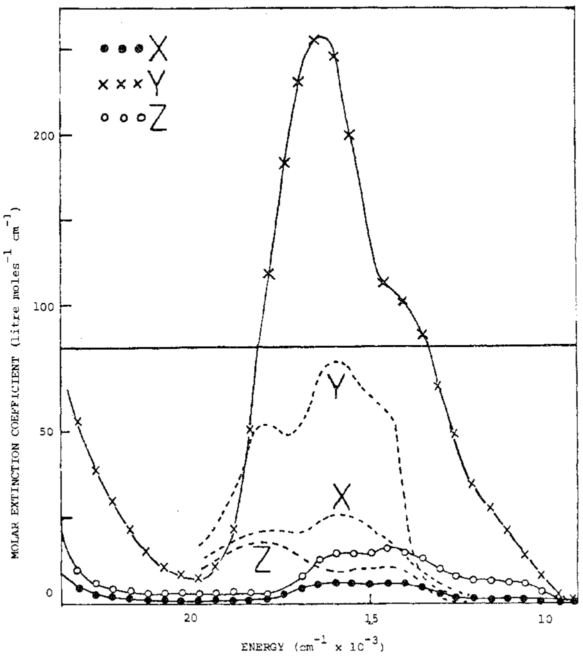

Figure 4. The molecular spectra of Cu(acac)$_2$·quin at 80°K (solid line). The spectrum of Cu(benzac)$_2$ at 4°K is shown for comparison (broken line; data from ref 6). Note the change in scale at ϵ 75 M^{-1} cm^{-1}.

The most striking feature of the molecular spectra of Cu(acac)$_2$·quin is the comparatively high intensity of the peak at 16,400 cm^{-1} in y polarization. This can confidently be assigned to the statically allowed transition $A_2(d_{xy}) \leftarrow B_1(d_{xz})$. The small temperature dependence of the peak (Figure 1B) is in agreement with the intensity having a static rather than a vibronic cause.

A second notable feature of the spectrum of Cu(acac)$_2$·quin when compared with that of a parent acetylacetonato complex is the peak at ~10,750 cm^{-1} in the x and z spectra. This can safely be assigned as $A_2(d_{xy}) \leftarrow A_1(d_{z^2})$ as this transition is expected to occur at comparatively low energy in the adduct because of the perturbing effect of the quinoline group (see following section).

The x spectrum of Cu(acac)$_2$·quin shows a pair of peaks at 16,000 and 14,300 cm^{-1} of comparable intensity and with extinction coefficients an order of magnitude less than that of the transition $A_2(d_{xy}) \leftarrow B_1(d_{xz})$ in y polarization. The fact that one transition does not have considerably greater intensity than each of the others is at first sight surprising, since the transition $A_2(d_{xy}) \leftarrow B_2(d_{yz})$ is statically allowed in x polarization. This feature will be discussed in a later section. However, the transition $A_2(d_{xy}) \leftarrow B_2(d_{yz})$ is unlikely to differ markedly from $A_2(d_{xy}) \leftarrow B_1(d_{xz})$ in energy, as each of the four bis(acetylacetonato)copper complexes which have been studied as single crystals by epr spectroscopy have been found to have g tensors with axial or near-axial symmetry.[8] This makes it highly probable that the peak at 16,000 cm^{-1} is $A_2(d_{xy}) \leftarrow B_2(d_{yz})$, with that at 14,300 cm^{-1} being $A_2(d_{xy}) \leftarrow A_1(d_{x^2-y^2})$. The alternative assignment is rendered even less likely by a comparison of the transition energies of Cu(acac)$_2$·quin with those of Cu(acac)$_2$ itself (see following section).

It is to be noted that the states A_1, B_1, and B_2 are connected by spin-orbit coupling. In particular, the close proximity of the peaks at 16,400 cm^{-1} in y polarization and at

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(6) M. A. Hitchman and R. L. Belford, *Inorg. Chem.*, 10, 984 (1971).

(7) A detailed discussion of the spectrum of Cu(benzac)$_2$ is given in ref 6.

(8) For a discussion of the reasoning behind this inference see M. A. Hitchman, *J. Chem. Soc., Faraday Trans. 2*, 846 (1972).

16,000 cm^{-1} in x polarization suggests that quite significant mixing of B_1 and B_2 must occur. This might well lead to a broadening or asymmetry of these peaks, due to the "borrowing" of y intensity by $A_2(d_{xy}) \leftarrow B_2(d_{yz})$ and x intensity by $A_2(d_{xy}) \leftarrow B_1(d_{xz})$. The spectra show little evidence of this, though this is hardly surprising in view of the breadth of the bands and the fact that they overlap significantly with the peaks due to neighboring transitions.

Comparison of the Transition Energies of Cu(acac)$_2$·quin with Those of Planar Bis(acetylacetonato) Complexes. The d-orbital energy sequence and consequent assignment of the electronic spectra of Cu(acac)$_2$ and related complexes have long been the subject of interest and controversy.[2,4,6,8-12] On the basis of simple molecular orbital calculations Cotton, *et al.*, tentatively proposed the sequence $d_{xy} \gg d_{z^2} > d_{yz} > d_{x^2-y^2} > d_{xz}$ in Cu[(t-$C_4H_9CO)_2CH]_2$(Cu(DPM)$_2$).[10,13] However, it has been noted that such an ordering is at variance with the axial symmetry of the g tensors of these complexes[8] and it seems likely that the transitions $d_{xy} \leftarrow d_{xz}$ and $d_{xy} \leftarrow d_{yz}$ give rise either to a single band or to neighboring bands in the electronic spectra of the compounds. Two other proposals have recently been put forward. Hathaway and coworkers have suggested the sequence $d_{xy} \gg d_{x^2-y^2} > d_{xz} \sim d_{yz} > d_{z^2}$,[11] while Belford, *et al.*,[2,6,12] and Hitchman[8] have proposed the ordering $d_{xy} \gg d_{z^2} > d_{x^2-y^2} > d_{xz} \sim d_{yz}$. The optical spectrum of Cu(acac)$_2$ has band maxima at 14,500, 15,600, and 18,000 cm^{-1} [14] (these values are virtually identical with those obtained from the spectrum of Cu(benzac)$_2$ shown in Figure 4; the crystal spectra of Cu(acac)$_2$ itself cannot be resolved into molecular spectra because of a crystal packing problem[14]). The d-orbital sequence of Hathaway assigns the 14,500 cm^{-1} transition as $d_{xy} \leftarrow d_{x^2-y^2}$, that at 15,600 cm^{-1} to $d_{xy} \leftarrow d_{xz}, d_{yz}$, and that at 18,000 cm^{-1} as $d_{xy} \leftarrow d_{z^2}$. Belford's assignment puts $d_{xy} \leftarrow d_{z^2}$ at 14,500 cm^{-1}, $d_{xy} \leftarrow d_{x^2-y^2}$ at 15,600 cm^{-1}, and $d_{xy} \leftarrow d_{xz}, d_{yz}$ at 18,000 cm^{-1}.

A comparison of the structure of Cu(acac)$_2$ with that of Cu(acac)$_2$·quin allows certain predictions to be made about the shifts in the energies of the "d-d" transitions to be expected on adduct formation. The Cu-O bond lengths in Cu(acac)$_2$ are each 1.92 Å and the metal ion lies in the plane of the four oxygen atoms; the nearest neighbors along the z axis are two carbon atoms at 3.09 Å.[14] In the quinoline adduct, each Cu-O bond has lengthened to 1.95 Å and the angle between the z axis and each Cu-O bond has increased from 90 to ~95°. Also, in Cu(acac)$_2$·quin the quinoline nitrogen atom forms a comparatively weak bond (2.36 Å) along the z axis. The net effect of these structural changes should be to lower the energy of all of the "d-d" transitions on going from Cu(acac)$_2$ to the quinoline adduct. The shift should be most marked for the transition $d_{xy} \leftarrow d_{z^2}$, followed by $d_{xy} \leftarrow d_{xz}, d_{yz}$, with $d_{xy} \leftarrow d_{x^2-y^2}$ being altered least.[2] A comparison of the transition energies shows that if the d-orbital sequence proposed by Hathaway, *et al.*, for the bis(acetylacetonato) complexes were correct, then adduct formation would be accompanied by a decrease of ~7500 cm^{-1} in $d_{xy} \leftarrow d_{z^2}$ with virtually no alteration in $d_{xy} \leftarrow d_{x^2-y^2}$ and a slight increase in energy of $d_{xy} \leftarrow d_{xz}$, d_{yz}, which disagrees with the above predictions. If the order suggested by Belford, *et al.*, is correct, the transition $d_{xy} \leftarrow d_{z^2}$ decreases by ~4000 cm^{-1} on adduct formation, while $d_{xy} \leftarrow d_{xz}, d_{yz}$ and $d_{xy} \leftarrow d_{x^2-y^2}$ decrease by ~1850 and ~1300 cm^{-1}, respectively, in agreement with the above prediction. It therefore seems highly probable that the orbital energy sequence in bis(acetylacetonato)copper complexes is that proposed by Belford, *et al.*, namely, $d_{xy} \gg d_{z^2} > d_{x^2-y^2} > d_{xz} \sim d_{yz}$.

The variation in the d-orbital energies on going from a planar, four-coordinate complex to a square-pyramidal adduct can be treated in a more quantitative fashion by means of the angular overlap model (AOM) developed by Schaffer and Jorgensen.[15,16] This simple molecular orbital model was recently used with some success to rationalize the energy levels observed for a series of tetragonal and square-pyramidal amine complexes of nickel chloride and bromide.[17] The AOM estimates the energy e by which a metal orbital is raised upon interaction with a ligand orbital as

$$e_\sigma = KS_\sigma^{\,2}, \quad e_\pi = KS_\pi^{\,2} \tag{1a}$$

where

$$K = H_L^{\,2}/(H_M - H_L) \tag{1b}$$

Here H_L and H_M are diagonal matrix elements of the ligand and metal orbitals, S is the diatomic overlap integral, and the σ and π subscripts designate the symmetry about the metal-ligand bond. The total energy of each orbital is obtained by summing the σ and π effects of all the ligands using the angular overlap matrix appropriate to the geometry of the complex. The constant K thus provides a way of parametrizing the bonding "power" of a ligand which, within the limitations of the model, is independent of the bond length or geometry of a complex. For a ligand such as the acetylacetonate anion, K can be separated into a σ component, K_σ, and two π components, $K_{\pi\parallel}$ and $K_{\pi\perp}$, where $K_{\pi\parallel}$ refers to the orbitals perpendicular to the plane of the chelate ring and $K_{\pi\perp}$ describes the effect of the orbitals lying in this plane. Once these constants have been estimated from the energy levels derived from the optical spectrum of one complex, the d-orbital energies in related complexes of known structure formed by the same ligand are readily calculated. It is to be noted that the method does not depend upon the *absolute* accuracy of any calculations; all that is required is that the *variation* in the overlap integrals as a function of bond distance and coordination geometry can be successfully represented.

The effects of changing the geometry of a complex from square planar to square pyramidal are conveniently discussed in terms of a model complex of C_{4v} symmetry in which the rhombic component to the ligand field is ignored. The virtual degeneracy of d_{xz} and d_{yz} and near-axial symmetry of the g tensors of these complexes suggest that this is a reasonable approximation as far as the *energies* of the orbitals are concerned. Clearly this approximation cannot be made when the *intensities* of the "d-d" transitions are considered. This distinction between the energy and intensity of the electronic transitions is not unreasonable, as orbital energies are determined by the total interaction of the d orbitals with

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(9) J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, 37, 1569 (1962).

(10) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, 6, 917 (1967).

(11) B. J. Hathaway, D. E. Billing, and R. J. Dudley, *J. Chem. Soc. A*, 1420 (1970).

(12) R. L. Belford and J. W. Carmichael Jr., *J. Chem. Phys.*, 46, 4515 (1967).

(13) F. A. Cotton, C. B. Harris, and J. J. Wise, *Inorg. Chem.*, 6, 909 (1967). Note that the x and y axes have been interchanged to agree with the notation used here.

(14) Structural details are quoted by T. S. Piper and R. L. Belford, *Mol. Phys.*, 5, 169 (1962).

(15) A discussion of this model and many original literature references are given by C. K. Jorgensen, "Modern Aspects of Ligand Field Theory," North-Holland Publishing Co., Amsterdam, 1970.

(16) C. E. Schaffer, *Struct. Bonding (Berlin)*, 5, 68 (1968).

(17) M. A. Hitchman, *Inorg. Chem.*, 11, 2387 (1972).

Table II. Diatomic Overlap Integrals between Ligand 2p and Copper(II) 3d Functions[a]

	Cu-N, A				Cu-O, A			
	3.2	2.5	2.3	2.1	1.92	1.94	1.96	1.98
S_σ	0.0158	0.04601	0.06181	0.07694	0.09236	0.09012	0.08808	0.08599
S_π	0.0030	0.01761	0.02818	0.04183	0.05039	0.04833	0.04625	0.04418

[a] Values taken from ref 20. The values at intermediate bond lengths may be obtained by interpolation.

the ligand σ and, to a lesser extent, π orbitals, while the band intensities are dominated by the comparatively minor ligand components of the relevant orbitals.[18] After application of the appropriate angular overlap matrix[16] the one-electron orbital energies for the model complex are given by

$$E(\mathrm{d}_{xy}) = 0.75(1 - \cos 2\theta)^2 e_\sigma(2) + (\sin^2 2\theta) e_{\pi\parallel}(2) \tag{2a}$$

$$E(\mathrm{d}_{x^2-y^2}) = 4(\sin^2 \theta) e_{\pi\perp}(2) \tag{2b}$$

$$E(\mathrm{d}_{z^2}) = e_\sigma(1) + 0.25[1 + 3(\cos 2\theta)]^2 e_\sigma(2) + 3(\sin^2 2\theta) e_{\pi\parallel}(2) \tag{2c}$$

$$E(\mathrm{d}_{xz}) = E(\mathrm{d}_{yz}) = e_\pi(1) + 2(\cos^2 \theta) e_{\pi\perp}(2) + 2(\cos^2 2\theta) e_{\pi\parallel}(2) + 1.5(\sin^2 2\theta) e_\sigma(2) \tag{2d}$$

Here, $e_\mathrm{i}(j)$ represents the energy by which the particular d-orbital is raised upon overlap with the orbital of symmetry i belonging to one ligand of type j ($j = 1$ refers to the axial ligand; $j = 2$, to the equatorial; θ defines the angle between the z axis and each in-plane metal-ligand bond; *i.e.*, $\theta = 90°$ for a planar complex and 95° for the quinoline adduct). Spin-orbit coupling has been neglected as no observable effects from this interaction have been reported for the molecules under consideration here. The bonding " power" of the acetylacetonate anion can be estimated by equating the differences between the d-orbital energies to the observed electronic transition energies of $\mathrm{Cu(acac)_2}$. Thus, $E(\mathrm{d}_{xy}) - E(\mathrm{d}_{x^2-y^2}) = 15{,}600\ \mathrm{cm}^{-1}$, $E(\mathrm{d}_{xy}) - E(\mathrm{d}_{z^2}) = 14{,}500\ \mathrm{cm}^{-1}$, and $E(\mathrm{d}_{xy}) - E(\mathrm{d}_{xz}) = 18{,}000\ \mathrm{cm}^{-1}$. Substitution of $\theta = 90°$ in eq 2a-d produces the values $e_\sigma = 7500\ \mathrm{cm}^{-1}$, $e_{\pi\parallel} = 2{,}250\ \mathrm{cm}^{-1}$, and $e_{\pi\perp} = 1725\ \mathrm{cm}^{-1}$. Here, the interaction with the π system of the two carbon atoms situated at 3.09 Å along the z axis of each molecule in solid $\mathrm{Cu(acac)_2}$ has been estimated to raise the energy of the d_{z^2} orbital by 500 cm^{-1}.[19,20] That is, $e_\sigma(1) = 500\ \mathrm{cm}^{-1}$ and $e_\pi(1) = 0$ in eq 2c. The diatomic overlap integrals between an oxygen 2p and copper(II) 3d orbitals have been calculated by Smith[20] and typical values used in the following discussion are listed in Table II. Substitution of the appropriate overlaps into eq 1a produces the values $K_\sigma = 0.879 \times 10^6\ \mathrm{cm}^{-1}$, $K_{\pi\parallel} = 0.852 \times 10^6\ \mathrm{cm}^{-1}$, and $K_{\pi\perp} = 0.653 \times 10^6\ \mathrm{cm}^{-1}$ for the bonding parameters of the acetylacetonate anion. These can now be used in eq 1 and 2 to calculate the d-orbital energies and consequent "d-d" transition energies in complexes with varying degrees of square-pyramidal distortion. As the ligand field strength of quinoline toward Cu(II) is unknown, the bonding parameters used for the axial ligand were those of $\mathrm{NH_3}$. The transition energies $\mathrm{d}_{xy} \leftarrow \mathrm{d}_{z^2} \approx 14{,}000\ \mathrm{cm}^{-1}$ and $\mathrm{d}_{xy} \leftarrow \mathrm{d}_{xz}, \mathrm{d}_{yz} \approx 18{,}000\ \mathrm{cm}^{-1}$ have been reported for several planar and near-planar complexes containing the $\mathrm{Cu(NH_3)_4}^{2+}$ chromophore,[21] yielding values of $e_\sigma = 7000\ \mathrm{cm}^{-1}$ and $e_\pi = 15{,}000\ \mathrm{cm}^{-1}$, and $K_\sigma = 0.946 \times 10^6\ \mathrm{cm}^{-1}$ and $K_\pi = 0.556 \times 10^6\ \mathrm{cm}^{-1}$ for the bonding parameters of the ammonia molecule toward copper(II) (the mean Cu-N bond length in these complexes is 2.0 Å). These values are likely to be fairly close to those of quinoline, as heterocyclic amines such as pyridine are known to have bonding parameters quite similar to those of ammonia.[17] Strictly speaking, the quinoline group should also be assigned two π-bonding parameters $K_{\pi\parallel}$ and $K_{\pi\perp}$. However, as this molecule is only weakly bound to the copper, the neglect of this asymmetry should not significantly affect the following discussion. The "d-d" transition energies calculated for a series of model complexes of varying degrees of square-pyramidal distortion are shown in Figure 5A, together with the Cu-O and Cu-N bond lengths and angle θ used to define each complex. In order to test the sensitivity of the model to the bonding "power" of the axial ligand the calculations were also performed with bonding parameters of $e_\sigma = 8000\ \mathrm{cm}^{-1}$, $e_\pi = 1750\ \mathrm{cm}^{-1}$ and $e_\sigma = 6000\ \mathrm{cm}^{-1}$, $e_\pi = 1300\ \mathrm{cm}^{-1}$ for this ligand. It can be seen that these alterations do not substantially change the overall manner in which the d-orbital energy differences vary.

The variation in the "d-d" transition energies estimated using the AOM is in agreement with the qualitative predictions outlined above. Each "d-d" transition moves to lower energy on adduct formation, with the shift being most marked for $\mathrm{d}_{xy} \leftarrow \mathrm{d}_{z^2}$, followed by $\mathrm{d}_{xy} \leftarrow \mathrm{d}_{xz}, \mathrm{d}_{yz}$, with $\mathrm{d}_{xy} \leftarrow \mathrm{d}_{x^2-y^2}$ being affected least. The transition energies observed for $\mathrm{Cu(acac)_2}$·quin are in good agreement with the values predicted by the AOM for a complex with this structure. This provides further evidence that the assignment of the spectrum of $\mathrm{Cu(acac)_2}$ used in these calculations is probably correct, as well as suggesting that the AOM provides a fairly realistic bonding model for treating the energy levels in complexes of this kind. The calculations were also performed using the assignment of the spectrum of $\mathrm{Cu(acac)_2}$ suggested by Hathaway, *et al.*,[11] and the results are shown in Figure 5B. The observed transition energies of $\mathrm{Cu(acac)_2}$·quin are then in poor agreement with the values calculated for this complex, supporting the conjecture that this assignment of the spectrum of $\mathrm{Cu(acac)_2}$ is incorrect.

Band Intensities of $\mathrm{Cu(acac)_2}$·quin. Perhaps the most unusual feature of the spectrum of $\mathrm{Cu(acac)_2}$·quin is its comparatively low intensity in x polarization. Despite the fact that the transition $\mathrm{A_2(d}_{xy}) \leftarrow \mathrm{B_2(d}_{yz})$ is formally allowed in this polarization, the x spectrum of the quinoline adduct is in fact less intense than that of the centrosymmetric bis(acetylacetonato) complexes (Figure 4). This suggests either that the distortion from $\mathrm{Cu(acac)_2}$ (D_{2h} symmetry) to $\mathrm{Cu(acac)_2}$·quin (C_{2v} symmetry) is inactive in inducing intensity into this transition or that the transition is so weak in the parent complex that even after intensification it does not dominate

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(18) This distinction is discussed further: M. A. Hitchman, *J. Chem. Soc. A*, 4 (1970); B. W. Moores and R. L. Belford, "Electron Spin Resonance of Metal Complexes," T. F. Yen, Ed., Plenum Press, New York, N. Y., 1969, p 17.

(19) This assumed that these carbon atoms have a similar bonding "power" to an oxygen atom of the acetylacetonate anion (or to an ammonia molecule). See ref 20 for the relevant overlaps; the calculated π interaction with the d_{xz} and d_{yz} orbitals is negligible. These estimates may well be quite inaccurate, but the effect is a small one and does not significantly alter the subsequent discussions.

(20) D. W. Smith, *J. Chem. Soc. A*, 1498 (1970); D. W. Smith, personal communication.

(21) B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).

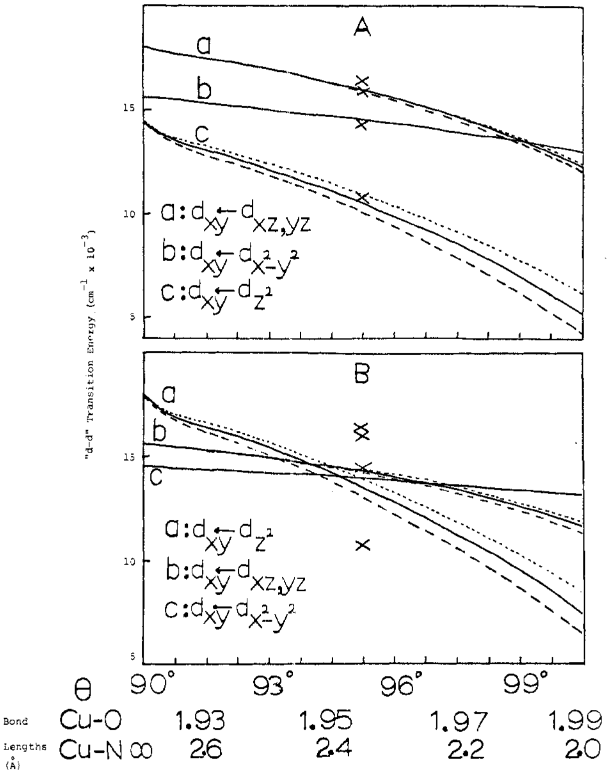

Figure 5. The variation of the "d–d" transition energies on the distortion of a β-ketoenolate–copper(II) complex from a planar to a square-pyramidal geometry. The full lines are for axial ligand bond parameters $K_\sigma = 0.946 \times 10^6$ cm^{-1}, $K_\parallel = 0.556 \times 10^6$ cm^{-1}; the dotted line, for $K_\sigma = 0.811 \times 10^6$ cm^{-1}, $K_\parallel = 0.519 \times 10^6$ cm^{-1}; the dashed line, for $K_\sigma = 1.08 \times 10^6$ cm^{-1}, $K_\parallel = 0.648 \times 10^6$ cm^{-1} (see text for the method used to calculate the transition energies). Diagram A is for an initial orbital sequence $d_{xy} >> d_{z^2} > d_{x^2-y^2} > d_{xz} = d_{yz}$, while B is for an initial orbital sequence of $d_{xy} >> d_{x^2-y^2} > d_{xz} = d_{yz} > d_{z^2}$. The experimental transition energies for Cu(acac)$_2$·quin are indicated by crosses.

the *x* spectrum. The likely explanation of this anomaly becomes apparent when the intensity mechanism proposed by Belford, *et al.*,[6,12] for the "d–d" transitions in copper-acetylacetonato complexes is considered.

The "d–d" spectra of the centrosymmetric bis(acetylacetonato)copper(II) complexes are unusual in that the *y* spectra are much more intense than those in *x* and *z* polarization (Figure 4). Belford has proposed[6,12] that the bulk of the intensity is derived from the admixture of a single charge-transfer state of B_{3u} symmetry into each excited d state, with all or most of the appropriate ungerade vibrational modes being active in this admixture. It was suggested that the *x* intensity is similarly derived from the admixture of an excited state of B_{2u} symmetry. The charge-transfer states involved in this process are supposedly those in which an electron is transferred from the B_{2u} and B_{3u} combinations of essentially nonbonding "lone-pair" electrons on the ligand oxygen atoms to the $B_{1g}(d_{xy})$ orbital. It is to be noted that these lone-pair orbitals are directed approximately along the *x* molecular axis (see Figure 3). If this mechanism is correct, then the intensity of each "d–d" transition is proportional to the magnitude of the matrix element $\langle\psi(\mathrm{d})\cdot|(\partial v/\partial Q)|\psi(\mathrm{ct})\rangle^2$ where $\psi(\mathrm{d})$ is the excited-state d wave function, $\psi(\mathrm{ct})$ is the wave function of the charge-transfer state, and $\partial v/\partial Q$ is the operator representing a vibrational distortion of the appropriate symmetry.[12,22] Thus, in order for intensity to be induced, the vibration must alter the overlap between the charge-transfer state and the excited d state in question. However, because of the spatial arrangement of the B_{2u} and B_{3u} states, only those d orbitals with components along the *x* axis can be so connected with these charge-transfer states. Thus, an ungerade vibration can admix the B_{2u} and B_{3u} states with every d orbital *except* d_{yz}.

The distortion which occurs on going from Cu(acac)$_2$ to Cu(acac)$_2$·quin consists of the addition of weak σ and π bonds along the *z* axis, together with the raising of the copper ion out of the plane of the four oxygen atoms. The latter alteration corresponds to a frozen out-of-plane bending mode (of B_{1u} symmetry) of the Cu(acac)$_2$ molecule. For the reasons given above, while this second distortion can admix the B_{3u} excited state with d_{xz}, it cannot be effective in mixing B_{2u} with d_{yz}. The fact that $d_{xy} \leftarrow d_{xz}$ undergoes a marked intensification when the *y* spectrum of Cu(acac)$_2$·quin is compared with those of planar bis(acetylacetonato)copper(II) complexes while the *x* spectrum does not is therefore in good agreement with the intensity mechanism proposed by Belford. Moreover, the above arguments suggest that the transition $d_{xy} \leftarrow d_{yz}$ should be inherently weak in all of the planar acetylacetonato complexes. The transitions $d_{xy} \leftarrow d_{xz}$ and $d_{xy} \leftarrow d_{yz}$ usually cannot be resolved in these compounds. However, for the complexes Cu(DPM)$_2$[10] and bis(3-phenylacetylacetonato)copper(II)[12] all four "d–d" transitions have been observed. Although the spectrum of Cu(DPM)$_2$ was only poorly resolved, for both of these complexes the transition at second to highest energy (which can be assigned as $d_{xy} \leftarrow d_{yz}$ by analogy with Cu(acac)$_2$·quin) occurs only as a weak shoulder, in agreement with the above arguments.

Conclusions

The present study suggests that the comparison of the optical spectra of compounds having closely related structures can be a powerful method of investigating the assignments and intensity mechanisms of the "d–d" spectra of transition metal complexes. The spectra of complexes having a slight distortion from a centrosymmetric structure are likely to be particularly valuable in this respect. It would also seem that the angular overlap model is a useful way of calculating the manner in which the d-orbital energies vary when a metal complex undergoes a structural alteration.

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Registry No. Cu(acac)$_2$-quin, 25948-21-4.

(22) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 186.