structure permits a ready rationalization for all of the available data.

Since retrodative nickel to sulfur electron donation is possible, this structure need exhibit little charge separation. Thus, the insensitivity of rate constants and activation parameters to the polarity of the medium is accommodated. The substantial, negative activation entropy is compatible with the restrictive geometry required for the hydrogen transfer to take place. Less compellingly, rationalization of the smallness of changes in rate constants resulting from variations in the mercaptan is possible. The greater the nucleophilic character of the mercaptan, the stronger should be the nickel–sulfur bond in the activated complex. Simultaneously, however, sulfur–hydrogen bond breaking should be rendered more difficult. Thus changing the nature of the mercaptan might be expected to have a small net effect on the stability of the transition state.

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The Single-Crystal Polarized Spectrum of Bis(benzoylacetonato)copper(II). Sources of Intensity[1a]

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The single-crystal polarized spectrum of bis(benzoylacetonato)copper(II) is reported. The "d–d" bands peak at {14.2}, {15.6}, and {18.1} kK, all are predominantly y polarized, and their temperature dependence and relative polarization suggest their assignment as $\{A_g(3z^2 - r^2)\}$, $\{A_g(x^2 - y^2)\}$, and $\{B_{2g}(xz), B_{3g}(yz)\} \leftarrow B_{1g}(xy)$, respectively. The relatively high intensity of the spectrum in y polarization in this and other similar complexes is apparently caused because the bulk of the intensity of the "d–d" bands is borrowed from a single charge-transfer state of B_{3u} symmetry. This B_{3u} state, which may lie at considerably lower energy than other u states which can mix with the d states, is probably that in which an electron is transferred from an orbital derived from "lone-pair" orbitals on the oxygen atoms to the $B_{1g}(xy)$ orbital on the copper ion.

Introduction

The sources of optical intensity as well as the identification of the various d–d transitions in copper β-keto-enolates and related systems have been subjects of considerable speculation and some controversy.[2–8] Early attempts to analyze the electronic spectrum of single crystals of copper acetylacetonate (Cu(acac)$_2$) in polarized light were rendered unsuccessful by the unfortunate mode of packing of molecules in the crystal.[4] Moreover, although most workers agreed that the transition intensities are gained by a vibronic mechanism, the manner in which this mechanism works to provide rather strongly polarized bands had not been understood.[4–7] Workers generally either resorted to an unfounded simplified assumption—conspicuously, the idea that only one or a few of the vibrational modes promote all the intensity—or else regarded the problem as being mired in hopeless complexity.

To overcome difficulties associated with the special crystal packing of Cu(acac)$_2$ and to probe details of the practical operation of the intensity mechanism, we undertook structure determination and temperature-dependent polarized spectroscopy on two copper β-keto-enolates—bis(3-phenyl-2,4-pentanedionato)copper(II) (Cu(3-phacac)$_2$) and bis(benzoylacetonato)copper(II) (Cu(benzac)$_2$). The spectral study on Cu(3-phacac)$_2$[2] revealed four "d–d" bands and showed them to be vibronically induced and single molecule in origin. The striking overall y polarization of all the bands suggested that the principal source of intensity was the lending (induced by several odd vibrations of various symmetry types) of some of the intensity of a single y-polarized charge-transfer band ($B_{3u} \leftarrow B_{1g}$ in D_{2h}) to each of the d–d bands. The temperature dependence of the spectra implied that the two lower-energy bands were probably $A_g(x^2 - y^2, 3z^2 - r^2) \leftarrow B_{1g}(xy)$ and the two higher energy bands $B_{2g}(xz)$ and $B_{3g}(yz) \leftarrow B_{1g}(xy)$. The predominance of y polarization in the spectra of two other copper β-keto-enolates has been demonstrated,[6] but without temperature dependence data the mechanism and energy level assignments had to be quite speculative. Some experimental problems with the Cu(3-phacac)$_2$ crystals[2] had led to unreliable features (no-

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[1] (a) Supported by ARPA, SD-131, through the Materials Research Laboratory, by an NSF grant, and by the University of Illinois Graduate Research Board. (b) ICI Postdoctoral Fellow at Oxford, 1968–1970.

[2] R. L. Belford and J. W. Carmichael Jr., *J. Chem. Phys.*, **46**, 4515 (1967); this reference contains a discussion of the various theories which have been proposed to explain the electronic spectra of copper β-diketonate complexes and has several references to prior work.

[3] D. P. Graddon, *J. Inorg. Nucl. Chem.*, **14**, 161 (1960).

[4] J. Ferguson, *J. Chem. Phys.*, **34**, 1609 (1961); T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962); J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, **34**, 1569 (1969).

[5] (a) C. Dijkgraaf, *Theoret. Chim. Acta*, **3**, 38 (1965); (b) R. L. Belford and G. G. Belford, *ibid.*, **3**, 465 (1965); (c) J. Ferguson, *ibid.*, **3**, 387 (1965).

[6] F. A. Cotton and J. Wise, *Inorg. Chem.*, **6**, 917 (1967); B. J. Hathaway, D. E. Billing, and R. J. Dudley, *J. Chem. Soc. A*, 1420 (1970).

[7] H. C. Allen Jr., *J. Chem. Phys.*, **45**, 553 (1966).

[8] G. N. La Mar, *Acta Chem. Scand.*, **20**, 1359 (1966).

tably, a highly suspect x spectrum). The spectra reported here for Cu(benzac)$_2$ do not suffer from the same difficulties and generally support the results of the Cu(3-phacac)$_2$ study. Here we describe the experiments, review the salient features of the intensity mechanism and its rough quantitative application to this case, draw conclusions about both the sources of intensity and the probable band assignments, and offer an opinion regarding the current state of knowledge and prospects for its improvement in this area.

Experimental Section

Cu(benzac)$_2$ was prepared as described previously.[9] Crystals suitable for spectroscopic measurements were grown by slow crystallization from acetonitrile. The crystals formed as blue needles with the faces (011) etc. well developed. These faces had extinction directions at 67 and −23° to the +a axis, the positive rotation being toward the +c axis. Spectra were measured over a temperature range down to 8°K (±4°K) on two crystals, with the electric vector along each of these extinction directions. As no other crystal faces were well developed, the (001) face was obtained by mounting crystals on their edges in glue upon glass slides with the c^* axis vertical. An optical goniometer was used to ensure that the orientation of the crystals was correct. These crystals were ground ⊥ to the c^* direction and then removed and placed upon this (001) face. Two crystals having (001) faces were successfully obtained in this manner and these were found to have essentially identical spectra, after correction for differences in thickness. The spectrum ‖ and ⊥ to the b axis of one of these crystals was measured down to 8°K.

The spectra were measured with a Cary 14RI spectrophotometer fitted with a high-intensity light source; an Air Products Cryotip AC3L-110 dewar (Joule-Thomson refrigerator) was used to cool the crystals. The temperature was measured by two iron-gold thermocouples, one of which was mounted next to the crystal while the other was embedded in the block surrounding the helium reservoir in the dewar. The crystals were mounted over holes cut in aluminum disks and secured with 1 drop of General Electric lacquer, No. 7031.

Results and Discussion

Molecular Coordinate System.—In order to resolve the measured spectra into their molecular components, it is necessary to define a molecular coordinate system. The molecular structure found[9] for Cu(benzac)$_2$ and the chosen coordinate system are shown in Figure 1.

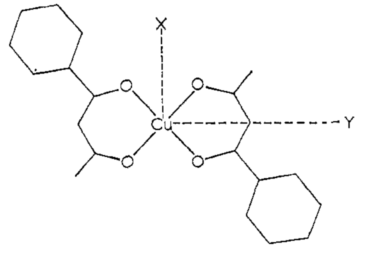

Figure 1.—The molecular structure and coordinate system of bis(benzoylacetonato)copper(II). The z axis is perpendicular to x and y.

The true symmetry of the complex is close to C_{2h}. However, the similarity of the electronic spectrum to those of Cu(acac)$_2$ and Cu(3-phacac)$_2$ suggests that the *effective spectroscopic symmetry* is close to D_{2h}. This is also suggested by the epr parameters of ∼0.5% of Cu^{2+} diluted into Pd(benzac)$_2$. The in-plane g axes ($g_\perp$ axes) were found[10] to lie very close to the axes as defined in Figure 1 although there are good theoretical reasons[11] for believing that any along-the-bonds perturbation to the ligand field should rotate the $g_\perp$ axes significantly toward the Cu–O bond directions. The following discussion therefore assumes a D_{2h} point group for Cu(benzac)$_2$. Note that all the molecules are on centrosymmetric crystal sites.

Spectra Referred to Molecular Axes.—The measured spectra for the two polarization directions of each face at room temperature and 8°K are shown in Figures 2 and 3. The molecular projections made by a unit electric vector for each spectrum are given in Table I.

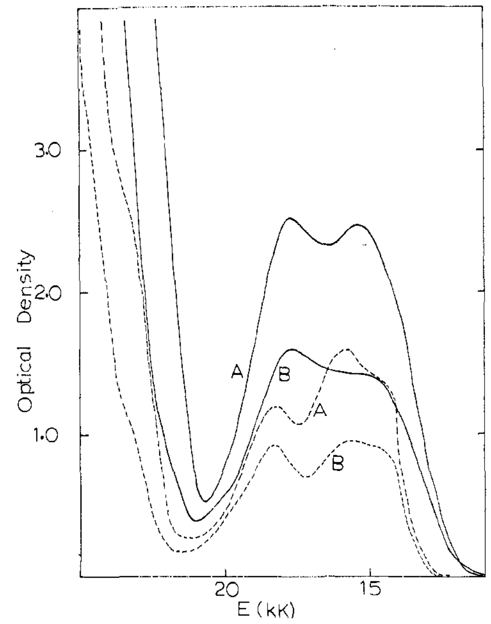

Figure 2.—The room-temperature (solid line) and 8°K (broken line) spectra of the (011) face of bis(benzoylacetonato)copper(II) with the electric vector at (A) 67° to the a axis and (B) −23° to the a axis, the positive rotation being toward the positive c axis.

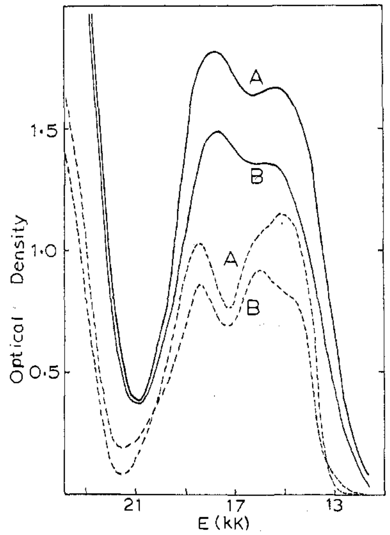

Figure 3.—The room-temperature (solid line) and 8°K (broken line) spectra of the (001) face of bis(benzoylacetonato)copper(II) with the electric vector (A) ⊥ to the b axis and (B) ‖ to the b axis.

The spectra were converted into molecular extinction coefficients in the following manner. For each face,

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[9] P. K. Hon, C. E. Pfluger, and R. L. Belford, *Inorg. Chem.*, **5**, 516 (1966).

[10] M. A. Hitchman and R. L. Belford in "Electron Spin Resonance of Metal Chelates," T. F. Yen, Ed., Plenum Press, New York, N. Y., 1969, p 97.

[11] M. A. Hitchman, C. D. Olson, and R. L. Belford, *J. Chem. Phys.*, **50**, 1195 (1969).

TABLE I

THE MOLECULAR PROJECTIONS FOR A UNIT ELECTRIC VECTOR ALONG THE EXTINCTION DIRECTIONS OF THE CRYSTAL FACES OF $Cu(benzac)_2$

i	Extinction direction, r_i	$\cos^2(x, r_i)$	$\cos^2(y, r_i)$	$\cos^2(z, r_i)$
1	(011), 67°[a]	0.4755	0.4543	0.0703
2	(011), −23°[a]	0.0904	0.2576	0.6520
3	(001), $\parallel b$	0.6341	0.1924	0.1735
4	(001), $\perp b$	0.0001	0.4875	0.5124

[a] See the Experimental Section for a precise definition of these extinction directions. The optical density corresponding to extinction direction i is denoted D_i.

the ratio of the optical densities at any wavelength can be equated to the ratio of the sum of the molecular projections squared. Thus, at any wavelength, two equations obtain (see Table I)

$$0.4755\epsilon_x + 0.4543\epsilon_y + 0.0703\epsilon_z = (D_1/D_2)(0.0904\epsilon_x + 0.2576\epsilon_y + 0.6520\epsilon_z)$$

$$0.6341\epsilon_x + 0.1924\epsilon_y + 0.1735\epsilon_z = (D_3/D_4)(0.0001\epsilon_x + 0.4875\epsilon_y + 0.5124\epsilon_z)$$

These equations are solved to give $\epsilon_x : \epsilon_y : \epsilon_z$, and these ratios are substituted into the equation $0.4755\epsilon_x + 0.4543\epsilon_y + 0.0703\epsilon_z = D_1/(cl)$, where c is the molar concentration of copper ions and l is the crystal thickness (in this case 0.009 ± 0.0008 cm), to convert the molecular spectra into approximate extinction coefficient units; this process is repeated for each of many wavelengths. This method of analysis has the great advantage that the ratios $\epsilon_x : \epsilon_y : \epsilon_z$ are calculated independently of the crystal thickness, which often can be measured only very approximately. Thus, while the *scale* of the molecular spectra is known only to the accuracy with which the crystal *thickness* can be measured, the *dichroic ratios* are known to the accuracy with which the *spectra* are measured (which is generally much higher) provided that the relevant equations are not ill conditioned.[12]

The spectra at 8°K referred to molecular axes are shown in Figure 4. As in $Cu(3\text{-}phacac)_2$[2] and also in the similar complex bis(dipivaloylmethanato)copper(II) ($Cu(DPM)_2$)[6] (note: the x and y axes in ref 6 are interchanged compared with those used in ref 2 and in the present work) the most striking feature of the spectrum of $Cu(benzac)_2$ is the relatively high intensity of the "d–d" bands in y polarization.

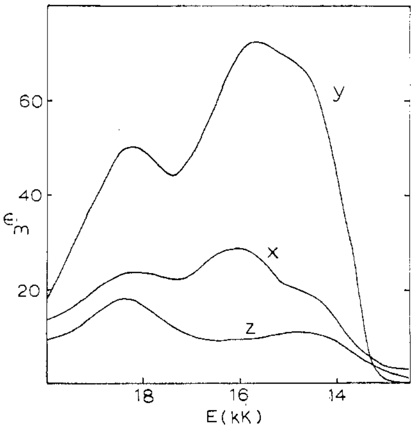

Figure 4.—The spectrum of bis(benzoylacetonato)copper(II) at 8°K referred to molecular axes.

The Overall y Polarization of the "d–d" Bands.—Within the framework of a vibronic mechanism[13] operating only on the excited d states, the intensity of a "d–d" transition $\psi_2 \leftarrow \psi_{1g}$ in r polarization for some distorted configuration of nuclei depends on the magnitude of $\Sigma_i|c_i\langle\psi_{iu}|r|\psi_{1g}\rangle|^2$. Here c_i is the coefficient representing the degree to which ψ_{iu} is mixed into ψ_2, ψ_{1g} is the lowest *gerade* (ground) state, and ψ_2 is the excited d state containing a small admixture of u states. First-order perturbation theory for small distortions gives $c_i = \Sigma_Q Q\langle\psi_{iu}|\partial V/\partial Q|\psi_{2g}\rangle/(E(\psi_{iu}) - E(\psi_{2g}))$ where ψ_{2g} is the pure g state, V is the energy of the electrons in the field of the nuclei, and Q is a normal coordinate of the molecule. The group theoretical criteria for a "d–d" transition to have nonzero intensity in r polarization by action of a Q-type distortion and an iu perturbing state are therefore that $\Gamma_{2g}\Gamma_Q\Gamma_{iu}^*$ and $\Gamma_{1g}\Gamma_r\cdot\Gamma_{iu}^*$ each contains A_{1g}. Assuming that for each Q some perturbing u state is available to be mixed into the excited d state, one can combine these equations to give the well-known yes-or-no selection rule that $\Gamma_{1g}^*\Gamma_{2g}\cdot\Gamma_r^*\Gamma_Q$ must contain A_{1g} for the "d–d" transition to be allowed.[5b] Also, as both r and $\partial V/\partial Q$ are one-electron operators, ψ_{iu} must be reached from both ψ_{1g} and ψ_{2g} by essentially single-electron excitations.[2,14]

Application of this simple group theoretical selection rule to Cu^{2+} in D_{2h} with a $B_{1g}(xy)$ ground state shows that all the "d–d" transitions are allowed in every polarization (Table II). Moreover each transition is allowed in each polarization by a different normal mode, so that the predominance of y polarization cannot be explained by the greater activity of a single vibrational type in producing intensity. However, it is apparent that a single polarization (*i.e.*, that of the $\psi_{ju} \leftarrow \psi_{1g}$ transition) will dominate the "d–d" spectrum if it is predominantly a single charge transfer state ψ_{ju} which is vibrationally mixed into the various excited d states. The symmetry of the perturbing state ψ_{iu} needed to produce y polarization is B_{3u}. As the states produced by both ligand←metal and ligand←ligand transitions differ from most or all of the d states by two electrons, it is likely that this B_{3u} state is produced by a metal←ligand charge-transfer transition. In like fashion, the x and z polarizations of the "d–d" bands are probably produced by admixtures of B_{2u} and A_u metal←ligand charge-transfer states, respectively, into the excited d states.

TABLE II

SYMMETRY OF THE VIBRATIONS ALLOWING TRANSITIONS FROM THE $B_{1g}(xy)$ GROUND STATE TO EACH EXCITED d STATE IN MOLECULAR POLARIZATIONS x, y, AND z

Excited d state	x	y	z
$B_{2g}(xz)$	α_u	β_{1u}	β_{2u}
$B_{3g}(yz)$	β_{1u}	α_u	β_{3u}
$A_g(x^2 - y^2, 3z^2 - r^2)$	β_{2u}	β_{3u}	α_u

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(12) Ill-conditioned equations are commonly discussed in elementary numerical analysis texts. See, for example, S. D. Conte, "Elementary Numerical Analysis," McGraw-Hill, New York, N. Y., 1965, p 164 ff.

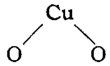
(13) For a discussion of the vibronic mechanism see, for example, C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 180; W. A. Yeranos, Ph.D. Thesis, University of Illinois, 1964; ref 5b.

(14) These restrictions have been used to explain the relative intensities of "d–d" bands in hexahalide complexes: R. F. Fenske, *J. Amer. Chem. Soc.*, **89**, 252 (1967).

It was suggested[2] that the B_{3u} and B_{2u} ligand orbitals involved in these charge-transfer transitions were probably combinations of "lone-pair" orbitals on the oxygen atoms. Some support for this idea is provided by a recent extended Hückel calculation performed[15] on a model copper keto–enolate complex. This calculation, which was adjusted to give fair agreement with both epr parameters and positions of the "d–d" bands, suggested that the highest filled orbitals of B_{3u} and B_{2u} symmetry were those derived essentially from oxygen "lone-pair" orbitals, and the transitions $B_{3u} \leftarrow B_{1g}(xy)$ and $B_{2u} \leftarrow B_{1g}(xy)$ were estimated to lie at 21.5 and 42.4 kK, respectively, with approximately equal oscillator strengths. The transition $A_u \leftarrow B_{1g}(xy)$ was estimated to lie at ~70 kK. The uv spectra of copper acetylacetonate and related complexes in inert solvents have been measured by several workers.[16–18] The principal constituents of these spectra are two intense bands at ~30 and ~40 kK, the former often being split into several components. On the basis of the mo calculation Cotton, *et al.*,[15] assigned the band at ~40 kK to the transition $B_{2u} \leftarrow B_{1g}(xy)$ and suggested that the transition $B_{3u} \leftarrow B_{1g}(xy)$ contributed to the broad absorption at ~30 kK. Moreover, although the measurements were hampered by the high intensity of the bands, Wise found[19] some evidence that a band at ~26 kK in the crystal spectrum of $CuDPM_2$ was y polarized. The approximate ratio of the transition moments of the "d–d" bands in the different polarizations is proportional to $(1/E_u - E_g)^2$ where E_u is the energy of the appropriate u charge-transfer state, and E_g is that of the excited d state, both relative to the ground state. If it is assumed that $B_{3u} \leftarrow B_{1g}$ is at ~28 kK, $B_{2u} \leftarrow B_{1g}$ at ~40 kK, and $A_u \leftarrow B_{1g}$ at ~70 kK, with these transitions having equal oscillator strengths, and if the average energy of the "d–d" transitions is taken as 16.5 kK, then the ratio calculated for $y:x:z$ is 1.0:0.24:0.05. Thus, this rough approximation does yield the experimentally correct ordering for the polarizations and also the approximate magnitude of $y:x$ (Figure 4).

Possible Ordering of the d Levels and Temperature Dependence of the Spectra.—The positions of the three "d–d" bands in Cu(benzac)$_2$ at 14.2, 15.6, and 18.1 kK (the mean positions of the bands at room temperature and helium) are very similar to those in Cu(acac)$_2$ (14.5, 16.3, and 18.0 kK).[4] The near equality of the $g_\perp$ values of Cu(benzac)$_2$ ($g_x = 2.049$, $g_y = 2.048$)[10] suggests that $|xz\rangle$ and $|yz\rangle$ are almost degenerate ($E(yz) - E(xz) \approx 0.5$ kK if the orbital coefficients of the two orbitals are identical), so that it is likely that one of the bands in the electronic spectrum is produced by the transitions to these two levels.

The only marked *relative* polarization of the bands in Cu(benzac)$_2$ is seen in the particularly low intensity around 15.6 kK in z polarization.[20] The selection rules in D_{2h} tell us that each transition is allowed in every polarization. However, in D_{4h} symmetry one transition is forbidden in one polarization, namely, $B_{2g}(xy) \leftrightarrow B_{1g}(x^2 - y^2)$ in z polarization. It therefore seems likely that if the effective point group as far as the vibronic perturbation is concerned does not depart too much from D_{4h}, the transition $A_g(x^2 - y^2) \leftarrow B_{1g}(xy)$ (in D_{2h}) in z polarization may be considerably weaker than the other transitions. It can be noted that the A_u state from which the z intensity is borrowed is probably that in which an electron has been transferred from a filled π orbital on the ligand to the $B_{1g}(xy)$ orbital on the copper. Unlike the nonbonding and antibonding orbitals of the σ system, the local symmetry of the four p_π orbitals on the oxygen atoms (as distinct from the ligand π-system molecular orbital in which they participate) is very close to D_{4h} (the angle



containing the chelate ring is 93°[9]). Thus, although the selection rules do not provide irrefutable evidence on this, there is an indication that the band at 15.6 kK is due to the transition $A_g(x^2 - y^2) \leftarrow B_{1g}(xy)$.

The temperature dependence of the spectrum yields further information on the band assignments. The x, y, and z spectra resolved into Gaussian components[21] at room temperature and 8°K are shown in Figure 5. The nature of the u-normal modes of different symmetry type is given in Table III. The simplest theory[22] predicts that the temperature dependence of a vibronically allowed band is given by $f_T = f_0 \coth(h\nu/2kT)$ where ν is the frequency of the perturbing vibration. The approximate "average" frequencies of the perturbing vibrations for the bands in each polarization calculated from this equation are given in Table IV. From Tables II and III it can be seen that the transitions $\{B_{2g}(xz), B_{3g}(yz)\} \leftarrow B_{1g}(xy)$ are allowed by in-plane stretches and bends in z polarization and out-of-plane bends in x and y polarization, while $A_g(x^2 - y^2, 3z^2 - r^2) \leftarrow B_{1g}(xy)$ are allowed by in-plane stretches and bends in x and y polarization and out-of-plane bends in z polarization. Table IV shows that in x and y polarization the bands at 14.2 and 15.6 kK are allowed by higher

TABLE III

Ungerade VIBRATIONAL MODES OF THE D_{2h} SQUARE-PLANAR COMPLEX

Type of vibration	Representation in D_{2h}
Stretch	β_{2u}, β_{3u}
In-plane bend	β_{2u}, β_{3u}
Out-of-plane bend	β_{1u}, α_u

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(15) F. A. Cotton, C. B. Harris, and J. J. Wise, *Inorg. Chem.*, **6**, 909 (1967).

(16) R L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

(17) R. H. Holm and F. A. Cotton, *J. Amer. Chem. Soc.*, **80**, 5658 (1958).

(18) J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

(19) J. J. Wise, Ph.D. Thesis, Massachusetts Institute of Technology, 1965.

(20) A strong word of caution is in order with respect to the arguments given in this section and indeed with respect to similar arguments in other work. For one point, we notice in examining Figure 4 that the middle band (15.6 kK) *seems* much weaker, relative to the other two bands in the z- than in the x- or y-polarized spectra. However, we also notice that a breakdown into possible approximate components (Figure 5) yields an extraordinarily broad low-energy component in the z spectrum; this fact arouses suspicion that some intensity of the 15.6-kK band has been artificially ascribed to the low-energy band in the breakdown of the z spectrum. For another point, we notice that the z-polarized spectrum of Cu(3-phacac)$_2$[9] displays different behavior, the third rather than second band being weak or absent in that case. To be sure, there were worse experimental difficulties with Cu(3-phacac)$_2$, leading to x and z spectra of low confidence level, but the apparent conflict must further alert us to be wary of arguments based on a weak feature of the already weak (and thus least reliable) z spectrum.

(21) A computer program written by Mr. B. Bird of the Inorganic Chemistry Laboratory, Oxford, England, was used to perform this Gaussian analysis. The true component shapes are certainly skewed, but we may hope that the simplified Gaussian components will behave semiquantitatively the same as the true components.

(22) A. D. Liehr and C. J. Ballhausen, *Phys. Rev.*, **106**, 1161 (1957).

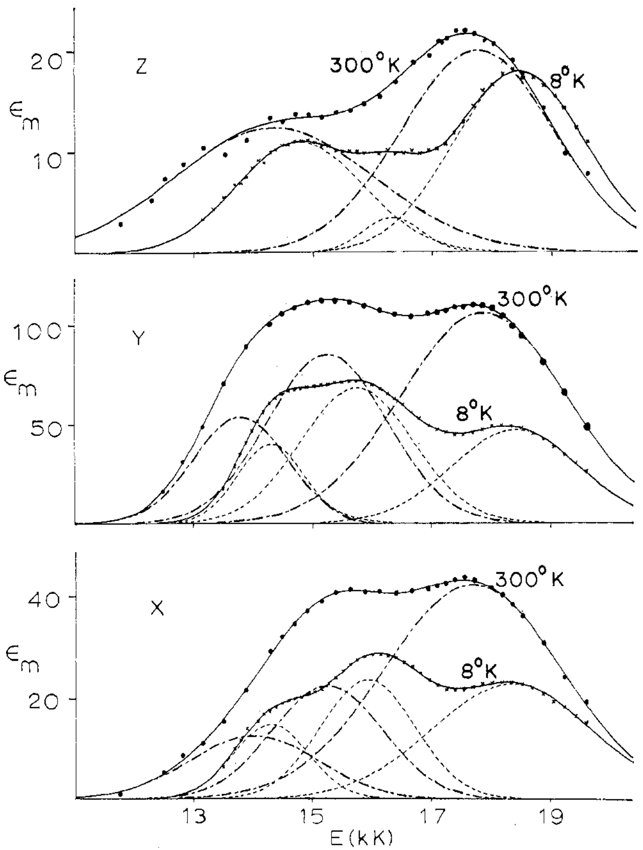

Figure 5.—The *x*, *y*, and *z* spectra of bis(benzoylacetonato)-copper(II) at room temperature and 8°K resolved into Gaussian components. Experimental points are shown as solid dots (300°K) and crosses (8°K). Components are shown as — — — for 300°K and - - - for 8°K. Sums of the components are shown as solid lines.

Table IV

Approximate "Average" Frequencies of the Perturbing Vibrations for the Bands in Molecular Polarizations *x*, *y*, and *z*

Band max, kK	Freq, K		
	x	*y*	*z*
14.2	340	240	250
15.6	590	380	*a*
18.1	220	150	420

[a] This band could not be resolved in the room-temperature spectrum.

energy vibrations than that at 18.1 kK, while in *z* polarization the band at 18.1 kK is allowed by higher energy vibrations than is that at 14.2 kK. As in-plane stretches and bends are expected to lie at considerably higher energies than out-of-plane bends, this behavior is consistent with assignments of the band at 18.1 kK to $\{B_{2g}(xz), B_{3g}(yz)\} \leftarrow B_{1g}(xy)$ and those at 14.2 and 15.6 kK to $A_g(3z^2 - r^2, x^2 - y^2) \leftarrow B_{1g}(xy)$. This ordering of the d levels is the same as that suggested for Cu(3-phacac)$_2$ by the temperature dependence of its spectrum.[2]

If, as we have discussed above,[20] the band at 15.6 kK can be assigned as $A_g(x^2 - y^2) \leftarrow B_{1g}(xy)$, the epr parameters found for Cu(benzac)$_2$ can be used to calculate approximate molecular orbital (mo) coefficients for the $|xz\rangle$, $|yz\rangle$ orbitals from the two possible remaining band assignments for the transitions to these levels. Taking $|xz\rangle$ and $|yz\rangle$ to be effectively degenerate, each with mo coefficient β, and using the standard expressions (neglecting overlap between metal and ligand orbitals for the g and hyperfine values[10]) we find that if $\{B_{2g}(xz), B_{3g}(yz)\} \leftarrow B_{1g}(xy) = 14.2$ kK, $\beta^2 \approx 0.52$ while if $\{B_{2g}(xz), B_{3g}(yz)\} \leftarrow B_{1g}(xy) = 18.1$ kK, $\beta^2 \approx 0.67$. In this approximation the squares of the mo coefficients of $|xy\rangle$ and $|x^2 - y^2\rangle$ are 0.76 and 0.77, respectively (with the D_{2h} symmetry axes defining these orbitals). Although these coefficients certainly are *not* to be considered as accurate bonding parameters, they probably do give a rough estimate of the relative covalency of the orbitals, and it is apparent that, in agreement with the suggestion of the temperature dependence of the bands, the assignment of $\{B_{2g}(xz), B_{3g}(yz)\} \leftarrow B_{1g}(xy)$ at 18.1 kK gives a more reasonable value for the mo coefficient than its assignment at 14.2 kK.

A Comment on Assignments.—Hathaway, *et al.*,[6] recently published polarized spectra of bis(3-methylpentane-2,4-dionato)copper. Notwithstanding an untrustworthy experimental technique,[23] they obtained spectra which appear satisfactory and which are rather similar to the spectra of Cu(benzac)$_2$ which we report here, but they made quite different assignments. The essential reason for the difference is that we have based our identifications upon the observed temperature dependences of the component bands, whereas Hathaway, *et al.*, had only room-temperature spectra and therefore had to make some simplifying assumptions about the sources of intensity. They chose to assume that vibrational modes of various symmetries can effectively induce *y* intensity but that the bulk of the *x* and *z* intensity is induced by a single mode, which they took to be α_u. We see no compelling justification for this *ad hoc* assumption or for the supporting arguments cited by Hathaway, *et al.*

Conclusion

The way in which the vibronic mechanism works to provide moderate-to-strong polarization of the d–d bands in copper bis(keto-enolates) now seems well established. The one-perturbing-mode model for vibronic intensity is untenable. Instead, several vibrational modes are active in mixing just a few strong ligand-to-metal electron-transfer states into the upper d states. The dominant polarization (*y* in all the cases studied) is most likely that of the charge-transfer band of lowest frequency. Perhaps new experiments designed to probe the polarization properties of the intense ultraviolet bands or visible polarized spectroscopy of chelates cleverly tailored to vary the relative properties of the B_{3u}, B_{2u}, and A_u charge-transfer states might be helpful, but in our opinion further studies on centric copper β-keto–enolates such as this paper reports are likely to contribute little more than confirmation of the established pattern.

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[23] The technique employed polarized light with the electric vector not parallel to crystal faces. The spectra are therefore subject to distortional effects of reflection, refraction, and depolarization. These effects are minimized by illumination at normal incidence with light polarized along a crystal extinction direction.