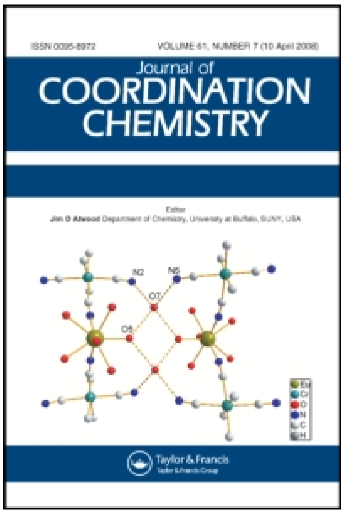

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POLARIZED CRYSTAL SPECTRA OF ACENTRIC COPPER COMPOUNDS. THREE CRYSTAL FORMS OF ETHYLENEBISACETYLACETONEIMINATO-COPPER(II)†

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Polarized absorption spectra on one face of single crystals of anhydrate, hemihydrate and monohydrate crystal modifications of N,N′-ethylene*bis*(acetylacetoneiminato)copper(II) are reported. Polarized spectra of the anhydrous form from 4° K to 300° K are analyzed with the aid of an oriented-gas model. Absorptions at about 16.4 kK and 18.4 kK are ascribed to the mainly "*d–d*" transitions $A_1(x^2-y^2) \leftarrow B_2(xy)$ and $A_1(3z^2-r^2) \leftarrow B_2(xy)$ which are electronically allowed along y in $C_{2v}(x)$. Vibronic components may also contribute to these transitions, as suggested by the temperature dependence of the integrated intensity along the x- and/or z-axes of the anhydrate in the 15 to 19 kK region. Similar methods and a comparison with the spectral frequencies of the monohydrate crystal suggest, but with less certainty, that the absorption at about 22.5 kK is not primarily associated with the "*d–d*" transitions. Crystal exciton effects for the anhydrate and hemihydrate spectra are also considered. Model calculations show a marginal possibility that excitons affect the polarization ratios to a measurable extent, but the main result that the molecular absorptions are mainly y-polarized is unchanged by consideration of intermolecular interactions.

I INTRODUCTION

In centrosymmetric copper chelates[1–6] the temperature dependence of polarized visible and near infrared absorption spectra has demonstrated that the *d*-electron levels are vibrationally mixed with certain *ungerade* excited electronic levels. Solution spectra of similar noncentrosymmetric chelates, in which *g*, *u* mixing can occur without the need for vibrations, were found[7,8] to be two to five times more intense than those of the centrosymmetric ones.

To provide more detailed information about the increased optical absorptivity associated with removal of the center of symmetry, we report here polarized crystal spectra of an acentric chelate, *N,N′*-ethylene*bis*(acetylacetoneiminato)Cu(II), in three different crystalline modifications.

The data are interpreted with reasonable consistency within the usual oriented gas model. Nevertheless, because of the possibility that crystal excitons can affect the polarization ratios for statically allowed transitions we also summarize the results of an extensive computation on crystal exciton intensity transfer. The calculations suggest that, in some copper complex crystals, exciton intensity transfer may be competitive with vibronic intensity for certain polarizations in the visible spectrum.

II EXPERIMENTAL

A Samples

N,N′-Ethylene*bis*(acetylacetoneiminato)Cu(II)[9] was prepared as previously described.[10] We studied three crystal forms—the anhydrate with space group $P2_1/c$,[11] the hemihydrate with space group *Pbcn*,[12] and the monohydrate with space group $P2_1/a$.[13,14] Anhydrate crystals with plate face (100) were slowly grown from a covered solution of the compound in 1 liter of petroleum ether (b.p., 30°–60° C) kept just below the boiling point. Slow evaporation of 1% and 20% aqueous ethanol solutions of the compound in flat dishes yielded rectangularly-shaped crystals of the hemihydrate with prominent face (001) and hexagonally-shaped

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crystals of the monohydrate with plate face (100), respectively. Efforts to obtain other faces with adequate area by slicing or growing in other solvents were unsuccessful.

Sufficiently thin single crystals of the hydrated forms were occasionally obtained by the above crystallization procedures but the anhydrate crystals required cleavage parallel to (100) for thicknesses of 30–80 μ. Thicknesses, measured by the micrometer eyepiece of a microscope, were precise to about 10%. There are thus uncertainties of about 10% in the scale of the reported crystal extinction coefficients.

The unit cell dimensions and space groups of the anhydrate and hemihydrate forms, as determined by X-ray diffraction methods conformed to those of the structural determinations.[11, 12] Precession camera, two-circle goniometer and rotating-eyepiece microscope data were used to find the crystallographic axes, interplanar angles and Miller indices of the faces used in the crystal spectra. The extinction directions of these crystals as viewed through crossed polarizers were perpendicular and parallel to the **b**-axis.

Crystals were fastened over a hole cut in an aluminum disc by pulling a similarly cut disc of black onionskin paper tautly over the edge of the crystal and gluing the paper to the aluminum with G.E. 7031 lacquer. These mountings were examined under a microscope before and after spectra were taken to insure that no light leaks were present. Base lines were determined after removing the crystal from the mounting.

Samples for unoriented spectra were obtained from finely ground anhydrate crystals treated in three alternative ways: mixed with nujol, mixed with spectroscopic KBr and pressed into fairly transparent discs, or dissolved in spectral grade chloroform. Base lines of these media were also determined.

B Spectra

A Cary Model 14 RI spectrophotometer, equipped with a high intensity lamp, was used for recording all spectra. Slit widths were always less than 0.1 mm in the visible. Neutral density filters were used when the optical density exceeded 2.0. The monochromatic illumination was polarized by a Rochon prism and polarized spectra were always taken with electric vector of the incoming light along an extinction direction.

For single-crystal spectra below room temperature we used an Air Products and Chemicals Model AC–3L Cryotip (a helium expansion refrigerator) equipped with a WMX–1A vacuum shroud and quartz windows. A special gas-filled cell with quartz windows was used for low temperature spectra of the hydrated crystals. Temperatures were obtained from the EMF (measured with a Leeds and Northrup Type 7556–A11 potentiometer) of a calibrated thermocouple (gold doped in iron vs. copper) placed in contact with the aluminum disc of the crystal mounting.

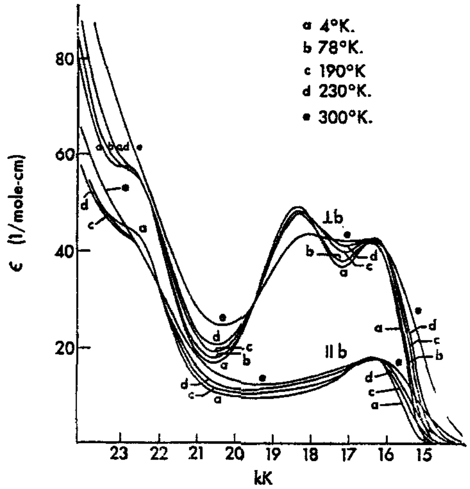

FIGURE 1 Polarized crystal spectra of the anhydrate form of Cu acac$_2$en on the (100) face at various temperatures.

III RESULTS AND DISCUSSION

A Experimental Results

Figure 1 shows the polarized spectra of the (100) face of the anhydrate crystal of Cu acac$_2$en with electric vector parallel and perpendicular to **b** at different temperatures. Figure 2 shows spectra of unoriented Cu acac$_2$en in nujol, KBr disc and chloroform; Figures 3 and 4 show the polarized crystal spectra of the (001) face of the hemihydrate and the (100) face of the monohydrate forms of Cu acac$_2$en.

B Exciton Treatment

Consider now the applicability of a weak-coupling exciton approach. The theory,[15] applied to the anhydrate (space group $P2_1/c$, 4 molecules per cell) and the hemihydrate (space group *Pbcn*, 8 molecules per cell), predicts that each transition of a free

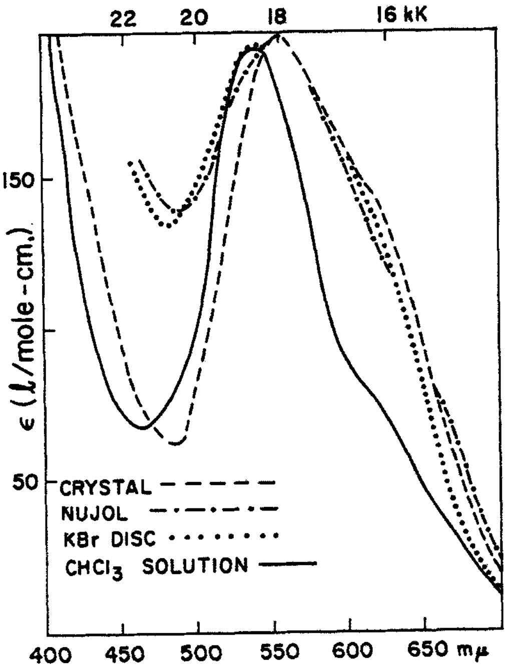

FIGURE 2 Unoriented spectra of Cu acac$_2$en.

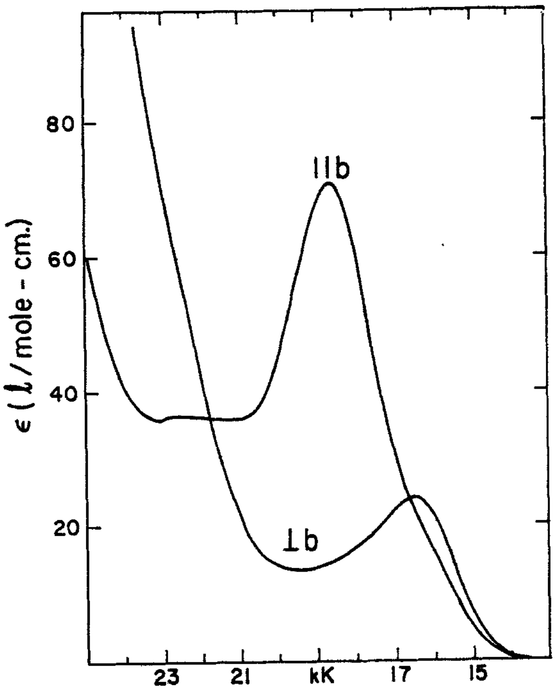

FIGURE 3 Polarized crystal spectra of the hemihydrate form of Cu acac$_2$en on the (001) face.

molecule is distributed into crystal transitions at different energies; one of the crystal transitions is allowed with electric vector of light $\parallel$**b** and another, $\perp$**b**.

In this connection, we note that it is very unlikely that the maxima at 18.4 kK in the $\perp$**b** spectrum and 16.4 kK in the $\parallel$**b** spectrum of the anhydrate (Figure 1) represent two crystal components split from one of the molecular transitions evident in chloroform solution (Figure 2). The crystal symmetry would then not allow the absorption that appears fairly strongly at 16.4 kK in the $\perp$**b** spectrum. We prefer to regard the 16.4 kK shoulder of the chloroform solution spectrum as evidence of a second absorption in the visible which, along with an 18.3 kK absorption, is reflected in the anhydrate crystal spectra with small energy shifts and splittings.

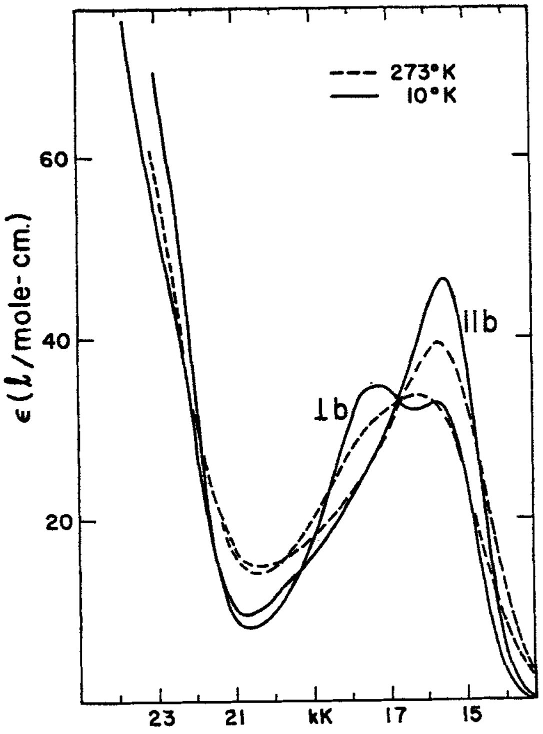

FIGURE 4 Polarized crystal spectra of the monohydrate form of Cu acac$_2$en on the (100) face at two temperatures.

Another effect of crystal forces is to mix molecular levels of the same crystal symmetry. The resulting deviations from oriented-gas intensities in the crystal may be treated[16] as "intensity transfer" among the free molecule transitions.

Extensive crystal-induced intensity transfer can weaken the utility of an oriented-gas model for the interpretation of crystal spectra. But experimental polarization information on the intense transitions in the u.v. is required if we are to rigorously assess the extent of intensity transfer into the visible absorptions. However, we have made estimates of these effects[17] by replacing the explicit calculation of intermolecular interactions[16] in the anhydrate and hemihydrate crystals with an approximation based on transition dipole-transition dipole interactions. Absorptions of Cu acac$_2$en in chloroform from 25 kK to 40 kK[18] were taken to have parallel transition moments; the sum of these moments was associated with the strongest absorption at 32 kK. For nine combinations of molecular polarization assignments for the concentrated absorption at 32 kK and each of the two visible absorptions, the sum of dipole–dipole interactions needed to fit crystal intensities with solution intensities was found and compared to the direct sum of dipole–dipole interactions computed from the crystal structure results.[17]

We found[17] that strong absorption along the **y**-axis (the long molecular axis as defined in the following section) at 18.4 kK and 16.4 kK would be required. This result will also be obtained from the oriented-gas model (cf. Section C below); however, crystal-induced mixing of levels appeared to be large enough to enable some of the ||**b** spectrum to be "stolen" from transitions at or above 32 kK *if* such u.v. transitions possess sufficiently large intensity in **x** and/or **z** polarization.

Our purpose here is not to argue for the presence of extensive crystal-induced intensity transfer in these crystals, but rather to suggest the possibility of some intensity transfer. That is, the oriented gas model cannot be accepted without reservations in this case. Detailed information about the molecule levels at u.v. energies remains unknown and other effects, such as higher multipole intermolecular interactions[19] or the influence of retardation effects in the intermolecular potential,[20] have not been taken into account. Keeping in mind the possible limitations imposed by the above exciton effects, we adopt an oriented-gas model for the remaining discussion.

C Oriented-gas Model

1 *Molecular axes* We assume an electric dipole transition localized in a molecule of the crystal. The squares of the components of an arbitrarily directed unit electric vector on a defined set of orthonormal molecular axes are computed from the atomic coordinates given in the crystal structure of the anhydrate.[21] These squares are given in Table I for a unit electric vector directed parallel or perpendicular to **b** in the (100) plane. The molecular axes are defined such that the **x**-axis is the normalized average of the bisectors of the N–Cu–N and O–Cu–O angles, the **y**-axis is set perpendicular to the **x**-axis and in the best plane of the coordinating atoms, and the **z**-axis is set perpendicular to the **x**- and **y**-axes. This procedure is also followed for the hemihydrate[12] with the results given in Table I for electric vector parallel or perpendicular to **b** in the (001) plane. Other definitions of a coordinate system which also attempt to average out the slight distortion of neighboring atoms about Cu in the crystal structures yield very similar results.

TABLE I

Squares of direction cosines in Cu acac$_2$en crystals

Direction of unit electric vector	Squares of the components of unit electric vector along molecular axes[c]		
	x	**y**	**z**
∥ b in (100) plane of anhydrate	0.506	0.000	0.494
⊥ b in (100) plane of anhydrate	0.466	0.051	0.483
∥ b in (001) plane of hemihydrate	0.000	0.145	0.855
⊥ b in (001) plane of hemihydrate	1.000	0.000	0.000
∥ b in (100) plane of monohydrate[a]	0.554	0.000	0.446
⊥ b in (100) plane of monohydrate[a]	0.439	0.017	0.544
∥ b in (100) plane of monohydrate[b]	0.491	0.000	0.509
⊥ b in (100) plane of monohydrate[b]	0.501	0.020	0.479

[a] Using z-axis as perpendicular to O_2N_2 plane. See text for details.

[b] Using z-axis as Cu to water oxygen direction. See text for details.

[c] In each case, the short, intermediate, and long axes of the molecule are, respectively, **z**, **x**, and **y**. In both anhydrate and monohydrate, where the **bc** face was observed, the long molecular axis is in the **ac** plane at ~77° (anhydrate) or ~82° (monohydrate) from **c**; the two shorter axes are almost equally inclined to **b** and **c**. In the hemihydrate, the intermediate molecular axis (**x**) is along **a** and the short axis is in the **bc** plane at ~22.5° from **b**.

A consequence of the choice of molecular axes in the anhydrate is that the **x**- and **z**-axes of one molecule are at nearly 45° to the **b** crystallographic axis. Thus two molecules, related by the glide plane parallel to the **ac** plane or the 2-fold screw axis parallel to **b** of $P2_1/c$, are oriented such that the **x**-axis of one molecule is less than 2° from being parallel to the **z**-axis of the other molecule and *vice* *versa.* Such a molecular packing then presents a limitation to the interpretation of polarized spectra of the anhydrate crystals reminiscent of that encountered in copper acetylacetonate:[1-3] absorption along the defined molecular **x**-axis is hardly distinguishable from that along the **z**-axis since only different fractions of their sum is observable for different orientations of the electric vector. This sum in the anhydrate will be referred to as **x** plus **z**.

The monohydrate is quite different in molecular structure from the anhydrate and hemihydrate forms of Cu acac$_2$en. A water molecule weakly coordinates to the copper ion at a distance of 2.43 Å; the copper ion, in turn, is displaced 0.14 Å from the best plane of the chelate's coordinating atoms.[14] The normal to this plane, however, differs by about 3.5° from a line from the copper to the oxygen of the water. This deviation raises the possibility of other "best" definitions of molecular axes as alternatives to the one described above, e.g., take the **z**-axis as the normalized copper to water oxygen vector, cross **z** with the normalized average of the bisectors of the N–Cu–N and O–Cu–O angles to obtain **y** and set **x** perpendicular to **y** and **z**. The squares of the components of a unit electric vector parallel and perpendicular to **b** in the (100) plane of the monohydrate on the molecular axes for the two definitions described above are then also presented in Table I.

2 *Polarizations of transitions* Table I may now be used to find the polarizations of absorption occurring at about 22.5, 18.4 and 16.4 kK in Figure 1 for the anhydrate. All of these absorptions are more intense for light polarized $_\perp$**b** in (100) than ||**b** in (100). Since the only molecular axis along which the fraction of incoming light increases on going from ||**b** to $_\perp$**b** is **y**, all of these absorptions have **y** components. Absorption at 18.4 and 16.4 kK is very intense in the **y** direction since only a small increase in the fraction of light along **y** produces the large difference between ||**b** and $_\perp$**b** in this region. But all three absorptions also have **x** and/or **z** components as there is intensity in the ||**b** spectrum.

The spectra of the anhydrate, referred to molecular axes **y** and **x** and/or **z**, may be estimated from Table I and Figure 1 since the component of electric vector along **x** and **z** is only slightly smaller in ||**b** than $_\perp$**b**. The **y** spectrum is presented in Figure 5 for various temperatures. The **x** plus **z** spectrum is essentially twice the intensity of the ||**b** spectrum of Figure 1.

Now in the absence of exciton effects, the sum of one third of the absorption along each of the three molecular axes should yield a spectrum similar to those of samples with random orientations of molecules. Such a spectrum at 300° K, $\epsilon_{\text{crystal}}$, is presented in Figure 2 along with a chloroform solution spectrum and spectra of a nujol mull and a pressed KBr disc, the latter two scaled such that their maxima equal the maximum extinction coefficient of the chloroform solution spectrum. General agreement is noted in Figure 2 between $\epsilon_{\text{crystal}}$, obtained from crystal thickness measurements and polarized spectra, and the extinction coefficient of the chloroform solution. $\epsilon_{\text{crystal}}$ also seems to describe reasonably well the shape of the absorption of the powdered solid near 18 kK, as judged by the nujol mull and pressed KBr disc spectra, although these unoriented solid samples presumably exhibit excessive light scattering at higher energies. The decomposition of the polarized spectra of the (100) face of the anhydrate into spectra along molecular axes thus appears to be generally adequate for this crystal at 300° K and is assumed to be so also at lower temperatures.

The room temperature polarized spectra of the (001) face of the hemihydrate, illustrated in Figure 3, also show absorption at about 22.5, 18.5 and 16.5 kK. Using Table I, one sees that the $_\perp$**b** spectrum of Figure 3 represents a spectrum with electric vector along the **x** molecular direction. It is very similar in shape to the room temperature ||**b** spectrum of the anhydrate in Figure 1 representing **x** and/or **z** absorption. This may indicate that absorption perpendicular to the molecular plane is quite weak. However, spectra of other faces of the hemihydrate are required to complete an unambiguous decomposition of the crystal spectra into molecular spectra.

Spectra of the monohydrate crystal at room temperature and 10° K, with electric vector ||**b** and $_\perp$**b** in the (100) plane, are presented in Figure 4. Three absorptions are apparent at 22.5, 17.5 and 15.5 kK. The latter two appear red-shifted from those of the anhydrate and hemihydrate crystals. Spectra of additional faces are also required for a full analysis of molecular polarizations in the monohydrate crystal, especially since some ambiguity remains in the choice of a first approximation to symmetry axes (see Table I).

3 *Symmetry considerations* The copper of the molecules in these crystals occupies a C$_1$ site[11-14] so that each electronic transition is allowed in all

electric vector directions. But since the arrangement of atoms about the Cu atom in the anhydrate and hemihydrate crystals approaches C_{2v}(x) (x axis taken as the 2-fold axis as in Figure 5), this symmetry is adopted for an analysis of the visible spectra.

TABLE II

Representations of coordinates and *d*-functions in $C_{2v}(x)$

Cartesian coordinates	$C_{2v}(x)$ representation	Half-filled molecular orbital containing *d* function	$C_{2v}(x)$ representation
x	A_1	xy	B_2
y	B_2	x^2-y^2	A_1
z	B_1	$3z^2-r^2$	A_1
		yz	A_2
		xz	B_1

Table II presents the $C_{2v}(x)$ representations spanned by the Cartesian coordinates and copper *d* functions. The direct products of representations of molecular levels and Cartesian coordinates are given in Table III. Some transitions are seen to be allowed since the direct product of representations of electric vector direction, ground state $B_2(xy)$, and final level contains the totally symmetric A_1.

In addition to the above static mechanism, a vibronic mechanism may also contribute observable intensity to the visible spectra of Cu acac$_2$en as in related centrosymmetric copper chelates.[1–6] Appropriate vibrations may slightly mix additional electronic levels into the level involved in an electronic transition and, consequently, alter the magnitude and distribution of intensity in the transition;[22] the symmetry criteria require that the direct product of the representations of initial and final electronic levels, perturbing vibration, and electric vector direction contain A_1.[23] The electric vector directions and vibrational modes by which such an admixture of electronic levels can be obtained in $C_{2v}(x)$ are presented in Table III.

Simple theory[24–26] relates the integrated intensity of the vibronic component of a transition, induced by an active vibrational mode Q, to the temperature by $\coth(h\nu_Q/2kT)$ where ν_Q is the frequency of the vibration. The $C_{2v}(x)$ representations of the types of vibrations among the coordinating atoms and the metal atom in Cu acac$_2$en are given in Table IV.

TABLE IV

Types of vibrations of CuN_2O_2 in $C_{2v}(x)$

Type of vibration	Representation in $C_{2v}(x)$
Stretches	$2\alpha_1$, $2\beta_2$
In-plane bends	$2\alpha_1$, β_2
Out-of-plane bends	α_2, β_1

4 *Possible assignments of transitions* As shown in Table III, two "*d–d*" transitions, $A_1(3z^2 - r^2) \leftarrow B_2(xy)$ and $A_1(x^2 - y^2) \leftarrow B_2(xy)$, possess statically allowed **y**-polarized components. The large intensity of the **y**-spectrum relative to the **x**-plus-**z** spectrum at 18.4 and 16.4 kK in the anhydrate (Figure 1 and Figure 5) indicate that these absorptions belong to $A_1(3z^2 - r^2) \leftarrow B_2(xy)$ and $A_1(x^2 - y^2) \leftarrow B_2(xy)$.

Negligible temperature dependence was observed in the integrated **y** intensity of these two absorptions (Figure 5). This is consistent with, but does not prove, the presence of statically allowed intensity. Vibronically induced components of $A_1 \leftarrow B_2$ transitions may also be present in the **y**-polarization but remain undetected due to either a relatively weak vibronic component or slowly changing $\coth(h\nu_Q/2kT)$ factors associated with α_1 vibrations of large frequencies.

TABLE III

Statically and vibronically allowed transitions in $C_{2v}(x)$

Transition	Direct product of states with coordinate			Polarization accompanied by vibrational mode			
	x	y	z	α_1	α_2	β_1	β_2
B_2-A_1, B_1-A_2	B_2	A_1	A_2	y	z	–	x
B_2-A_2, B_1-A_1	B_1	A_2	A_1	z	y	x	–
B_2-B_1, A_2-A_1	A_2	B_1	B_2	–	x	y	z
B_2-B_2, B_1-B_1 A_2-A_2, A_1-A_1	A_1	B_2	B_1	x	–	z	y

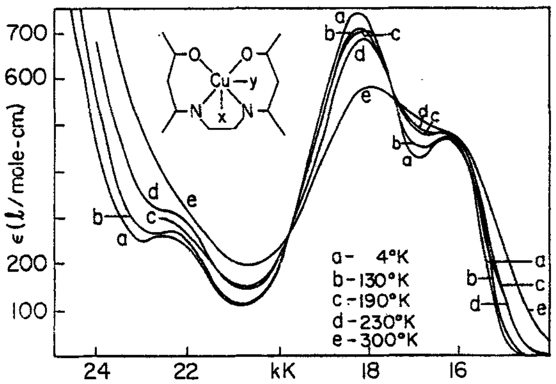

FIGURE 5 Spectra analyzed with electric vector along the y-axis of Cu acac$_2$en in the anhydrate form at various temperatures.

However, the negligible temperature dependence of the y-spectrum at these two absorptions makes it improbable that they originate in the $A_2(yz) \leftarrow B_2(xy)$ and $B_1(xz) \leftarrow B_2(xy)$ transitions, which are statically forbidden. y-polarized intensity could be induced into these transitions by vibrational modes α_2 or β_1 (Table III), but α_2 and β_1 correspond to out-of-plane bending motions about the metal (Table IV) and are associated with frequencies much less than 500 cm^{-1}. The y integrated intensity of the $A_2(yz) \leftarrow B_2(xy)$ and $B_1(xz) \leftarrow B_2(xy)$ transitions would then be expected to exhibit an observable increase with increasing temperature following $\coth(h\nu_Q/2kT)$ which is contrary to the observed result at 18.4 and 16.4 kK in Figure 5.

Assuming a Gaussian line shape for the 16.4 kK absorption in the x-plus-z spectrum (Figure 1), the absorption's integrated intensity changes with temperature to an extent described by an "average" ν_Q of 320 cm^{-1}. This is consistent with α_2 and β_2 vibrations' promoting $A_1 \leftarrow B_2$ intensity in the **z** and **x** directions.

Because of the overlapping strong absorption from higher energies, the amount of temperature dependence in the absorption at 22.5 kK in the anhydrate is more difficult to measure, but the alteration of the y intensity of this absorption with temperature also appears to be minor. The previous argument would then indicate that this absorption also does not mainly involve $A_2(yz)$ or $B_1(xz)$ excited states. Indeed, if the absorption at 22.5 kK in the monohydrate (Figure 4) is of the same origin as the absorption at that energy in the anhydrate, its apparent lack of a red-shift on fifth coordination,[27] compared to the lower energy absorption, also indicates that it is not mainly due to $A_2(yz)$ or $B_1(xz) \leftarrow B_2(xy)$.

D *Conclusion*

The calculations show that exciton effects can influence the crystal polarization ratios for rather weak visible transitions in acentric metal complexes similar to those studied here. The experimental data do not suggest any substantial exciton influences in these particular systems, and we use an oriented gas model for the discussion. Whatever model applies, the main part of the visible intensity is attributable to y-polarized molecular transitions just as in related centric complexes.[4,5,6,28] These findings reinforce the proposition[4,6] that the asymmetric molecular distortions, whether vibrational or static, are causing all the "*d–d*" transitions to borrow intensity chiefly from a single *y*-polarized charge-transfer band. In our opinion, this feature of the spectra of both centric and acentric copper β-ketoenolates and β-iminoenolates is now well established; similar spectroscopic experiments on such molecules are most unlikely to produce any substantially new or different results.

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