

Optical and Magnetic Spectra of Bis-*N*-Propylsalicylaldiminato Copper (II)

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The electronic and electron spin resonance spectra of bis-*N*-propylsalicylaldiminato copper (II) have been measured. The measurements show that the *g*-tensor has some rhombic character with $g_z = 2.225$, $g_x = 2.064$, and $g_y = 2.038$. Four *d-d* transitions were observed in the electronic spectrum at 14,800, 16,800, 19,800, and 22,000 cm^{-1} . A consistent set of assignments has been made based on the polarization data of the bands. These results are compared to the results from other similar molecules.

Key Words: Bis-*N*-propylsalicylaldiminato copper (II), optical spectra—four *d-d* transitions, paramagnetic resonance—three *g* values, square planar complex.

1. Introduction

Considerable data are now available on the electronic spectra and magnetic properties of bis-copper (II) complexes with bidentate ligands attached to ring systems [1–9].¹ Almost without exception, for a square planar configuration, the ligand field axes in the molecular plane have been found to point toward the ligand ring system even though the molecular geometry about the copper would seem to favor axes along the copper ligand bonds. These complexes generally contain a center of symmetry so that in the simplest approximation the *d-d* transitions are forbidden. To account for the observation of these transitions a vibronic mechanism is usually invoked.

The spectra of bis-salicylaldiminato copper (II) [CuSal_2] and bis-*N*-methylsalicylaldiminato copper (II) [$\text{Cu}(m\text{-Sal})_2$], for which the crystal structures are known, have been studied [2]. These spectra have been interpreted by assuming that the ligand field symmetry at the cupric ion is described by the point group D_{2h} . Unfortunately all four possible *d-d* transitions could not be observed for either molecule making it necessary to speculate on the reasons why only certain transitions are active. Although the interpretation seems reasonable, there are still some unanswered questions about it [3].

Preliminary data on bis-*N*-propylsalicylaldiminato copper (II) [$\text{Cu}(p\text{-Sal})_2$] indicated that this complex would be particularly suited for a detailed study that might resolve some of the unanswered questions even though the complete crystal structure of the molecule is not known. Four *d-d* transitions are observed in the optical spectrum and the *g*-tensor has a rhombic distortion. Preliminary x-ray data revealed that there is only one molecule per unit cell thus ruling out any spectral ambiguities arising from crystallographically nonequivalent sites.

2. Experimental Procedure

Samples of $\text{Cu}(p\text{-Sal})_2$ were kindly supplied by Mrs. Paula Wood. Suitable single crystals were grown by evaporation from an acetone solution.

Analysis: Calculated, C—61.92%, H—6.24%, N—7.22%, Cu—16.38%.

Found, C—61.9%, H—6.2%, N—7.2%, Cu—16.4%.

X-ray examination showed that the crystals of $\text{Cu}(p\text{-Sal})_2$ are triclinic with a measured cell volume of 462\AA^3 . The calculated density based on one molecule per unit cell is 1.39 gm/cm^3 which is to be compared to the measured value of 1.40 gm/cm^3 .

The magnetic studies were carried out at 25°C and -196°C using a X-band spectrometer with 100 kHz modulation and a K-band spectrometer with 6 kHz modulation. The principal axes of the *g*-tensor were determined by trial and error because of the absence of crystal symmetry. The principal *g*-values are given in table 1. The uncertainties quoted represent primarily a measure of the uncertainty in the alinement of the crystals in the applied magnetic field. The spectrum of a powdered polycrystalline sample was also observed. It was interpreted by the method of Kneubuhl [10] yielding results in agreement with the single crystal measurements. The peak-to-peak line widths at 77°K are about 18 G in the *xy*-plane and about 60 G along the *z*-axis. Such line widths indicate a considerable amount of exchange interaction.

Optical spectra were taken on a spectrophotometer. Light incident on the crystal was polarized by means of Glan-Thomsen polarizers. Spectra were taken in two crystal faces whose orientation with respect to the experimentally determined magnetic axes is shown in figure 1. The *ab* face is nearly perpendicular to the molecular plane which is assumed to be the magnetic *xy*-plane. The other face corresponds very nearly to this *xy*-plane.

¹Figures in brackets indicate the literature references at the end of this paper.

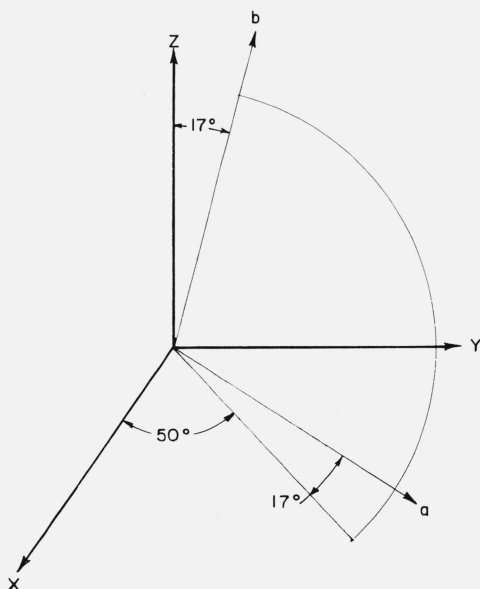


FIGURE 1. Orientation of the *ab* face with respect to the principal magnetic axes.

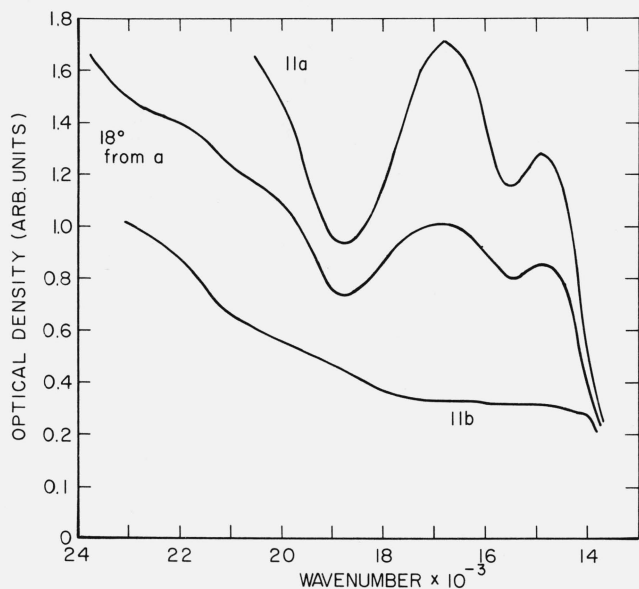


FIGURE 2. Polarized absorption spectra of $\text{Cu}(\text{p-Sal})_2$ at 77 °K with light incident on the *ab* face.

Figure 2 shows the polarized spectra along *a* and *b*. The parallel to *a* spectrum shows two strong bands (14,800 and 16,800 cm^{-1}) while the parallel to *b* spectrum shows two relatively weak bands (19,800 and 22,000 cm^{-1}). The presence of four bands is clearly revealed in the spectrum taken approximately 18° from *a* in the *ab* face.

The spectra taken with light polarized parallel to *x*

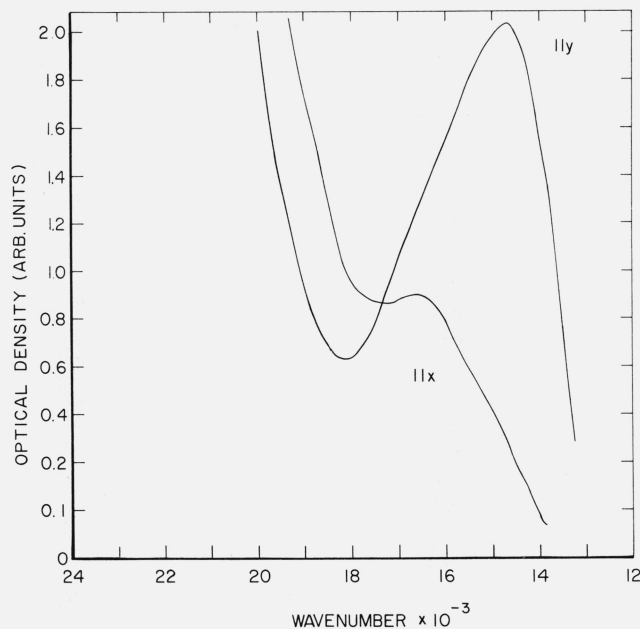


FIGURE 3. Polarized absorption spectra of $\text{Cu}(\text{p-Sal})_2$ at 77 °K with light incident in the *xy*-plane.

and to *y* in the *xy*-plane is shown in figure 3. Charge transfer and/or ligand absorption above 20,000 cm^{-1} preclude the observation of the two high frequency bands in this orientation. The two low-frequency bands are strongly polarized in the plane of the molecule while the two high-frequency bands have a *z*-component. Whether these latter bands also have an *x* or *y* component could not be established because of the strong overlapping absorption mentioned previously. These data are summarized in table 1.

TABLE 1. Optical transitions (cm^{-1})

$\text{Cu}(\text{p-Sal})_2$	$\text{Cu}(\text{m-Sal})_2$	$\text{Cu}(\text{Sal})_2$
14,800 (<i>x, y</i>) 16,800 (<i>x, y</i>) 19,800 (<i>z</i>) 22,000 (<i>z</i>)	15,000 (<i>x, y</i>) 17,000 (<i>x, y</i>) 20,500 (<i>z</i>)	16,500 (<i>x, y</i>) 18,500 (<i>x, y</i>)
e.p.r. data		
	$\text{Cu}(\text{p-Sal})_2$	$\text{Cu}(\text{Sal})_2^a$
g_x	2.064 ± 0.004	2.050 ₀
g_y	$2.038 \pm .004$	2.040 ₂
g_z	$2.225 \pm .006$	2.200 ₀

3. Interpretation of Results

The geometry for this type molecule is shown in figure 4 [11, 12]. The highest symmetry consistent with this model is the point group C_{2h} . This symmetry leaves the position of the *x*- and *y*-axes in the molecular plane undefined. In CuSal_2 and $\text{Cu}(\text{m-Sal})_2$ the *y*-

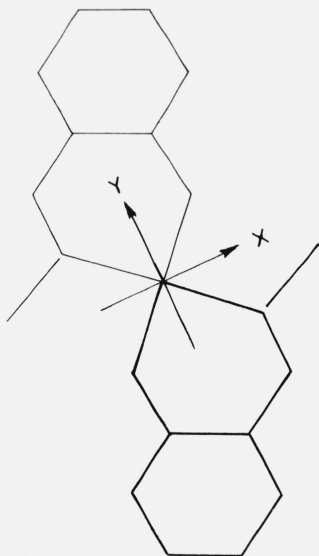


FIGURE 4. Schematic representation of the geometry of the $\text{Cu}(\text{Sal})_2$ -type complex showing the location of the x- and y-magnetic axes.

axis was found to pass through the interior N-Cu-O angle as shown. The ligand field axes of $\text{Cu}(p\text{-Sal})_2$ were found to be identical from both optical and magnetic measurements and are assumed to be oriented in the same manner as in the closely related molecules.

The observed g -values can be accounted for on the basis of a ground state that is essentially $d_{x^2-y^2}$ or essentially d_{xy} . The polarized electronic spectrum does not lead to a differentiation either, since in C_{2h} both states belong to the symmetry species A_g . In table 2, the polarization of the various expected transitions is summarized assuming that the appropriate point group is C_{2h} and that the transitions become allowed through a vibronic mechanism. This same table would hold if the roles of d_{xy} and $d_{x^2-y^2}$ were interchanged.

TABLE 2. Polarization of allowed vibronic transitions in C_{2h}

Transition	Species of vibration	
	A_u	B_u
$ xy\rangle \rightarrow z^2\rangle$	z	x,y 14,800
$ xy\rangle \rightarrow x^2-y^2\rangle$	z	x,y 16,800
$ xy\rangle \rightarrow xz\rangle$	x,y	z 19,800
$ xy\rangle \rightarrow yz\rangle$	x,y	z 22,000

The assignment given in table 2 seems to be the most logical and agrees with the assignments made previously in CuSal_2 and $\text{Cu}(m\text{-Sal})_2$ [1-3]. This means that the transitions become allowed through a vibronic mechanism involving a B_u vibration. Again this is in accord with the previous work [1-2].

The disturbing part of this interpretation is that it does not provide an unambiguous determination of

the electronic ground state. However, intuitive arguments based on the fact that the d_{xy} orbital points directly at the ligands lead to the conclusion that d_{xy} must be the orbital containing the unpaired electron.

4. Bonding Parameters

The magnetic and optical data can be used to gain some insight into the nature of the bonding in $\text{Cu}(p\text{-Sal})_2$. The wavefunctions which describe this complex are taken to be a linear combination of copper d -orbitals and ligand orbitals of the same symmetry species. The d_{z^2} , d_{xy} , and $d_{x^2-y^2}$ orbitals belong to the irreducible representation A_g in the point group C_{2h} and can therefore mix. As a first approximation, however, we have assumed they may be treated separately. The wavefunctions [6] are:

$$|xy\rangle = \alpha d_{xy} - \frac{1}{2} \alpha' [-\sigma_{xy}^{(1)} + \sigma_{xy}^{(2)} + \sigma_{xy}^{(3)} - \sigma_{xy}^{(4)}]$$

$$|x^2-y^2\rangle = \beta d_{x^2-y^2} - \frac{1}{2} (1-\beta^2)^{1/2} [-p_{xy}^{(1)} - p_{xy}^{(2)} + p_{xy}^{(3)} + p_{xy}^{(4)}]$$

$$|z^2\rangle = \gamma d_{z^2} = \frac{1}{2} (1-\gamma^2)^{1/2} [\sigma_{xy}^{(1)} + \sigma_{xy}^{(2)} - \sigma_{xy}^{(3)} - \sigma_{xy}^{(4)}]$$

$$|yz\rangle = \delta' d_{xy} - \frac{1}{2} (1-\delta'^2)^{1/2} [p_z^{(1)} + p_z^{(2)} - p_z^{(3)} - p_z^{(4)}]$$

$$|xz\rangle = d_{xz}$$

The g -values which are the experimental parameters in the usual spin Hamiltonian can then be related to the free ion spin-orbit coupling constant, the electronic energy levels and the bonding parameters by the equations

$$g_z = 2.002 - \frac{8\lambda}{\Delta_{x^2-y^2}} [\alpha^2\beta^2 - \alpha\alpha'\beta^2S - \alpha\alpha'\beta(1-\beta^2)^{1/2} \frac{T(n)}{2}]$$

$$g_x = 2.002 - \frac{2\lambda}{\Delta_{xz}} [\alpha^2 - \alpha\alpha'S]$$

$$g_y = 2.002 - \frac{2\lambda}{\Delta_{yz}} [\alpha^2\delta'^2 - \alpha\alpha'\delta'^2S]$$

The values for the S and $T(n)$ integrals are assumed to be the average of calculated values for oxygen and nitrogen. Using the assignments $\Delta_{x^2-y^2} = 16,800 \text{ cm}^{-1}$, $\Delta_{xz} = 19,800 \text{ cm}^{-1}$, and $\Delta_{yz} = 22,000 \text{ cm}^{-1}$, the bonding parameters are found to be $\alpha = 0.89$, $\beta = 0.85$, and $\delta' = 0.76$. The values indicate that the pi bonding to the ring system can play an important role in stabilizing some chelating complexes. Gersmann and Swalen [6] also calculated values for bonding parameters in chelating complexes. In their studies the two in-plane g -values were approximately equal and differences in the optical transitions were used to

reach conclusions about the strength of the pi bond. In $\text{Cu}(p\text{-Sal})_2$ the $|xz\rangle$ and $|yz\rangle$ energy levels are found to be rather close together and the nature of the bonding manifests itself in rather different in-plane g -values.

It is interesting to use the magnetic data of Maki and McGarvey and estimates of the bonding parameters for $\text{Cu}(\text{Sal})_2$ to calculate the expected positions of the $|xz\rangle$ and $|yz\rangle$ levels in that complex. The work of Kivelson and Neiman [7] suggests that α^2 would be about 0.76 and we assume that δ' is about the same as in $\text{Cu}(p\text{-Sal})_2$. The $|xz\rangle$ level is then expected to be at $18,200\text{ cm}^{-1}$ and the $|yz\rangle$ level is calculated to be at about $24,700\text{ cm}^{-1}$. The latter band would be masked by the charge transfer spectra, while the former falls in the same region of the spectrum as the two more intense $A_g \rightarrow A_g$ transitions. Ferguson [2] has suggested that a small z component in the spectrum might indeed be present in this spectral region. This assignment of energy levels is also in qualitative agreement with the work of Gersmann and Swalen.

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5. Conclusions

The electronic and magnetic spectra of $\text{Cu}(p\text{-Sal})_2$ support the contention that the effective symmetry at the cupric ion is lower than axial. Moreover, these data appear to be best accounted for in terms of a model which supposes the ground-state molecular orbital is essentially d_{xy} .

6. References

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