TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE REPLACEMENT OF HALIDE LIGANDS OF Pt(dien)X^+ BY HALIDE AT 25° AND CONVERTED TO IONIC STRENGTH = 0

	Entering group		
	Cl^-	Br^-	I^-
Leaving group	10^4k_2, sec^{-1} M^{-1}		
Cl^-	150^a	89 78^a	3200^b
Br^-	23	228^c	4200^b

[a] Reference 4. [b] Reference 13. [c] Reference 6.

zero ionic strength was 78 sec^{-1} M^{-1} which is in satisfying agreement with our value of 89 sec^{-1} M^{-1}.

The plot of log k_2 *vs.* n_{Pt} in Figure 3 for the zero ionic strength conditions is generally consistent with the expected linear behavior. Without the correction to zero ionic strength there was a much greater scatter for the points. The rate constant for the reaction of Cl^- with Pt(dien)Cl^+ appears the only inconsistency in the set. This rate was determined by $^{36}Cl^-$ exchange in which a silver chloride precipitation was used for the separation process.[4] Silver halide separations have proven unsatisfactory for the exchange studies of a number of platinum(II) complexes in this laboratory. It would therefore seem advisable to reexamine that system with an ion-exchange procedure.

It appears that bromide is only a slightly better leaving group than chloride for these complexes in which differences such as ionic charge and differences in the *cis* and *trans* neighbors have been eliminated. Perhaps the most striking feature which is emerging for these reactions is that chloride and bromide behave so similarly as a leaving group.

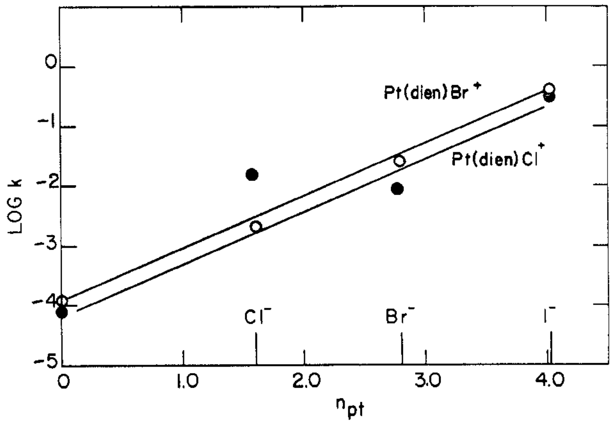

Figure 3.—The dependence of the second-order rate constant, k_Y sec^{-1} M^{-1}, upon the nucleophilic reactivity of the entering group for the halide interchange reactions of Pt(dien)Cl^+ (●) and Pt(dien)Br^+ (○) where k_Y is for 25° and is adjusted to ionic strength of zero. Points at n_{Pt} = 0 are k_1 sec^{-1}.

In view of the rather modest differences in extinction coefficients for the chloro and bromo complexes, Pt(dien)X^+, the ion-exchange and tracer technique appears to be definitely superior to spectrophotometric methods. In addition, it has the very important advantage that the concentrations of the equilibrium state can be evaluated, and an equilibrium quotient can therefore be tested over a variety of conditions. The presence of the reverse reaction does not pose the serious obstacle which is difficult to treat from spectrophotometric data. In addition, it has permitted an evaluation of the equilibrium quotient for the aquation of the complex.

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Optical and Magnetic Measurements on Single Crystals of Copper(II)-Doped Tris(phenanthroline)zinc(II) Nitrate Dihydrate

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The electron paramagnetic resonance spectrum in single crystals of copper(II)-doped tris(phenanthroline)zinc(II) nitrate dihydrate has been observed between 4 and 350°K. The results have been interpreted in terms of a Jahn–Teller effect for the copper(II) ion. At 350°K the spectrum is nearly isotropic with $g = 2.13$ and no observed hyperfine splitting. At 77°K anisotropy of the g tensor is observed with $g_{||} = 2.273$, $g_{\perp} = 2.064$, $A = 160 \times 10^{-4}$ cm^{-1}, $B < 7 \times 10^{-4}$ cm^{-1}, $A' = 12.5 \times 10^{-4}$ cm^{-1}, and $B' = 10.5 \times 10^{-4}$ cm^{-1}. No significant change in the spectrum was observed at temperatures below 77°K. The optical d–d transitions and their polarization properties are reported. Two bands are observed at 7000 and 14,900 cm^{-1}. The 14,900-cm^{-1} band is split at 77°K into components at 14,700 and 15,200 cm^{-1}. The optical axes do not coincide with the principal magnetic axes.

Introduction

Electron paramagnetic resonance measurements on some tris complexes of copper(II) were reported recently[2] in which the magnetic parameters were obtained from polycrystalline samples of the copper(II) complexes in a matrix of the corresponding diamagnetic zinc(II) complex. The temperature variation of the epr spectra suggested that these complexes were ex-

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(1) (a) National Bureau of Standards; (b) University of Maryland.

(2) H. C. Allen, Jr., G. F. Kokoszka, and R. G. Inskeep, *J. Am. Chem. Soc.*, **86**, 1023 (1964).

hibiting dynamical Jahn–Teller distortions.[2–4] This effect had been observed in copper fluorosilicate[5,6] as well as in other copper compounds,[7] but there had been no previous example reported for a tris chelate of copper(II). In the earlier studies[5–7] the copper(II) ion was reported to reside in a trigonal site which manifested itself in the epr spectrum as three equivalent distortions. It might be expected that in the tris-phenanthroline complex, the local ligand field would also have approximately trigonal symmetry. Hudson[8] has interpreted the results of our previous investigation in terms of a simple hopping model in which the complex is assumed to jump at random between the three equivalent distortions. His calculated spectra are in substantial agreement with the observed spectra.

While numerous investigations of the magnetic properties of Jahn–Teller complexes have been carried out, relatively little attention has been directed toward their electronic spectra. Liehr and Ballhausen,[3a] in an earlier study, and O'Brien[3b] have made estimates which indicate that in these complexes a transition in the near-infrared region as well as one or more transitions in the visible region should be observed. Palmer and Piper[9] have reported the electronic spectra of some tris(2,2′-bipyridine)copper complexes with electronic transitions near 7000 and 15,000 cm^{-1}. These data have been interpreted in terms of trigonal molecular symmetry, but they indicated that some difficulties were encountered in attempting to reconcile their preliminary magnetic data with this model. Since the earlier magnetic studies on the polycrystalline tris complexes of copper(II) as well as the previous studies[5–7] on the copper(II) ion in a trigonal site have been interpreted on the basis of the Jahn–Teller induced tetragonal distortions in the ligand field, the results of Palmer and Piper would seem to require that the magnetic and optical data should be related to noncoincident sets of molecular axes. Experimentally, this lack of coincidence should be readily observable.

Studies on single crystals of tris-chelate complexes of copper(II) should provide information concerning the number and relative orientation of the magnetic z axes at low temperatures. More importantly, such studies would provide an opportunity to obtain experimental data on the orientation of the principal magnetic axes with respect to the direction of polarization in the same complex.

It has now been possible to obtain single crystals of copper-doped tris(phenanthroline)zinc(II) nitrate dihydrate, $(C_{12}H_8N_2)_3Zn(Cu)(NO_3)_2 \cdot 2H_2O$. The purpose of this paper is to report the results of an investigation of the epr spectra which were observed at various temperatures between 4 and 350°K and the optical spectra which were recorded at 77°K and at room temperature.

Experimental Section

Suitable crystals were grown from an alcohol solution which contained a mole ratio of one part zinc nitrate to nine parts of phenanthroline and small amounts of copper(II) nitrate. Chemical analysis showed that the crystals corresponded to the tris-phenanthroline complex.[10] *Anal.* Calcd for $Zn(phen)_3(NO_3)_2 \cdot 2H_2O$: Zn, 8.53; C, 56.44; H, 3.67; N, 14.62. Found: Zn + Cu, 8.5; C, 57.8; H, 3.8; N, 14.2. Only the Cu^{63} isotope was used for reasons previously discussed.[2]

Preliminary X-ray studies indicated that the crystal was triclinic with a unit cell volume of 1801 A^3. The density was found to be 1.46 g/cc which corresponds to two tris(phenanthroline)-zinc(II) nitrate dihydrate molecules per unit cell. Examination of the morphology of the crystals with a two-circle goniometer showed them to be centrosymmetric. These measurements were all made at room temperature.

The epr data were obtained at X band (Varian Model 4500 spectrometer) and K band (Strand Labs Model 601 spectrometer) on crystals which contained a Zn to Cu^{63} ratio of about 200. X-Band data were obtained in the temperature range from 77 to 350°K and K-band data were obtained at 4 and at 77°K. Since the crystals were triclinic and the complete crystal structure was unknown, the initial experiments were devoted to finding the maximum g value at 77°K. The crystals were mounted in various orientations until the maximum g value at 77°K was the same as that obtained from the powdered polycrystalline material at the same temperature. Then the spectrum was observed in the plane perpendicular to this direction. A second maximum g value was found in that plane. Further measurements were made in various directions but only two magnetic z axes were observed.

When the magnetic field is directed along one of the magnetic z axes, the superhyperfine structure is composed of nine components with a relative intensity very nearly in the ratio 1:4:10:16:19:16:10:4:1. The separation between these components is approximately 10 gauss and we attribute this splitting to the interaction of four equivalent nitrogen atoms. Reasonably well-resolved spectra were also obtained in other directions where the nitrogen ligands are also assumed to be equivalent. Very low resolution was observed when the magnetic field was directed along the line perpendicular to the two z axes (see Figure 1). In this direction two of the nitrogen atoms would be expected to contribute with a splitting A', the parallel component of the interaction, while the other two would be expected to produce an additional splitting of B', the perpendicular hyperfine component. This is consistent with the suggestion that the principal magnetic axes are directed along copper(II)–nitrogen bonds.

Figure 1 shows the epr spectrum at various temperatures in the direction perpendicular to the two z axes where the two magnetic units are equivalent and where they show a minimum g value. The epr spectrum in a direction bisecting the two low-temperature z axes is shown in Figure 2 at two different temperatures. At about 350°K the epr spectrum was nearly isotropic with $g = 2.13 \pm 0.01$ with no observed hyperfine splitting. A summary of the epr results at 77°K is shown in Table I. The estimated uncertainty in the g values is associated mainly with the uncertainty in the alignment of the crystal.

Polarized optical absorption spectra in the region from 5000 to 21,000 cm^{-1} were taken in dilute crystals of the copper complex in a zinc complex with a spectrophotometer (Cary 14) and Glan-Thompson polarizers. Three bands were observed whose polarization properties were essentially the same at room temperature and liquid nitrogen temperature. The position of the 7000-cm^{-1} band was invariant with temperature, but the position of the other bands changed slightly with temperature as is shown in Table II. Polarized spectra are shown in Figure 3 in which the directions of maximum and minimum intensity are given with

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(3) (a) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **3**, 304 (1958); (b) M. C. M. O'Brien, *Proc. Roy. Soc.* (London), **A281**, 323 (1964).

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(7) B. Bleaney, K. D. Bowers, and R. S. Trenam, *Proc. Roy. Soc.* (London), **A228**, 157 (1955).

(8) A. Hudson, *Mol. Phys.*, **10**, 575 (1966).

(9) R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966).

(10) R. G. Inskeep, *J. Inorg. Nucl. Chem.*, **24**, 763 (1962).

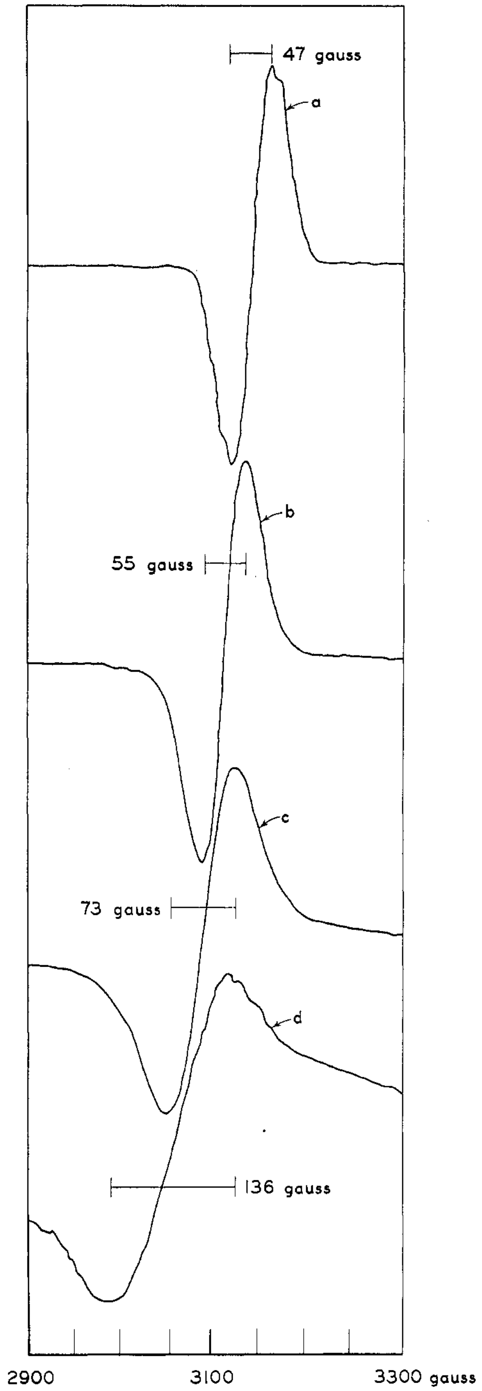

Figure 1.—Epr spectrum in the direction of the minimum g value: (a) spectrum at 77°K, g = 2.06; (b) spectrum at 210°K, g = 2.08; (c) spectrum at 300°K, g = 2.10; (d) spectrum at 350°K, g = 2.12.

respect to the magnetic z axes. The magnetic axis, z_2, lies 45° out of the plane of the figure while z_1 lies in this plane.

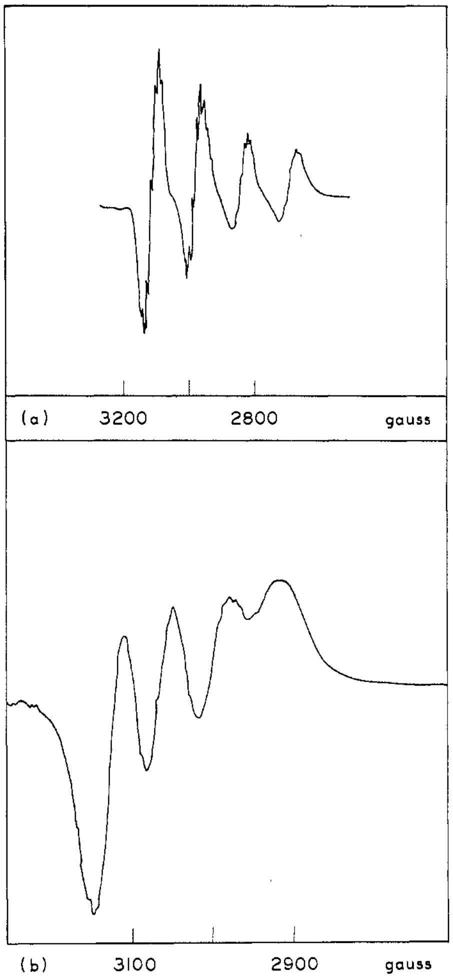

Figure 2.—Epr spectrum in a direction between the two low-temperature z axes: (a) spectrum at 77°K, g = 2.16, A = 0.012 cm^{-1}; (b) spectrum at 210°K, g = 2.14, A = 0.006 cm^{-1}.

TABLE I

ELECTRON PARAMAGNETIC RESONANCE RESULTS AT 77°K

$g_{\|} = 2.273 \pm 0.007$	$g_{\perp} = 2.064 \pm 0.008$
$A = 160 \pm 3 \times 10^{-4}$ cm^{-1}	$B < 7 \times 10^{-4}$ cm^{-1}
$A' = 12.5 \pm 1.7 \times 10^{-4}$ cm^{-1}	$B' = 10.5 \pm 0.7 \times 10^{-4}$ cm^{-1}

TABLE II

OPTICAL TRANSITIONS FOR $Cu(phen)_3(NO_3)_2$ (CM^{-1})

	77°K	300°K
Δ_1	7,000	7,000
Δ_2	14,700	14,900
Δ_3	15,200	14,900

Discussion

The Epr Results.—The low-temperature spectrum could be fit to the usual $S = {}^1/_2$ (spin Hamiltonian).[11] The observed superhyperfine structure indicates that the unpaired electron is coupled to four equivalent nitrogen ligands. Four equivalent nitrogen atoms are compatible with a tetragonal distortion as are the observed g values.

Above about 120°K the nitrogen superhyperfine structure was not observed. The copper hyperfine structure was barely resolvable in certain directions at room temperature. No evidence for the copper hyperfine structure appeared in the minimum g value spectra as can be seen from Figure 1. The epr spectrum taken between the two z axes (Figure 2) is similar to those reported by McGarvey[12] for cupric ions in solution. Orton,[13] *et al.*, have observed a similar spectrum in their studies of copper-doped magnesium oxide.

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[11] J. H. M. Thornley, B. W. Mangum, J. H. E. Griffiths, and J. Owen, *Proc. Phys. Soc.* (London), **A78**, 1263 (1961).

[12] B. R. McGarvey, *J. Phys. Chem.*, **61**, 1232 (1957).

[13] J. W. Orton, P. Augins, J. H. E. Griffiths, and J. E. Wertz, *Proc. Phys. Soc.* (London), **A78**, 554 (1961).

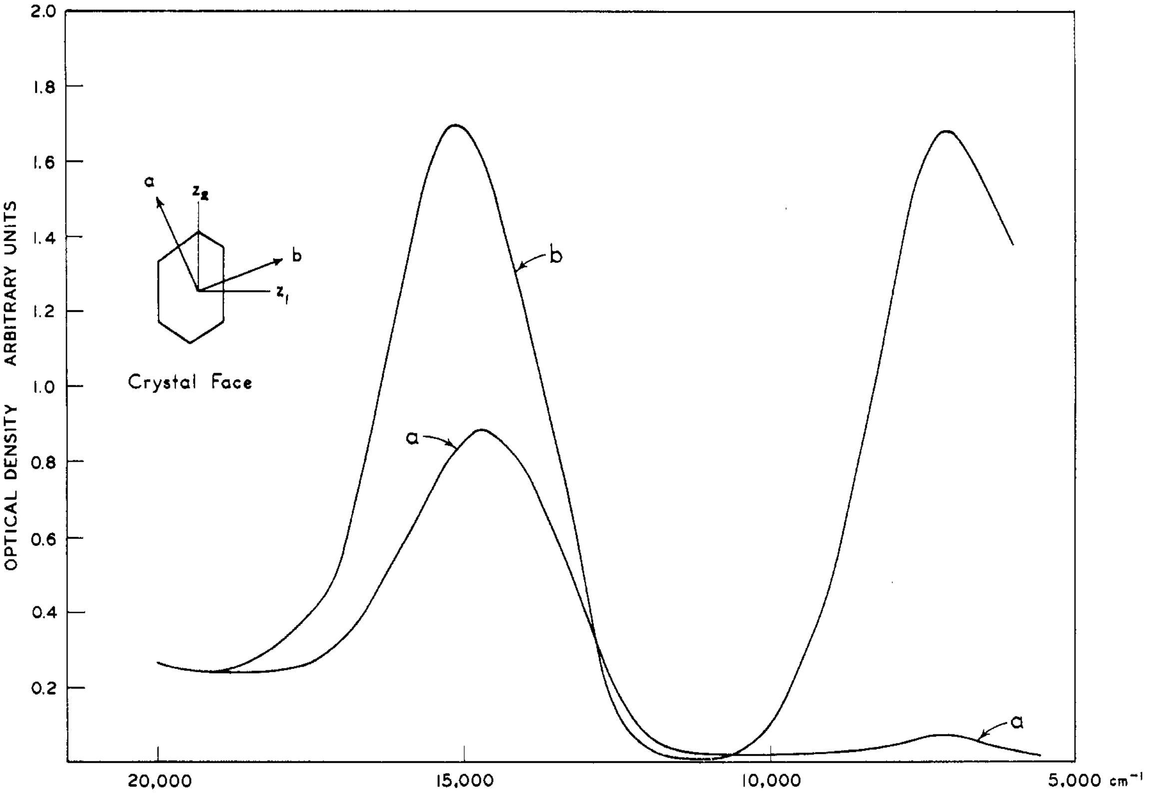

Figure 3.—Polarized absorption spectra of copper-doped tris(phenanthroline)zinc(II) nitrate dihydrate. Spectra were taken in the crystal face which contains a unique magnetic axis, z_1. The z_1, a, and b directions lie in the plane of the paper while z_2 makes an angle of 45° with this plane. The direction of propagation of the light is perpendicular to the plane of the figure.

There have been many theoretical treatments of the Jahn–Teller effect in nearly octahedral complexes of copper(II) and the experimental results appear to conform to the proposed models.[3-7] In general these models predict that at sufficiently low temperatures three equivalent distortions will be observed along each of the three ligand–metal–ligand axes. The g values for the distorted configurations then correspond to those obtained for a tetragonally elongated octahedron

$$g_{\parallel} = 2 - \frac{8\lambda}{\Delta_{xy}}$$

$$g_{\perp} = 2 - \frac{2\lambda}{\Delta_{xz,yz}}$$

At sufficiently high temperatures the complex resonates among the three equivalent distortions giving rise to an isotropic g value

$$g = 2 - \frac{4\lambda}{\Delta}$$

A continuous variation from the low-temperature spectra to the high-temperature spectra is expected, consistent with our observations. O'Brien[3b] has shown that the three equivalent distortions arise as a result of a relatively high-energy barrier between the three possible configurations. This has been assumed by Hudson[8] in his treatment of the temperature dependence of the epr spectrum of the polycrystalline tris complexes. Since the epr results show that an isotropic g value is not observed until the temperature is about 350°K, it would appear that his assumption is quite reasonable.

At room temperature, the unit cell is centrosymmetric, which implies that any distortion in one of the two complexes in the unit cell is accompanied by a parallel distortion in the other. Therefore, if the unit cell remains centrosymmetric at low temperatures, the experimental results show that only two rather than three configurations are stable. These results imply that a modification in the theoretical treatments to accommodate the case of two relatively deep stable minima and a third minimum at somewhat higher energies is needed. An examination of the epr spectrum at high gain in the direction perpendicular to the two z axes at 77°K revealed no evidence for the expected third z axis. This result indicates that the third minimum is at least 100 cm^{-1} above the two more stable configurations. Liehr[14] has discussed a case in which a slightly distorted octahedral complex can show only one stable distortion. The results reported here suggest that conditions exist under which two stable distortions prevail.

If the g values are interpreted on the basis of a tetragonal distortion, then $-\lambda/\Delta_{xy}$ and $-\lambda/_{xz,yz}$ at low temperatures are 0.034 ± 0.001 and 0.032 ±0.004, respectively. At 350°K, $-\lambda/\Delta$ is 0.033 ± 0.003. With Δ = 14,900 cm^{-1} the effective spin–orbit coupling constant is about −492 cm^{-1}. In this case the low value of the effective spin–orbit coupling constant relative to the free-ion value of −828 cm^{-1} may be associated pri-

(14) A. D. Liehr, *J. Phys. Chem.*, **67**, 389 (1963).

marily with covalency effects.[4] The appearance of nitrogen superhyperfine structure also supports this conclusion. In general, the magnetic parameters indicate that the extent of covalency is comparable to that found in other copper complexes.[15-18] A recent discussion of the relationship between the magnetic properties and covalency in transition metal ions can be found in the review of Owen and Thornley.[19]

The Optical Results.—The absorption bands observed in copper-doped tris(phenanthroline)zinc(II) nitrate dihydrate are similar to those reported by Jørgensen[20] for solutions containing phenanthroline and copper nitrate in a mole ratio greater than 3. Jørgensen reported a band centered around 14,900 cm^{-1} with an extinction coefficient of ≈ 50, and an additional absorption which set in near the low-energy end of the spectral region was studied. In solution we find a band centered at 7000 cm^{-1} with an extinction coefficient of ≈ 35. The ratio of the extinction coefficients for these two bands did not vary when the mole ratio of phenanthroline to copper nitrate was 3.5 or greater. Thus the bands at 14,900 and 7000 cm^{-1} are associated with the same species. Additional evidence for this latter interpretation is provided by our epr studies of the frozen solutions. When a large excess of phenanthroline was present, the epr spectrum was characteristic of a single species.[2] When the phenanthroline to copper ratio was less than 3.5, the epr spectra of these solutions indicated that more than one species was present.

The 14,900-cm^{-1} band with an extinction coefficient of about 50 is typical for a d–d transition in a nearly octahedral copper complex. The 7000-cm^{-1} band is also assigned as a d–d transition. This latter assignment is in accord with predictions of Liehr and Ballhausen as well as O'Brien. They show that a Jahn–Teller distortion can result in the splitting of the E_g octahedral degeneracy of about 7000 cm^{-1}.

The polarized optical spectra of single crystals of copper-doped tris(phenanthroline)zinc nitrate dihydrate showed that the 14,900-cm^{-1} band is split and at 77°K the maxima occur at 14,700 and 15,200 cm^{-1} along the directions of minimum and maximum integrated intensity, respectively. The observed polarization properties of these absorption bands cannot be made to conform to a simple tetragonal distortion in which the observed magnetic z axes correspond to the principal molecular axis. This leads to the important result that the optical and magnetic axes do not coincide. An unambiguous assignment of electronic energy levels cannot be attempted without the detailed crystal structure. If the assumption is made, however, that the two magnetic axes and the normal to the plane defined by these axes lie in the direction of copper–nitrogen bonds, then the a direction (Figure 3) could correspond to a trigonal axis of the molecule. The observed polarization properties of this complex would then be similar to those reported for the $Cu(bipy)_3^{2+}$ system by Palmer and Piper.[9] Such a trigonal model for the optical data would appear to conflict with the essentially tetragonal model proposed for the magnetic data. It is interesting to note that although Palmer and Piper assigned the electronic transition in $Cu(bipy)_3^{2+}$ on the basis of trigonal symmetry, they pointed out that their epr data are not readily reconciled with the conclusion of essentially trigonal symmetry.

Conclusions

Magnetic and electronic spectra of copper-doped tris(phenanthroline)zinc(II) nitrate dihydrate have been obtained. The principal results and conclusions of this investigation follow.

(1) The temperature variation of the epr spectra indicated that the distorted configurations were separated by relatively high-energy barriers which are consistent with the assumptions made by Hudson.[8] However, only two rather than the expected three equivalent distortions were observed which indicates that existing theoretical models cannot be applied in detail to this complex.

(2) The ligand superhyperfine structure observed at 77°K is consistent with the assignment of the ground state as primarily $d_{x^2-y^2}$ and suggests that the symmetry is approximately tetragonal. This observation is inconsistent with the application of the trigonal model since the latter symmetry would require equivalence of the six nitrogen ligands.

(3) Electronic transitions were observed near 7000 and 15,000 cm^{-1}. These transition energies are approximately equal to those reported by Palmer and Piper for the $Cu(bipy)_3^{2+}$ complexes. The optical axes did not coincide with the principal magnetic axes. This result is consistent with the tentative interpretation of previous optical and magnetic studies of some tris copper complexes but a satisfactory theoretical model accounting for both these observations is not presently available.

(4) The gross features of the optical and magnetic data are in accord with a model based on the dynamical Jahn–Teller effect. However, the detailed features of the experimental results do not conform with existing models.

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(16) R. Neiman and D. Kivelson, *ibid.*, **35**, 149, 156, 162 (1962).

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