

also, which indicates that the effect cannot arise solely in the excited state. Since the observation of stereoselectivity was found only in the energy-transfer results, it may be concluded that the other measurements are not sufficiently sensitive to detect the effect. Our previous work^{12,13} has shown that intermolecular energy transfer is the most sensitive technique for probing polynuclear association among lanthanide complexes in solution, and the present work indicates how effective the method can be. It is concluded here that a stereoselective association of lanthanide complexes derived from potentially chiral ligands exists in the hydrolysis region but that only sensitive emission measurements are able to detect this association. Further studies are under way to examine these stereoselective effects in greater detail.

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Registry No. Tb^{3+} , 22541-20-4; Eu^{3+} , 22541-18-0; DL-Asp, 617-45-8; D-Asp, 1783-96-6; L-Asp, 56-84-8; Ho^{3+} , 22541-22-6.

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Polarized Crystal Spectrum of Bis(methylphenethylammonium) Tetrachlorocuprate(II): Analysis of the Energies, Vibrational Fine Structure, and Temperature Dependence of the "d-d" Transitions of the Planar $CuCl_4^{2-}$ Ion

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The electronic spectra of two crystal faces of bis(methylphenethylammonium) tetrachlorocuprate(II) are reported. The polarization properties of the transitions suggest the d-orbital energy sequence $d_{x^2-y^2} \gg d_{xy} > d_{xz} > d_{yz} > d_{z^2}$ for the planar, centrosymmetric $CuCl_4^{2-}$ ion present in this compound. The d-orbital energies are in agreement with a simple angular-overlap treatment of the bonding in a square-planar complex, except that the d_{z^2} orbital is $\sim 5000\text{ cm}^{-1}$ lower in energy than expected. This depression is rationalized in terms of configuration interaction with the copper 4s orbital. At low temperature, each band in the electronic spectrum exhibits considerable vibrational fine structure. The three lower energy transitions each consist of a single progression, and this is assigned to the a_{1g} stretching mode. The spacing is in each case $\sim 272\text{ cm}^{-1}$, and the half-widths of the components are $\sim 140\text{ cm}^{-1}$. The relative intensities of the components in y polarization imply a lengthening of the Cu-Cl bonds of $\sim 8.9 \pm 0.3\text{ pm}$ in these excited states, while the overall temperature dependence of the bands suggests that the intensity in each case is probably induced largely by coupling with the out-of-plane bending mode of b_{2u} symmetry with this having an energy of $\sim 105\text{ cm}^{-1}$. The highest energy band in xy polarization consists of four progressions, three of these being much weaker and sharper (half-widths $\sim 30\text{ cm}^{-1}$) than the fourth (half-width $\sim 120\text{ cm}^{-1}$). Each of these progressions is also assigned to the a_{1g} mode with an energy of $\sim 267\text{ cm}^{-1}$. The relative intensities of the components imply a lengthening of the Cu-Cl bond of $\sim 10.3 \pm 0.3\text{ pm}$ in this excited state. The separations between the progressions suggest that the bulk of the intensity at 10 K is derived by coupling with the in-plane stretching mode of e_u symmetry (energy 188 cm^{-1}), with the three weaker progressions being assigned to coupling with lattice modes of energy 108, 63, and $\sim 20\text{ cm}^{-1}$. The overall temperature dependence of the band is consistent with this interpretation. The three sharper progressions show a marked broadening of their components as the energy of the peaks increases, and this is rationalized in terms of the different vibrational frequencies expected for the various isotopic isomers expected for the $CuCl_4^{2-}$ ion. Although the energies of the a_{1g} mode are lower in the excited electronic states than those in the ground state (276 cm^{-1}), the difference is not as large as might be expected from the changes in the Cu-Cl bond lengths. It is possible that this results from a distortion toward a tetrahedral geometry in the excited electronic states.

Introduction

The tetrachlorocuprate(II) ion generally has either a flattened tetrahedral geometry or a tetragonally distorted octahedral arrangement of chloride ions about the copper(II).¹ Recently, however, it was found that the compound $(C_6H_5CH_2CH_2NH_2CH_3)_2CuCl_4$, (nmph)₂CuCl₄, contains discrete, planar $CuCl_4^{2-}$ ions in which no axial ligation is present.² The assignment of the energy levels in this complex is particularly

important, first because there are widely conflicting theoretical predictions³⁻⁷ concerning the d-orbital energies in this ion and second because a comparison with the energy levels of chlorocuprate(II) complexes having other geometries should provide a useful test of the self-consistency of simple models used to describe the bonding in transition-metal complexes.^{8,9}

The complex (nmph)₂CuCl₄ is also unusual in that preliminary investigations of the low-temperature electronic

spectra of single crystals revealed considerable vibrational fine structure.¹⁰ Structure of this kind is not usually observed in the spin-allowed "d-d" spectra of centrosymmetric metal complexes as several ungerade vibrational modes are generally responsible for inducing intensity, and the resulting peaks overlap to produce a smooth, featureless band envelope.¹¹ Among the few complexes for which fine structure comparable to that seen for (nmph)₂CuCl₄ is observed are the analogous ions PdCl₄²⁻ and PtCl₄²⁻, and the electronic spectra of these have been the subject of numerous investigations.¹²⁻¹⁷ The analysis of vibrational structure of this kind has been found to provide important information on the geometries of the complexes in their excited electronic states, as well as on the mechanisms by which the "d-d" transitions gain their intensity.^{11,14,15,18}

The present paper describes the electronic spectra of two crystal faces of (nmph)₂CuCl₄ and their resolution into the molecular spectra of the CuCl₄²⁻ ion. The excited-state energies are deduced and compared with those of other chlorocuprate(II) compounds by using the angular-overlap simple molecular orbital model. The vibrational fine structure and temperature dependence of the bands have been analyzed and used to deduce the probable bond lengths of the complex in the excited electronic states, as well as the nature of the ungerade vibrations inducing the intensity in the "d-d" transitions.

Experimental Section

The complex was prepared by mixing equimolar methanolic solutions of the amine hydrochloride and CuCl₂·2H₂O. Anal. Calcd for [C₆H₃CH₂CH₂NH₂CH₃]₂CuCl₄: C, 45.25; H, 5.91; N, 5.86. Found: C, 45.30; H, 5.84; N, 5.71. Large, well-formed crystals were obtained by slow diffusion of an acetone solution of the complex into ether. At room temperature the compound crystallizes in the monoclinic space group *P*2₁/*c* (a high-temperature modification of the complex also exists, in which flattened tetrahedral CuCl₄²⁻ groups occur²). The crystals generally formed as thick plates with the (010) face well developed.

Electronic spectra of the (010) face were obtained by slicing suitable crystals and mounting the resulting sections (typical dimensions ~5 × 3 × 0.1 mm) over a hole in an aluminum foil mask by using a spot of silicone grease. The extinction directions of the crystal face were found to lie at angles of +6 and -84° to the *a* axis, the + sign corresponding to a rotation of the electric vector into the quadrant containing an obtuse angle. These directions were not observed to vary as a function of either wavelength or temperature. A second crystal face, designated face X, was obtained by slicing large crystals to produce a section containing the *b* crystal axis and cutting the (010) plane at an angle of +45° to the *a* axis. Two such faces were studied in detail (dimensions ~3 × 2 × 0.1 mm). The morphology was checked by measuring the EPR spectrum of each face, the single-crystal EPR spectrum of (nmph)₂CuCl₄ being well characterized.¹⁹ Electronic spectra were measured over a temperature range with the electric vector of light along each of the crystal extinction directions by using a Cary 17 spectrophotometer (the spectrum of one face of type X was also recorded on a McPherson spectrometer with identical results). The crystals were cooled with an Oxford Instruments CF200 cryostat, and the light was polarized with a Glan-Thompson polarizer. Temperatures were measured with two carbon resistors, placed one above and one below the sample. Thicknesses of the various faces were measured with a graduated microscope eyepiece and were estimated to be accurate to ±10%. The spectral band-pass was found to be always significantly less than the half-widths of the observed peaks. Base line corrections were made by repeating the measurements after removal of the crystals. Infrared spectra were measured over the range 50–500 cm⁻¹ as Nujol mulls between polythene windows with a Perkin-Elmer 80 spectrometer. Raman spectra were measured on a Cary 82 spectrometer by using the 514.5-nm excitation line of an argon laser.

Results and Discussion

Derivation of the Molecular Spectra. The single molecule in the asymmetric unit of (nmph)₂CuCl₄ is rigorously centrosymmetric with two slightly different Cu–Cl bond lengths

Table I. Molecular Projections Made by an Electric Vector along the Extinction Directions of the (010) and X Crystal Faces

crystal face	angle, ^a deg	<i>x</i> ²	<i>y</i> ²	<i>z</i> ²
010	+6	0.6102	0.0007	0.3891
	-84	0.1996	0.5188	0.2817
X	+45	0.1066	0.2241	0.6693
	+90	0.1876	0.4821	0.3303

^a Angle made with the *a* axis; where relevant, a positive sign indicates a rotation in the (010) plane into the quadrant containing the obtuse angle.

(224.8 and 228.1 pm) and ClCuCl bond angles which differ from 90° by less than one standard deviation. No bonding interactions occur out of the plane of the CuCl₄²⁻ ion, so that the copper is truly four-coordinate.² Crystallographically, the symmetry about the copper(II) ion is *C*₁. However, considering just the CuCl₄²⁻ unit, this belongs to the *D*_{2h} point group, with the departure from *D*_{4h} symmetry being caused by the relatively small difference between the two Cu–Cl bond lengths. The molecular coordinate system used to interpret the electronic spectrum was defined with *x* along the shorter Cu–Cl bond direction, *z* orthogonal to *x* and the second Cu–Cl bond direction, and *y* orthogonal to *x* and *z*. The matrix which transforms a vector expressed in an orthogonal set of crystal coordinates defined by the relationships

$$a' = a \sin \beta^* \quad b' = b \quad c' = c - a \cos \beta^*$$

into molecular coordinates is

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -0.5790 & -0.4332 & 0.6907 \\ 0.2743 & 0.6943 & 0.6653 \\ 0.7678 & -0.5747 & 0.2833 \end{bmatrix} \begin{bmatrix} a' \\ b' \\ c' \end{bmatrix}$$

The molecular projections made by an electric vector lying along the extinction directions of the (010) and X crystal faces are given in Table I.

The mathematical procedure used to derive the molecular spectra from those measured on the crystal faces has been described in detail elsewhere.²⁰ This consists essentially of solving the set of equations obtained from the four crystal spectra

$$x_i^2 \epsilon_x + y_i^2 \epsilon_y + z_i^2 \epsilon_z = D_i / ct$$

where *x*_{*i*}² etc. represent the molecular projections, *D*_{*i*} is the measured optical density, *c* is the concentration of metal ions, *t* is the crystal thickness, and ϵ_x , ϵ_y , and ϵ_z are the desired molecular extinction coefficients. The whole process is repeated at as many wavelengths as is necessary to fully resolve the spectra. The experimental points from the (010) and X crystal faces measured at 10 K are shown in Figure 1, and the molecular spectra derived from these are shown in Figure 2. The accuracy with which the molecular spectra can be defined depends not only upon the quality of the crystal spectra but also upon the degree of independence of the set of equations which must be solved to produce them, that is, upon the extent to which the relative magnitudes of the projections *x*_{*i*}², *y*_{*i*}², and *z*_{*i*}² change with the polarization direction. This in turn depends upon the orientation of the molecules in the unit cell. It can be seen from Table I that in the (010) plane the major change occurs between the *x* and *y* molecular axes. Unfortunately, the molecular packing is such that the *z* molecular spectrum is never well resolved. Face X was chosen to maximize the resolution of this projection. This "packing problem", which has sometimes meant that it is impossible to fully resolve molecular from crystal spectra,²¹ is probably responsible for the comparatively poor quality of the molecular spectra of (nmph)₂CuCl₄. The reliability of the spectra was checked by repeating the process on a second pair of crystal faces. The spectrum of the second (010) face was found to be identical

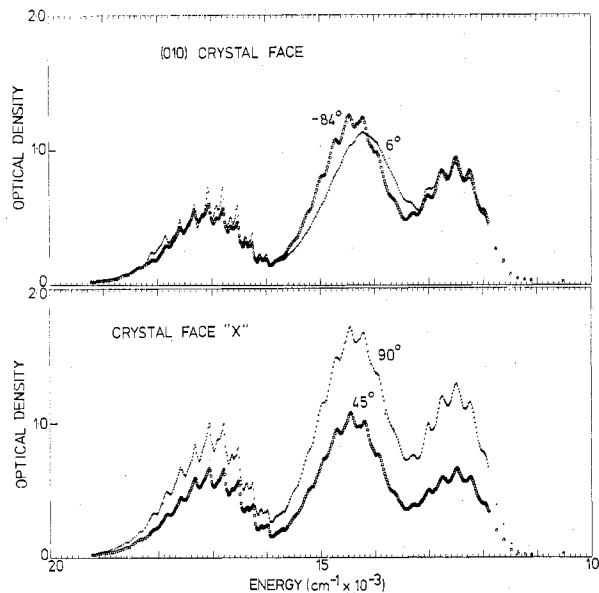


Figure 1. Experimental points from the polarized electronic spectra of the (010) crystal face and a crystal face of type X of $(nmpH)_2CuCl_4$ measured at 10 K. The angles made by the electric vector of light with the a crystal axis are shown with a positive sign indicating rotation into a quadrant of the (010) plane containing an obtuse angle.

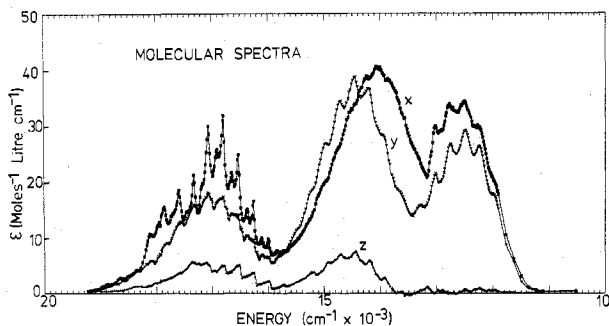


Figure 2. Molecular spectra of the planar $CuCl_4^{2-}$ ion in $(nmpH)_2CuCl_4$.

with that of the first; the spectrum of the second face of type X, shown measured over a temperature range in Figure 3, differed from that of the first solely in the slightly greater relative intensity of the highest energy peak in 45° polarization. The only significant difference in the molecular spectra derived from the second pair of crystal faces was a slightly greater relative intensity of the highest energy band in z polarization.

Assignment of the Excited-State Band Energies. On the assumption of D_{2h} symmetry for the chromophore in $(nmpH)_2CuCl_4$, the only transitions to be forbidden by the electric dipole vibronic selection rules are ${}^2B_{1g}(xy) \leftarrow {}^2A_g(x^2 - y^2)$ in z polarization, ${}^2B_{2g}(xz) \leftarrow {}^2A_g(x^2 - y^2)$ in y polarization, and ${}^2B_{3g}(yz) \leftarrow {}^2A_g(x^2 - y^2)$ in x polarization (the unpaired electron in each case occupying the d orbital indicated in parentheses). The polarization properties of the bands in the molecular spectra are clearly in agreement with these selection rules, with three of the four bands each being absent in a different polarization (Figure 2). The band maxima therefore suggest the following assignments of the excited-state energies: ${}^2B_{1g}(xy)$ at $12\,500\text{ cm}^{-1}$, ${}^2B_{2g}(xz)$ at $14\,050\text{ cm}^{-1}$, ${}^2B_{3g}(yz)$ at $14\,450\text{ cm}^{-1}$, ${}^2A_g(z^2)$ at $17\,000\text{ cm}^{-1}$.

It is interesting to note that the z spectrum is considerably weaker in intensity than that in xy polarization. This would seem to be a general feature of many copper(II) complexes with planar or tetragonal geometries.²² Simple vibronic theory suggests that in a complex like $CuCl_4^{2-}$ the intensity is "stolen" from ligand \rightarrow metal charge-transfer transitions.¹¹ It has been

suggested by Belford^{20,23} that when there is a large overall difference in intensity with polarization, this may be because a particular charge-transfer transition dominates in the intensity-stealing process. In the present case, neglecting for the moment the departure from D_{4h} symmetry, the z intensity comes from transitions to B_{2u} states, while the xy intensity comes from those to E_u states. In planar $CuCl_4^{2-}$ there is only one state of B_{2u} symmetry, derived from the out-of-plane π orbitals on the chloride ions, but two states of E_u symmetry, one derived from the in-plane π orbitals and one from the σ orbitals of the chloride ion. It may be noted that the intensities of the "d-d" transitions of planar complexes of copper(II) and nickel(II) with aliphatic amines, where covalent π -bonding interactions must be negligible, are quite similar to those observed for $(nmpH)_2CuCl_4$.^{24,25} This suggests that in all of these compounds the bulk of the intensity is probably "stolen" from the xy -polarized ligand \rightarrow metal charge-transfer transition originating from the e_u σ -bonding orbitals.

Interpretation of the d-Orbital Energies. The assignment of the excited-state energies suggests the d-orbital energy sequence $d_{x^2-y^2} \gg d_{xy} > d_{xz} > d_{yz} > d_z$ for the planar $CuCl_4^{2-}$ ion. This agrees with the interpretation of the molecular g values of this ion,¹⁹ and also with some theoretical calculations,^{3,7} though not with others.⁴⁻⁶ Because of their comparatively simple electronic structure and the wide range of stereochemistries which they exhibit, chlorocuprate(II) complexes have often been used to test the self-consistency of simple models of the bonding in metal complexes.^{8,9,26} One of the most useful bonding schemes of this kind is the angular-overlap model (AOM) developed by Jørgensen and Schäffer.^{27,28} The AOM relates the energy e by which a d orbital is raised upon interaction with a ligand orbital to the square of the diatomic overlap integral S as in eq 1, where K

$$e = KS^2 \quad (1)$$

is a constant dependent upon the nature of the metal and the ligand.²⁷ Both σ and π interactions are considered, and the total energy of each d orbital, E , is obtained by summation of the effects of all the ligands by using the angular-overlap matrix appropriate to the geometry of the complex in question. For a planar complex such as $CuCl_4^{2-}$, the d-orbital energies are given by eq 2. Here e represents the energy by which a

$$E(x^2 - y^2) = 3(e_\sigma(x) + e_\sigma(y))/2 \quad (2a)$$

$$E(xy) = 2e_\pi(x) + 2e_\pi(y) \quad (2b)$$

$$E(xz) = 2e_\pi(x) \quad (2c)$$

$$E(yz) = 2e_\pi(y) \quad (2d)$$

$$E(z^2) = (e_\sigma(x) + e_\sigma(y))/2 \quad (2e)$$

d orbital is raised by the σ or π interaction with one ligand situated along the axis indicated in parentheses. For an isotropic ligand such as Cl^- , the AOM in this simple form predicts that the metal-ligand interaction can be represented by a single constant K , with the differences in σ and π interaction and bond length being accommodated by the variation in the overlap integral S . Substitution in eq 1 and 2a-e of the values $S_\sigma^2 = 6.56 \times 10^{-3}$, $S_\pi^2 = 1.75 \times 10^{-3}$ and $S_\sigma^2 = 6.1 \times 10^{-3}$, $S_\pi^2 = 1.54 \times 10^{-3}$ estimated²⁹ for the Cu-Cl bond lengths of 224.8 and 228.1 pm in $(nmpH)_2CuCl_4$, respectively, allows the excited-state energies to be calculated as a function of K , and the excited-state energies estimated in this manner are shown in Figure 4. Reasonable agreement with experiment is obtained for $E(xy)$, $E(xz)$, and $E(yz)$ on the assumption of a value of $K = 0.95 \times 10^6\text{ cm}^{-1}$. This is in excellent agreement with the value $K = 0.94 \times 10^6\text{ cm}^{-1}$ obtained by fitting the excited-state energies of a series of chlorocuprate(II) complexes with stereochemistries ranging from distorted tetrahedral through tetragonal octahedral to

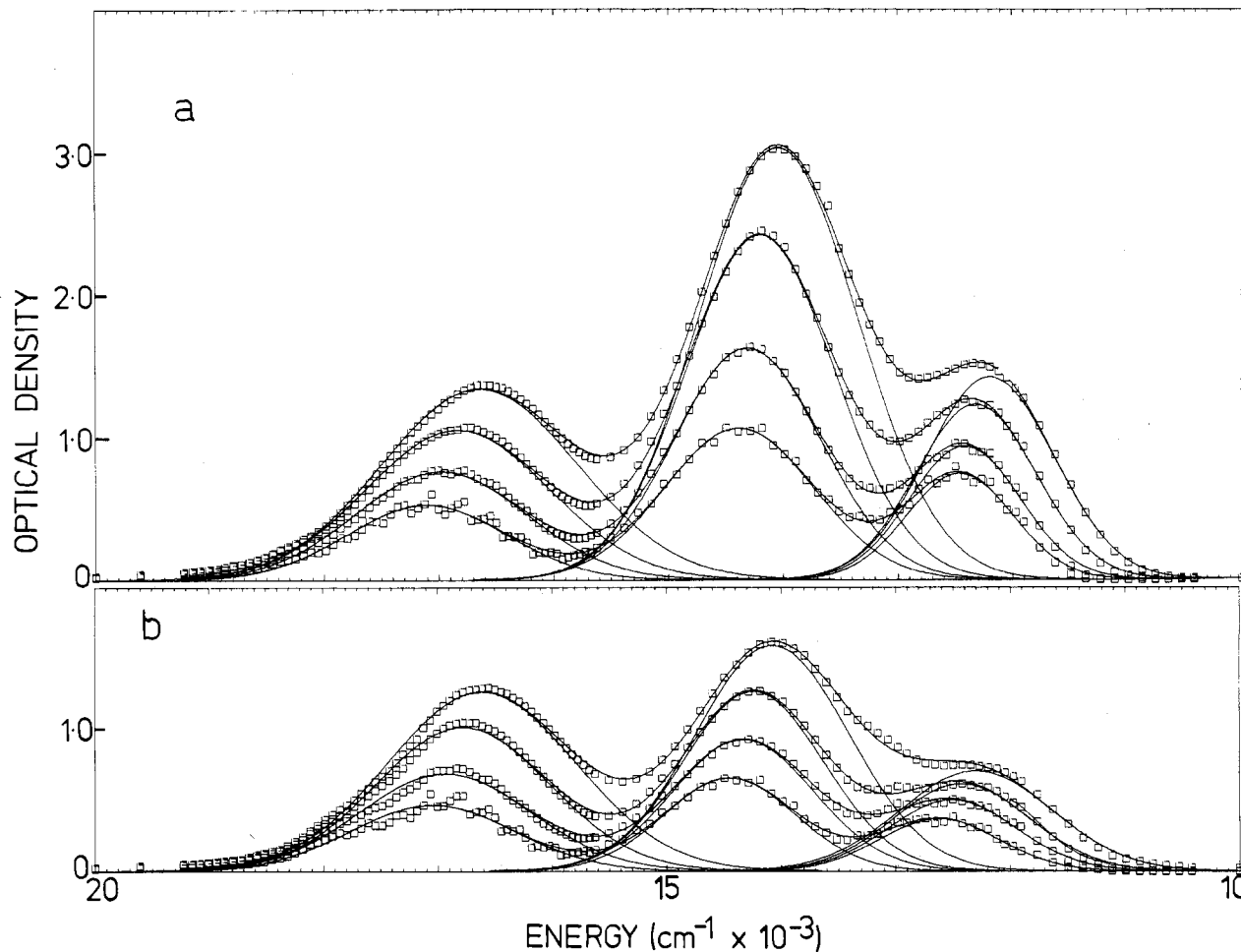


Figure 3. Experimental points and best-fit Gaussian curves for the electronic spectra of a crystal face of type X of $(nmph)_2CuCl_4$ with the electric vector (a) along the b crystal axis and (b) at an angle of 45° to the a axis in the (010) plane. The four pairs of spectra were measured at temperatures of 10, 77, 120, and 185 K, the intensities in each case increasing regularly with temperature.

trigonal bipyramidal.⁹ However, this value of K places $E(z^2) \sim 5000 \text{ cm}^{-1}$ lower in energy than the observed transition to this state in $(nmph)_2CuCl_4$. In fact, the AOM predicts similar energies for the d_{z^2} and d_{xy} orbitals in a planar complex of this kind. This is because the energy ratio $E(z^2)/E(xy) = e_\sigma/4e_\pi$ (see eq 2b and 2e); as $S_\sigma \approx 2S_\pi$, the σ bonding with the d_{z^2} orbital should about match the π -bonding interaction with the d_{xy} orbital for a planar complex with a ligand such as Cl^- . The very high energy of the transition ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ suggests that the d_{z^2} orbital is hardly raised in energy at all in $(nmph)_2CuCl_4$ and is probably even shifted to lower energy by $\sim 1000 \text{ cm}^{-1}$ on complex formation. Smith has suggested that an effect of this kind is to be expected in a truly planar copper(II) complex because of configuration interaction between the $a_g(d_{z^2})$ and $a_g(4s)$ orbitals.³⁰ The extent of this interaction depends on the difference in metal-ligand bonding along z and in the xy plane. Because of the diffuse nature of the $4s$ orbital, this difference is only large when axial ligation is completely absent. Thus, in a complex such as $(C_2H_5NH_3)_2CuCl_4$, which contains planar $CuCl_4^{2-}$ units ($Cu-Cl$ lengths 229 pm) linked by long axial bonds ($Cu-Cl$ lengths 304 pm),³¹ the excited state energies $E(xy) = 12390 \text{ cm}^{-1}$, $E(xz, yz) = 13300 \text{ cm}^{-1}$, and $E(z^2) = 11130 \text{ cm}^{-1}$ ¹⁹ fit the energy scheme suggested by the simple AOM quite well (see Figure 4). Although distant axial ligands therefore have little *direct* effect on the d orbitals, it seems clear that a significant indirect effect is present and that simple perturbation bonding schemes such as the AOM or a crystal field approach,²⁶ which limit their attention solely to the metal d orbitals, cannot adequately account for the energy of the d_{z^2} orbital in a planar

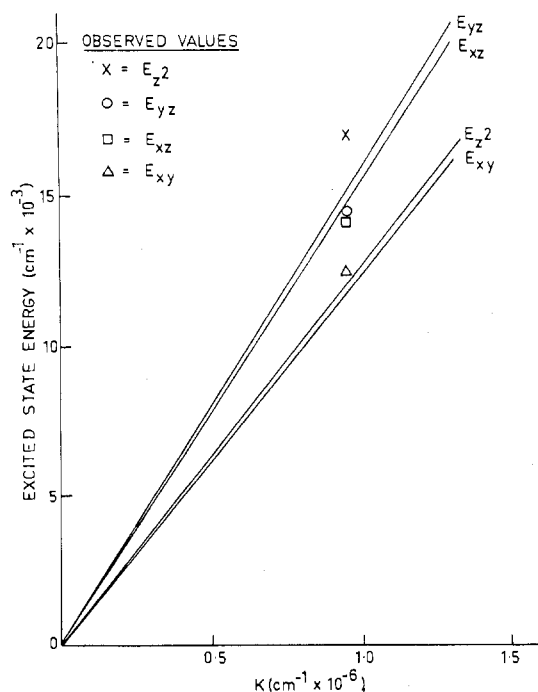


Figure 4. Plot of the excited-state energies of planar $CuCl_4^{2-}$ as a function of the angular overlap parameter K .

metal complex. If the energy of the $4s$ orbital is $\sim 80000 \text{ cm}^{-1}$ relative to the $3d$ orbitals,³² a depression of $\sim 5000 \text{ cm}^{-1}$ of

the $a_g(d_{z^2})$ orbital indicates a coefficient of ~ 0.25 for the copper 4s orbital in this wave function. This figure agrees well with estimates of the 4s orbital participation in the $a_{1g}(d_{z^2})$ ground-state wave functions of various planar cobalt(II) complexes obtained by EPR spectroscopy.³³ Although the assignment of the $a_{1g}(d_{z^2})$ orbital energies in the analogous $PdCl_4^{2-}$ and $PtCl_4^{2-}$ ions has been the subject of some controversy,¹²⁻¹⁷ it seems likely that a similar depression occurs here also. Moreover, recent studies of the electronic structures of planar nickel(II)²⁴ and iron(II)²⁴ complexes also indicate an anomalously low energy for the d_{z^2} orbital, suggesting that this is probably a general feature of square-planar transition-metal complexes.

Assignment of the Vibrational Fine Structure. Below ~ 100 K the spectrum of $(nmph)_2CuCl_4$ shows vibrational fine structure on each of the main bands (Figures 1-3). At 10 K the three lower energy bands each consist of a regular progression in a single vibrational frequency, while the highest energy band exhibits four separate progressions in approximately the same vibrational frequency. It is generally accepted that in centrosymmetric complexes the intensity of the Laporte forbidden "d-d" transitions is derived from higher energy allowed transitions via coupling with u vibrational modes of the complex.^{11,35} The theory of vibronic coupling suggests that at temperatures close to 0 K each "d-d" transition involves the excitation of the electronic wave function plus one quantum of the vibrational mode inducing the intensity. On the assumption that only a single u mode is active, if the ground and excited electronic states have identical equilibrium geometries, each transition should give rise to a single spectral peak. However, if the equilibrium geometry of the excited state differs from that of the ground state, which will almost always be the case, then quanta of the vibrational mode which converts the ground-state geometry into that of the excited state will also be excited. If the bond lengths change uniformly, the a_g "breathing" mode will be excited, while if the shape alters, the mode which converts the ground-state shape into that of the excited state may be promoted. In either case, the result will be a progression in which the overall band intensity results from the overlap between the electronic wave functions perturbed by the u vibrational mode or modes, while the intensities of the individual component peaks depend on the overlap between the vibrational wave functions concerned with the change in geometry.¹¹ According to the Franck-Condon principle, this process can be represented by vertical transitions connecting the potential energy surfaces of the ground and excited electronic states drawn as a function of the normal mode involved in the progression. This is illustrated in Figure 5 for the a_g mode by using the estimated vibrational frequencies and change in bond length for the lowest energy electronic transition of $(nmph)_2CuCl_4$.

A cursory examination of the spectra shows that all the progressions are regular, the spacings between the peaks being in each case ~ 265 cm^{-1} . This implies that the progressions occur in the same vibrational mode in each excited electronic state. In order to identify this mode it is necessary to consider the probable geometry of the $CuCl_4^{2-}$ ion in its excited electronic states. Since each transition involves promotion of an electron to the σ -antibonding $d_{x^2-y^2}$ orbital it is highly probable that the Cu-Cl bonds will be longer in every excited state. This implies that a progression in the a_g stretching mode is quite likely. However, the isolated $CuCl_4^{2-}$ ion generally has a flattened tetrahedral geometry¹ (indeed above ~ 350 K $(nmph)_2CuCl_4$ exists in a crystal modification containing this form of the ion²). Since a planar geometry is only strongly favored by metal-ligand interactions when the unpaired electron occupies the $d_{x^2-y^2}$ orbital, it seems plausible that in the excited electronic states the $CuCl_4^{2-}$ ion could well have

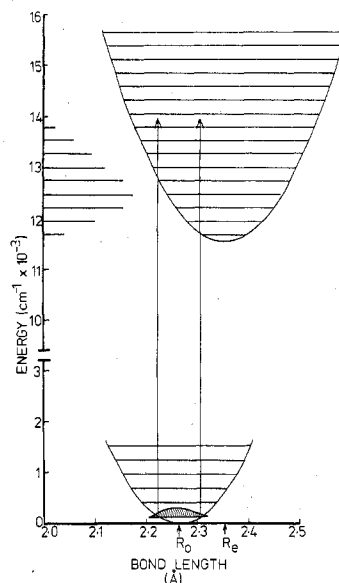


Figure 5. Diagram of the potential energy surfaces of the ground and first excited electronic state of planar $CuCl_4^{2-}$. R_0 and R_e indicate the equilibrium Cu-Cl bond lengths in the ground and excited states. The observed intensities of the transitions to the first nine vibrational levels of the a_{1g} mode of the excited state are shown, as well as the form of the wave function of the 0 vibrational state of the ground state.

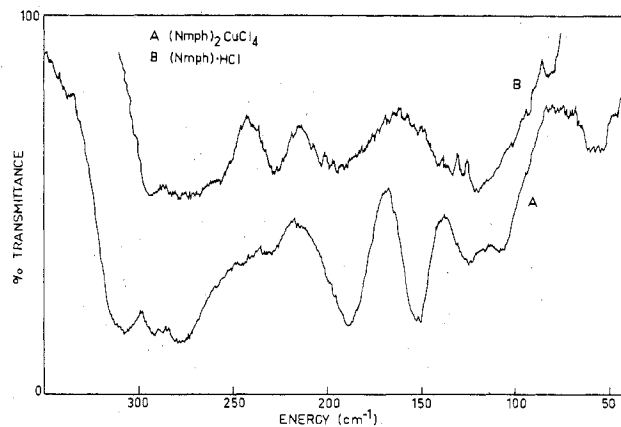


Figure 6. Infrared spectrum of a Nujol mull of $(nmph)_2CuCl_4$ together with that of the cation hydrochloride for comparison.

a distorted tetrahedral structure. This would imply that the progressions could be in the out-of-plane bending mode (b_{2u} in D_{4h} symmetry; as no effects due to the inequivalence of the Cu-Cl bonds could be detected in the infrared or Raman spectra of $(nmph)_2CuCl_4$, this point group will be used to discuss the vibrational spectrum of the compound). In order to assign the ground-state vibrational frequencies of the planar $CuCl_4^{2-}$ ion, the Raman and far-infrared spectra of $(nmph)_2CuCl_4$ were recorded. The infrared spectrum of the compound, together with that of the cation hydrochloride for comparison, is shown in Figure 6. The vibrational frequencies attributed to the $CuCl_4^{2-}$ group, and their assignments, are shown in Table II, together with the corresponding frequencies reported for the analogous $PtCl_4^{2-}$ and $PdCl_4^{2-}$ ions for comparison. Unfortunately, the b_{2u} out-of-plane bending mode is both Raman and infrared inactive, so that the precise energy of this in $(nmph)_2CuCl_4$ is unknown. However, force-field calculations suggest an energy of 150 ± 30 cm^{-1} for this mode in $PdCl_4^{2-}$ and $PtCl_4^{2-}$, and an even lower value is likely in planar $CuCl_4^{2-}$. Thus, the observed fine structure in the electronic spectra of $(nmph)_2CuCl_4$ clearly cannot be a simple progression in the b_{2u} mode. It is conceivable that the pro-

Table II. Vibrational Frequencies of Planar CuCl_4^{2-} together with Those Reported for PtCl_4^{2-} and PdCl_4^{2-} for Comparison

mode ^a D_{4h} sym- metry	activity	motion	energies, ^g cm^{-1}		
			CuCl_4^{2-}	PdCl_4^{2-}	PtCl_4^{2-}
ν_1 (a_{1g})	Raman	sym str	276 s	310 s ^a	329 s ^e
ν_2 (b_{1g})	Raman	str	210 vw	275 w ^a	302 w ^e
ν_3 (a_{2u})	IR	out-of-plane bend	152 s	170 ^b	173 ^b
ν_4 (b_{2g})	Raman	in-plane bend	182 s	198 s ^a	194 mw ^e
ν_5 (b_{2u})	inactive	out-of-plane bend		(157 ^c)	(174, ^c 120 ^f)
ν_6 (e_u)	IR	str	~300 s	336 s ^d	325 ^b
ν_7 (e_u)	IR	in-plane bend	188 s	193 m ^d	195 ^b

^a Reference 36. ^b Reference 37. ^c Calculated value.¹⁵ ^d Reference 38. ^e Reference 39. ^f Calculated value.⁴⁰ ^g s = strong, m = medium, mw = medium weak, w = weak, vw = very weak.

^h Note that the assignments of ν_2 and ν_4 for PtCl_4^{2-} are as given in ref 15.

gressions involve just double excitations of this mode. However, the complete absence of any peaks midway between those composing the progressions, which would correspond to the excitation of an odd number of quanta of the b_{2u} mode, argues strongly against this assignment, and we shall not consider it further. The energy of the a_{1g} Cu-Cl stretching mode, 276 cm^{-1} , on the other hand, is very similar to the spacings in the electronic spectra ($\sim 265 \text{ cm}^{-1}$) making it highly likely that the progressions are in this mode of the excited electronic states. This assignment is supported by the fact that a strong progression in this mode is also seen in some of the electronic transitions of the PtCl_4^{2-} and PdCl_4^{2-} ions¹²⁻¹⁶ and that where vibrational fine structure has been observed in the spin-allowed "d-d" transitions of other metal complexes, it has usually involved this vibration.^{11,17,41}

In order to characterize the peaks comprising the vibronic progressions more accurately, the spectra in which these were best resolved were subjected to Gaussian analysis.⁴² The transitions to the ${}^2B_{3g}(yz)$, ${}^2B_{1g}(xy)$, and ${}^2B_{2g}(xz)$ states each exhibit a single regular progression, these being best resolved for the two former transitions in y polarization. The y spectrum was therefore analyzed over the range $10000\text{--}16000 \text{ cm}^{-1}$. It was assumed that each progression has a constant spacing and is composed of symmetrical Gaussian peaks with a constant half-width. The best fit to the observed spectral intensities was obtained with the first resolved component of ${}^2B_{1g}(xy) \leftarrow {}^2A_g(x^2 - y^2)$ at 11680 cm^{-1} (3.3) and that of ${}^2B_{3g}(yz) \leftarrow {}^2A_g(x^2 - y^2)$ at 13655 cm^{-1} (3.4); the progressional frequencies were 271.5 cm^{-1} (0.9) and 272.2 cm^{-1} (0.9), and the half-widths were 135.0 cm^{-1} (0.8) and 144.7 cm^{-1} (0.9), respectively. The standard errors are given in parentheses. The intensities of the components and the calculated spectrum are shown in Figure 7, and it can be seen that the agreement with the measured spectral intensities is good.

In y polarization both electronic transitions are formally allowed by vibrations of a_{2u} and b_{2u} symmetry,⁴³ and an isolated CuCl_4^{2-} ion has a single normal mode of each symmetry type (Table II). Since only a single progression is observed in each band, it follows for both electronic transitions either that a single u mode dominates in inducing intensity or that if both modes are active, the excited-state energy of the b_{2u} mode must be close to that of the a_{2u} mode (152 cm^{-1} in the ground state). However, the temperature dependence of the spectrum suggests that for each transition the energy of the perturbing u mode is considerably less than this, ~ 90 and $\sim 115 \text{ cm}^{-1}$ for ${}^2B_{3g}(yz) \leftarrow {}^2A_g(x^2 - y^2)$ and ${}^2B_{1g}(xy) \leftarrow {}^2A_g(x^2 - y^2)$, respectively (see following section). The most reasonable explanation is therefore that the bulk of the intensity of both these electronic transitions in y polarization

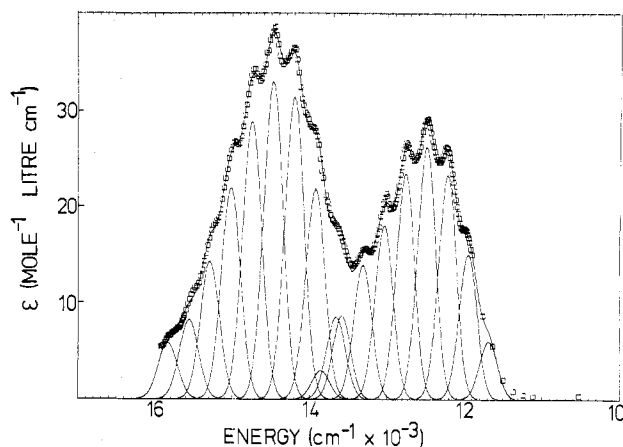


Figure 7. Experimental points and the calculated best-fit Gaussian curves and their sum for the vibrational progressions of the first two electronic transitions observed in the y molecular spectrum of $(\text{nmph})_2\text{CuCl}_4$ at 10 K.

is derived from coupling with the b_{2u} mode and that this has an energy of $\sim 105 \text{ cm}^{-1}$ in the ground state (judging by the behavior of the a_{1g} mode, the energy in the excited state should not be very different from this). In principle, the z spectrum should provide further information on the nature of the u-perturbing modes, as in this polarization the transitions ${}^2B_{2g}(xz)$, ${}^2B_{3g}(yz) \leftarrow {}^2A_g(x^2 - y^2)$ are allowed by vibrations of e_u symmetry. Unfortunately, however, the comparatively poor resolution of the z spectrum (Figure 2), combined with the fact that these transitions overlap strongly, precludes any analysis of the fine structure in this polarization. The above reasoning therefore suggests that at 10 K in x and y polarization the energy of each progressional peak of the transitions to the ${}^2B_{1g}(xy)$ and to the ${}^2B_{2g}(xz)$ or ${}^2B_{3g}(yz)$ states is given by eq 3, where $\bar{\nu}_0$ is the energy of the pure electronic transition

$$\bar{\nu} = \bar{\nu}_0 + \bar{\nu}_u + n\bar{\nu}_{a_{1g}} \quad (3)$$

(which is not observed), $\bar{\nu}_u$ is the energy of one quantum of the u-perturbing mode in the excited electronic state (in this case the b_{2u} mode, $\bar{\nu}_u \approx 105 \text{ cm}^{-1}$), $\bar{\nu}_{a_{1g}}$ is the energy of the a_{1g} mode in the excited electronic state ($\sim 272 \text{ cm}^{-1}$), and n is the number of quanta of this last mode excited in conjunction with the electronic transition. If, as seems likely, the first peak resolved in the ${}^2B_{1g}(xy) \leftarrow {}^2A_g(x^2 - y^2)$ transition corresponds to the vibronic origin ($n = 0$), then the following approximate values of $\bar{\nu}_0$ may be estimated: ${}^2B_{1g}(xy) \approx 11575 \text{ cm}^{-1}$, ${}^2B_{2g}(xz) \approx 13150 \text{ cm}^{-1}$, and ${}^2B_{3g}(yz) \approx 13550 \text{ cm}^{-1}$, with the most intense component in each case occurring at $n = 3$.

The highest energy band in $(\text{nmph})_2\text{CuCl}_4$ exhibits considerably more fine structure than those at lower energy. At 10 K, four separate progressions in the a_{1g} mode can be resolved, with at least one of these involving quite narrow peaks (half-widths $\sim 30 \text{ cm}^{-1}$; see Figures 1 and 2). In this situation it is possible that the differing vibrational frequencies associated with the two naturally occurring isotopes ${}^{35}\text{Cl}$ and ${}^{37}\text{Cl}$ (relative abundance 75 and 25%) may affect the spectrum. On the assumption of a statistical distribution of the two isotopes, for a complex such as CuCl_4^{2-} , a transition from the 0 to the n th vibrational state of the a_{1g} mode should be split into five peaks.¹⁶ In order of increasing energy, the intensities will be in the ratio 1:12:54:108:81, and the separation between each pair of peaks will be $n\delta \text{ cm}^{-1}$, where $\delta = \bar{\nu}(\text{Cu-}^{35}\text{Cl}_4)[1 - (35/37)^{1/2}]/4$. Substitution of the value $\bar{\nu}(\text{Cu-}^{35}\text{Cl}_4) = 265 \text{ cm}^{-1}$ yields the separation $\delta = 1.82 \text{ cm}^{-1}$. In the spectral analysis, each component peak was thus represented as a sum of five Gaussian curves with the above relative intensities and a separation between neighboring lines of $1.82n \text{ cm}^{-1}$, where n is the quantum number assigned to the a_{1g} level in the excited

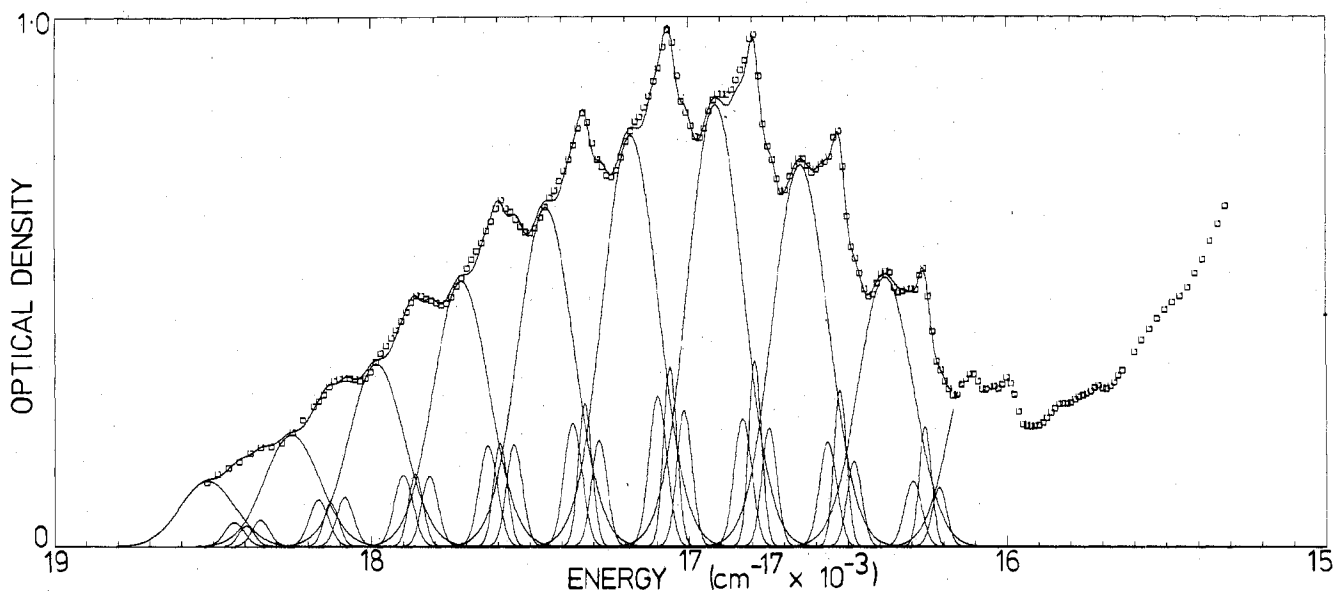


Figure 8. Experimental points and the calculated best-fit curves and their sum for the highest energy peak in the spectrum of a crystal face of type X in 90° polarization at 10 K. See the text for the way in which the component peaks were represented.

state. Since the resolution of the molecular spectra was comparatively poor, particularly in the higher energy region (Figure 2), a detailed analysis was only made of the 90° polarization spectrum of face X. Initially, the analysis was carried out on the three sets of best-resolved lines, occurring from 16 200 to 17 000 cm^{-1} . It was assumed that the progressions are regular and in the same excited-state frequency and that the first set of lines observed (occurring between 15 750 and 15 900 cm^{-1}) involve transitions to the $n = 0$ state. It was also assumed that the peaks in each progression are derived from components with a fixed half-width. Having used this analysis to estimate the basic half-widths of the Gaussian lines, the progressional frequency, and the origins of the peaks composing each progression, we calculated the "best-fit" intensities for the spectral range 16 200–18 600 cm^{-1} , corresponding to transitions to the vibrational states $n = 3$ to $n = 11$.⁴² The calculated spectrum, with the peaks obtained by summing the Gaussian components for each progression, are shown in Figure 8, together with the measured absorbances. The fit is reasonably good. Although the transitions of the individual isotopic forms of CuCl_4^{2-} are not resolved, as they have been in the fluorescence spectrum of PtCl_4^{2-} ,¹⁶ the model predicts a significant broadening of the three sharper peaks as the progressions move to higher energy, and this is borne out by experiment (Figure 8). The spectral simulations imply that the resolution of the fine structure of this band could be significantly improved by using isotopically pure ^{35}Cl , and it is hoped to measure the spectra of crystals prepared in this way in the near future. The energy of the a_{1g} mode of the excited state was estimated to be 268.9 cm^{-1} (0.6). This value applies to pure $\text{Cu}^{35}\text{Cl}_4^{2-}$; a value ~ 2 cm^{-1} lower would be expected for CuCl_4^{2-} with natural isotopic abundances. The energies of the first member of each progression were estimated to be 15 678.4 cm^{-1} (4.0), 15 722.9 cm^{-1} (1.3), 15 761.5 cm^{-1} (7.0), and 15 846.8 cm^{-1} (2.9), with the respective half-widths of the Gaussian components being 26.9 cm^{-1} (3.6), 22.6 cm^{-1} (2.1), 31.7 cm^{-1} (5.6), and 100.6 cm^{-1} (5.3), the standard errors being shown in parentheses.

The spectrum of the X crystal face in 90° polarization is dominated by the xy molecular spectra (Table I), and in these polarizations the transition ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ is allowed by vibrations of e_u symmetry.⁴³ At 10 K the bulk of the intensity of the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ band resides in one progression (initial member at 15 847 cm^{-1}). As the band

shows a large temperature dependence, it seems likely that this progression is induced by the lower energy metal–ligand e_u mode (ground-state energy 188 cm^{-1}). On the assumption of a similar frequency for e_u in the excited electronic state (as has been observed in PdCl_4^{2-}),¹⁵ substitution of this value for $\bar{\nu}_u$ in eq 3 implies an energy $\nu_{00} \approx 15 659$ cm^{-1} for the electronic origin of the ${}^2A_g(z^2)$ state. Substitution of the energies of the vibronic origins of the other three progressions in eq 3 indicates values of $\bar{\nu}_u \approx 19$, 64, and 103 cm^{-1} , respectively, for the u modes inducing intensity in each of these progressions. In agreement with this, peaks are observed at 57 and 108 cm^{-1} in the infrared spectrum of $(\text{nmph})_2\text{CuCl}_4$ (Figure 6), these being presumably due to lattice modes. It is therefore suggested that the three weaker progressions in the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition gain their intensity by coupling with lattice modes of effective e_u symmetry. It is noteworthy that peaks assignable to coupling with low-energy lattice modes (14–40 cm^{-1}) have also been observed in the low-temperature fluorescence spectrum of the PdCl_4^{2-} and PtCl_4^{2-} ions substituted in various host lattices.^{14,15} It is interesting that the half-width of the most intense progression is very similar to those occurring in the three lower energy bands, being ~ 4 times those of each of the other three progressions. The factors determining the widths of the individual vibronic peaks of the spin-allowed "d–d" transitions of metal complexes are at present obscure, but it would seem that in $(\text{nmph})_2\text{CuCl}_4$ the peaks induced by the metal–ligand vibrations are significantly broader than those induced by what are formally lattice modes. Unfortunately, the quality of the molecular spectra does not allow a detailed analysis of the polarization properties of the vibrational fine structure (Figure 2). However, it would seem that the major change in the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition on going from x to y polarization is in the relative intensities of the sharp peaks whose intensity has been assigned to coupling with lattice modes. This seems reasonable, as while the metal–ligand interaction changes very little in the xy plane, the environment of the CuCl_4^{2-} unit as a whole is quite different along the x and y axes.² In z polarization, the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition exhibits only a single progression, rather poorly resolved. The first member of this occurs at $15 760 \pm 30$ cm^{-1} . On the assumption that this represents the vibronic origin, the assignment of the electronic origin of the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition at $\bar{\nu}_{00} \approx 15 659$ cm^{-1} implies an energy of $\bar{\nu}_u \approx$

$100 \pm 30 \text{ cm}^{-1}$ for the mode-inducing intensity in this transition in z polarization. As modes of b_{2u} and a_{2u} symmetry may be active in this case, this agrees well with the energy estimated for the u -perturbing mode responsible for the intensity of the lower energy transitions in y polarization and implies that in each case it is the b_{2u} vibration which dominates the vibronic coupling process.

The planar arrangement of the CuCl_4^{2-} groups in $(\text{nmph})_2\text{CuCl}_4$ is thought to be stabilized by hydrogen bonding.² The amine hydrogens were therefore replaced by deuterium, with the idea that this might produce a shift in the lattice modes active in inducing intensity. However, the Raman spectrum of this complex in the range $300\text{--}100 \text{ cm}^{-1}$ and the electronic spectrum of the (010) face at 10 K were found to be indistinguishable from the undeuterated complex. Clearly the definitive assignment of the vibrational structure would be greatly helped if the quality of the molecular spectra could be improved. The major obstacle to this is the rather unfavorable orientation of the CuCl_4^{2-} groups in the unit cell. Attempts are therefore being made to grow crystals by using various cations similar to those in $(\text{nmph})_2\text{CuCl}_4$, in the hope that in one of these the planar arrangement of the CuCl_4^{2-} ions will be retained, but with a crystal packing more favorable to spectroscopic investigations.

Variation of the Band Intensities with Temperature. Simple vibronic theory suggests that for a centrosymmetric complex the intensity f of a "d-d" electronic transition is related to temperature T by the expression¹¹

$$\coth^{-1}(f/f_0) = h\nu/2kT$$

where f_0 is the intensity at 0 K, k is the Boltzmann constant, and ν is the frequency of the u -perturbing mode. A plot of $\coth^{-1}(f/f_0)$ against $1/T$ should therefore yield a straight line passing through the origin, with a slope proportional to ν . If more than one mode is active in inducing intensity, the value of ν suggested by the temperature dependence will represent an "average" value dependent on the effectiveness and frequencies of the perturbing modes. Unfortunately, the molecular spectra of $(\text{nmph})_2\text{CuCl}_4$ are not of good enough quality to warrant a detailed analysis of their temperature dependence. However, the spectrum of the thinner face X was studied over the range 10–185 K (the large absorbance precluding measurements at higher temperatures). The spectra were analyzed into the three best-fit Gaussian components at each temperature, and the resulting curves and experimental points are shown in Figure 3. As the temperature was raised, each band showed a large increase in intensity, with the band maximum shifting to lower energy and the half-width increasing. Very similar changes were observed in the (010) spectra, though these were not studied quantitatively.

Taking the values of f_0 to be the band areas at 10 K, the function $\coth^{-1}(f/f_0)$ was plotted against $1/T$ for each band in the 90° polarization spectra (Figure 9). An approximately linear relationship was obtained in each case, with the straight line passing through the origin. From the slopes of the lines, the energies of the perturbing frequencies were estimated to be 115, 90, and 90 cm^{-1} for the transitions to the ${}^2B_{1g}(xy)$, ${}^2B_{3g}(yz)$, and ${}^2A_g(z^2)$ states, respectively, with an estimated error of $\sim \pm 15 \text{ cm}^{-1}$. In this polarization, the crystal spectrum is dominated by the x molecular spectrum, with a smaller y contribution and very little contribution from z (Table I). The fact that the z spectrum makes a negligible contribution to the temperature dependence is confirmed by the very similar behavior of each band as a function of temperature in the spectrum at 45° polarization (Figure 3). In xy polarization the ${}^2B_{1g}(xy)$, ${}^2B_{2g}(xz)$, and ${}^2B_{3g}(yz) \leftarrow {}^2A_g(x^2 - y^2)$ transitions are allowed by modes of b_{2u} and a_{2u} symmetry.⁴³ The a_{2u} mode in $(\text{nmph})_2\text{CuCl}_4$ occurs at 152 cm^{-1} (Table II), which is considerably higher in energy than the values suggested by

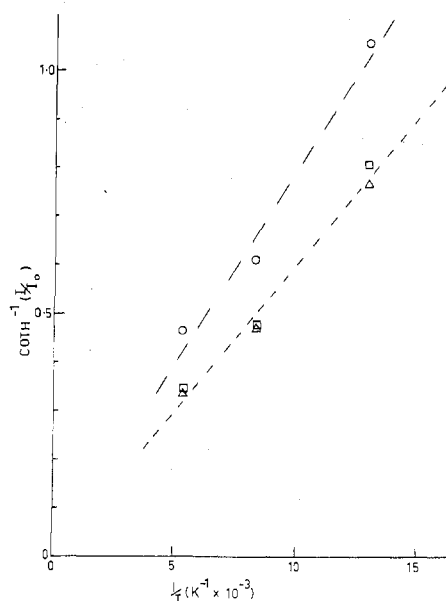


Figure 9. Plot of $\coth^{-1}(I/I_0)$ against $1/T$ for the three peaks in the spectrum of a crystal face of type X in 90° polarization. I is the estimated intensity at temperature T and I_0 is that at 10 K; \circ = band 1, \square = band 2, and \triangle = band 3, in order of increasing energy.

the temperature dependence of the bands. Since each band apparently consists of only a single vibronic progression, the most reasonable explanation seems to be that the b_{2u} mode is active in each case, with this having an energy of $\sim 105 \text{ cm}^{-1}$.

The temperature dependence of the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition, which is allowed by u modes of e_u symmetry in xy polarization, also indicates an effective perturbing mode of very low energy, $\sim 90 \text{ cm}^{-1}$. This is considerably lower than either of the e_u metal-ligand vibrations (Table II). However, this band consists of four vibrational progressions, and these have been assigned to coupling with the e_u in-plane stretch ($\bar{\nu} = 188 \text{ cm}^{-1}$) and lattice modes of energy $\bar{\nu} = 108, 57, \text{ and } \sim 20 \text{ cm}^{-1}$ (see previous section). The total band intensity f at any temperature should thus be a sum of the contributions from these four progressions:

$$f = \sum_{i=1}^4 f_{i0} \coth(h\nu_i/2kT)$$

The variation of the total band intensity with temperature calculated in this way, with the areas of the progressions deduced from Gaussian analysis, is shown in Figure 10, together with the intensity changes estimated for the individual progressions. The main error in this procedure results from the uncertainty in the lowest energy lattice mode, which occurs at too low a frequency to be observed in the infrared spectrum. The error limits shown for the calculated intensity were obtained by allowing an uncertainty of $\pm 5 \text{ cm}^{-1}$ in this energy, as well as including the uncertainty in the area of this progression indicated by the Gaussian analysis. It can be seen that the observed variation in band intensity lies close to the upper limit of that calculated. The agreement is probably good enough to suggest that the proposed intensity mechanism and assignments are feasible. It is hoped to test the model further by studying the temperature dependence of this band in the range 10–50 K by using isotopically pure $(\text{nmph})_2\text{Cu}^{35}\text{Cl}_4$. If the mechanism proves correct, it is interesting to note that while the contributions to the band intensity from what are formally lattice modes is quite small ($\sim 20\%$) at $\sim 10 \text{ K}$, they rise quite dramatically with temperature, being $\sim 50\%$ by 185 K. This suggests that conclusions drawn from the temperature dependence of bands based upon the "oriented gas" model of solid metal complexes, in which lattice contributions to the

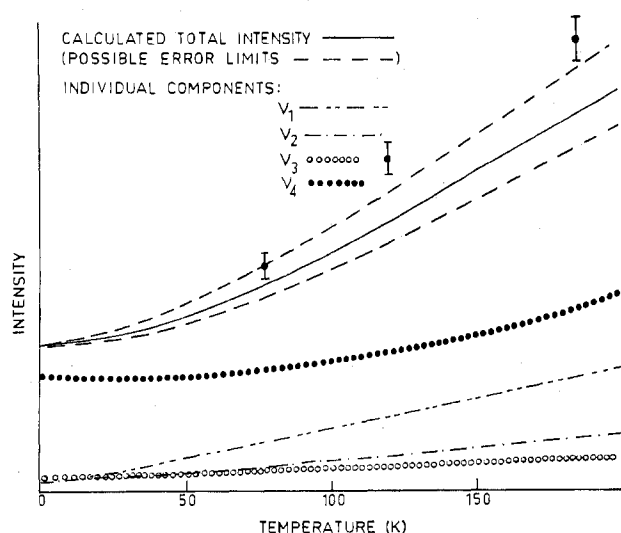


Figure 10. Plot of intensity against temperature calculated for the highest energy band in the spectrum of a crystal face of type X in 90° polarization. The intensities of the individual components are also shown, estimated by using the following energies for the perturbing ν modes: $\nu_1 = 20 \pm 5 \text{ cm}^{-1}$, $\nu_2 = 57 \text{ cm}^{-1}$, $\nu_3 = 108 \text{ cm}^{-1}$, and $\nu_4 = 188 \text{ cm}^{-1}$. The observed intensities are also indicated, together with the error limits suggested by Gaussian analysis.

intensity are ignored, must be treated with caution.^{20,23}

Geometry of the Excited Electronic States. The fact that the electronic spectrum shows vibrational progressions in the a_{1g} breathing mode suggests that the equilibrium bond lengths in the excited states of planar $CuCl_4^{2-}$ differ from those in the ground state. The relative intensities of the transitions to the various vibrational levels of each excited electronic state depend on the change in bond length, Δ , as well as the vibrational frequencies in the ground and excited states,⁴⁴ and they have been tabulated as a function of these parameters by Henderson et al.⁴⁵ By means of these tables, the areas of the component peaks deduced by Gaussian analysis were used to estimate Δ for each excited state of $CuCl_4^{2-}$. For the ${}^2B_{1g}(xy)$ and ${}^2B_{3g}(yz)$ states, the intensity pattern was found to be very similar, being reproduced best by a value of $\Delta = \pm 8.9 \text{ pm}$. For the ${}^2A_g(z^2)$ state, a similar intensity distribution was observed for all the progressions (Figure 8), and for the two most intense progressions this was best reproduced by a value of $\Delta = \pm 10.5 \text{ pm}$. The agreement between the calculated and observed intensity ratios was in each case fairly good (Figure 11). The intensity distribution is quite sensitive to Δ , so that a significantly poorer fit was obtained if this was changed by $\pm 0.3 \text{ pm}$. However, it must be remembered that the analysis depends upon the assignment of the first observed transition in each band to the vibronic origin. For the ${}^2B_{1g}(xy)$ state, this seems reasonably certain, as any lower energy transitions should have been clearly resolved (Figure 7). For the ${}^2B_{3g}(yz)$ and ${}^2A_g(z^2)$ transitions, however, any lower energy peaks could have been obscured by the absorption due to the previous bands. For these, therefore, the magnitudes of Δ must be considered as a lower limit.

The fact that the a_{1g} mode is lower in energy in each excited state, compared with the ground state, implies that Δ is negative, indicating a lengthening of the equilibrium Cu-Cl bond lengths on excitation. This is expected from the increase in antibonding character of the bonds. It may be noted that the calculated changes are about equal to the increase in bond length of $\sim 10 \text{ pm}$ which has been observed to occur when an electron occupies an e_g orbital rather than a t_{2g} orbital in comparisons of the structures of octahedral complexes of divalent first-row transition-metal ions.⁴⁶ The changes in bond length in planar $CuCl_4^{2-}$, however, are somewhat less than

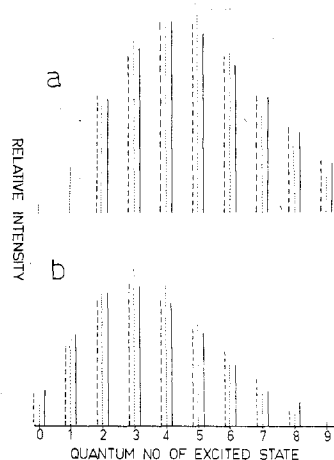


Figure 11. Calculated and observed relative intensities of the vibrational components of the bands in planar $CuCl_4^{2-}$. (a) Relative intensities (dotted line) calculated for a difference between ground- and excited-state Cu-Cl bond lengths; $\Delta = 10.5 \text{ pm}$. The full and dashed lines indicate the observed intensities, estimated by least-squares analysis, for the most intense and second most intense components of the highest energy band observed for a crystal face of type X of $(nmph)_2CuCl_4$ in 90° polarization at 10 K. (b) Relative intensities (dotted line) calculated for a value of $\Delta = 8.0 \text{ pm}$. The dashed and full lines indicate the observed intensities, estimated by Gaussian analysis, for the lowest energy and second lowest energy bands in the y molecular spectrum of $(nmph)_2CuCl_4$ at 10 K. The calculated intensities were estimated by using the tables of Henderson et al.⁴⁵

those deduced from the "d-d" spectra of $PtCl_4^{2-}$ ($\Delta = -16 \text{ pm}$)¹⁴ and $PdCl_4^{2-}$ ($\Delta = -21 \text{ pm}$).¹⁵ The fact that a greater reduction in frequency of the a_{1g} mode occurs for the ${}^2A_g(z^2)$ state than for the ${}^2B_{1g}(xy)$ and ${}^2B_{3g}(yz)$ states ($\sim 9 \text{ cm}^{-1}$ compared with $\sim 4 \text{ cm}^{-1}$) agrees with the greater increase in bond length in the former state. This implies a more antibonding character in ${}^2A_g(z^2)$, which is consistent with its higher excitation energy. However, it is noteworthy that the decreases in frequency of the a_{1g} mode in $(nmph)_2CuCl_4$ are considerably less than might be expected from the changes in bond length. Several simple relationships between stretching frequency and bond length have been developed,⁴⁷ perhaps the best known being due to Badger.⁴⁸ When comparing molecules related simply by a difference in bond length Δ , Badger's rule may be written

$$\Delta = c(\bar{\nu}_1^{-2/3} - \bar{\nu}_2^{-2/3})$$

where $\bar{\nu}_1$ and $\bar{\nu}_2$ are the energies of the two stretching modes and c is a constant. With $\bar{\nu}$ measured in cm^{-1} and Δ in pm, a value of $c = 1.11 \times 10^4$ provides an excellent correlation between the observed stretching frequencies and the estimated bond lengths of $PdCl_4^{2-}$ and $PtCl_4^{2-}$ in the ground and excited states. Thus, for $PdCl_4^{2-}$ the estimated value of $\Delta = -21 \text{ pm}$ predicts that the a_{1g} mode should lower from 307 cm^{-1} in the ground state to 271 cm^{-1} in the excited state, compared with the observed value of 269 cm^{-1} .¹⁴ Similarly, for $PtCl_4^{2-}$ the value $\Delta = -16 \text{ pm}$ implies a lowering of this mode from 329 to 298 cm^{-1} , which agrees exactly with experiment.¹⁵ For $(nmph)_2CuCl_4$, however, the bond lengthening suggested by the analysis of the vibrational structure, $\Delta = -8.9 \text{ pm}$ for the ${}^2B_{1g}(xy)$ and ${}^2B_{3g}(yz)$ states and $\Delta = -10.5 \text{ pm}$ for the ${}^2A_g(z^2)$ state, implies a lowering of the a_{1g} mode from the ground state value of 276 cm^{-1} to 262 and 260 cm^{-1} , respectively. The observed values are 10 cm^{-1} and 7 cm^{-1} higher than this, and self-consistent results cannot be obtained by choosing a different value for c . It is possible that the discrepancy may be due to a distortion toward a tetrahedral geometry in the excited electronic states of the copper(II) complex, as the a_{1g} mode in the flattened tetrahedral $CuCl_4^{2-}$ ion in Cs_2CuCl_4 occurs

at 295 cm^{-1} , some 20 cm^{-1} higher than the value in $(\text{nmph})_2\text{CuCl}_4$.⁴⁹ However, the influence of lattice effects and the fact that the Cu-Cl bond lengths in Cs_2CuCl_4 are marginally shorter (by $\sim 3\text{ pm}$) than those in $(\text{nmph})_2\text{CuCl}_4$ ⁵⁰ make any quantitative comparisons of the frequencies impossible. It may be significant in this context that although no vibronic progressions appear in the b_{2u} mode, as might be expected if a distortion toward a tetrahedral geometry occurs in the excited electronic states, yet this mode apparently does predominate in the vibronic intensity stealing process.

Conclusions

The overall polarization properties of the bands in the electronic spectrum of $(\text{nmph})_2\text{CuCl}_4$ provide an unambiguous assignment of the excited-state energies of the planar CuCl_4^{2-} ion. The d-orbital energies are in good agreement with simple theory, except that the d_{z^2} orbital is $\sim 5000\text{ cm}^{-1}$ lower in energy than expected. This depression is rationalized in terms of configuration interaction with the metal 4s orbital.

Each band in the "d-d" spectrum exhibits vibrational progressions in the a_{1g} stretching mode. The intensities of the components suggest a lengthening of the Cu-Cl bond length of 8.9 pm in the ${}^2B_{1g}(xy)$ and ${}^2B_{3g}(yz)$ excited states and 10.5 pm in the ${}^2A_g(z^2)$ state. In agreement with this, the a_{1g} mode has lower energies in the excited states than the ground state, though the shift to lower energy is rather less than that expected. The vibrational fine structure and temperature dependence of the bands are consistent with the intensity of the ${}^2B_{1g}(xy) \leftarrow {}^2A_g(x^2 - y^2)$ and ${}^2B_{3g}(yz) \leftarrow {}^2A_g(x^2 - y^2)$ transitions in y polarization being derived from coupling with the out-of-plane bending mode of b_{2u} symmetry, with this having an energy of $\sim 105\text{ cm}^{-1}$. The ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition in xy polarization consists of a superimposition of four progressions in the a_{1g} mode. The separations between these, together with the temperature dependence of the band, is consistent with the intensity being derived from coupling with the in-plane metal-ligand bending mode of e_u symmetry and three low-energy lattice modes. The narrow peaks due to coupling with the lattice modes show a progressive broadening as the vibrational quantum number of the excited state increases which may be explained by the different energies of the a_{1g} mode predicted for the various isotopic isomers of the CuCl_4^{2-} ion.

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References and Notes

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