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Electronic Spectra and Bonding of the Planar Complexes $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$ and $\text{Cu}(4\text{-methylpyridine } N\text{-oxide})_2\text{Cl}_2$

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The vibrational and single-crystal "d-d" electronic spectra of the compounds $[\text{CuCl}_2(\text{H}_2\text{O})_2]\cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$ and $\text{Cu}(4\text{-methylpyridine } N\text{-oxide})_2\text{Cl}_2$ are reported. The temperature dependence of the band intensities of the former complex are interpreted in terms of vibronic coupling, and the energies of the ungerade vibrations inducing intensity are consistent with those derived from the infrared spectrum. Vibrational fine structure observed in the electronic spectra at low temperature is apparently due to progressions in the two totally symmetric a_g vibrations expected for each complex, and for the planar $\text{CuCl}_2(\text{H}_2\text{O})_2$ group present in the former compound an estimate of the changes in the Cu-Cl and Cu-O bond lengths accompanying the electronic excitations has been made. A weak band observed at high energy in the spectrum of $[\text{CuCl}_2(\text{H}_2\text{O})_2]\cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$ has been assigned to coupling of the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition with O-H stretching vibrations of the water ligands, though the precise mechanism by which the band gains intensity is uncertain. The transition energies of the complexes have been interpreted in terms of angular overlap metal-ligand bonding parameters, and these have been compared with those of other planar complexes.

Introduction

Recent studies of the electronic spectrum of the planar CuCl_4^{2-} ion in a range of crystal lattices have provided considerable information about the bonding properties of both the ground and excited electronic states of this complex.¹⁻⁶ The band energies have been used to deduce the angular overlap metal-ligand bonding parameters for chloride toward Cu^{2+} , and it was inferred that the ${}^2A_g(z^2)$ excited state is considerably higher in energy than is predicted by simple bonding schemes.¹ This feature has been confirmed for a range of other planar complexes.⁷ Analysis of the temperature dependence of the band intensities has provided a means of probing the energies of the ungerade vibrations, and it was deduced that the out-of-plane bending mode of b_{2u} symmetry, which is both infrared and Raman inactive and so cannot be observed directly, is of very low energy.^{2,6} This vibration carries the complex from a planar toward a tetrahedral stereochemistry, and its "softness" is consistent with analysis of the vibrational fine structure observed in the electronic spectra at low temperature^{5,6} and the temperature dependence of the band maxima,³ both of which suggest that the potential surfaces of the excited electronic states are distorted in the b_{2u} coordinate, with minima corresponding to pseudotetrahedral geometries. Band-shape analysis also allowed the lengthening of the Cu-Cl bonds in each excited state to be estimated,^{1,2} providing a useful test of simple models relating bond distance to the d-electron configuration of a transition-metal complex.⁸

In view of the above, the electronic spectra of mixed-ligand complexes related in a simple fashion to planar CuCl_4^{2-} should be of interest, and we have therefore studied several complexes of general formula $\text{trans-CuCl}_2\text{X}_2$, where X is either a nitrogen or oxygen donor ligand. The compound $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ (Ph = C_6H_5) is unusual in that it contains isolated, planar $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$ groups, with the triphenylphosphine oxide molecules being hydrogen-bonded to the water ligands.⁹ This paper describes the spectral properties of this compound and the planar molecule $\text{Cu}(4\text{-picO})_2\text{Cl}_2$ (4-picO = 4-methylpyridine *N*-oxide) and compares the spectral and bonding characteristics with those of planar CuCl_4^{2-} and other complexes involving oxygen donor ligands.

Experimental Section

Infrared spectra were measured as Nujol mulls between polythene disks with a Digilab FTS 20E spectrometer using 6.25- or 25- μ Mylar beam-splitters between 50-500 and 20-100 cm^{-1} , respectively. Raman spectra were recorded by using a Cary 82 spectrophotometer fitted with an argon laser, using the 488- or 514.5-nm excitation line. Powdered samples were pressed into disks and rotated in a "spinning cell" arrangement to minimize decomposition. The Stokes shifts were calibrated with reference to the argon ion emission lines. Electronic spectra were measured on a Cary 17 spectrophotometer using polarized light with the crystals mounted by a technique described previously.^{2,10} The samples

Table I. Energies of the Metal-Ligand Vibrations of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ and $\text{Cu}(4\text{-picO})_2\text{Cl}_2$ Compared with Those Reported¹⁶ for $\text{K}_2\text{CuCl}_4\cdot 2\text{H}_2\text{O}^a$

| mode | sym | activity | $\text{K}_2\text{CuCl}_4\cdot 2\text{H}_2\text{O}^b$ | $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ | $\text{Cu}(4\text{-picO})_2\text{Cl}_2$ |
|---------|----------|----------|--|---|---|
| ν_1 | a_g | R | 404 | 444 w | 137 s, 413 w ^c |
| ν_2 | a_g | R | 224 | 252 s | 292 vs |
| ν_3 | b_{1g} | R | 246 | obscured | 229 m |
| ν_4 | b_{1u} | IR | 218 | 167 m | 156 m |
| ν_5 | b_{1u} | IR | 139 m | 71 vw | uncertain |
| ν_6 | b_{2u} | IR | 316 vs | 333 vs | 332 sh |
| ν_7 | b_{2u} | IR | 267 ms | 277 w | 203 m |
| ν_8 | b_{3u} | IR | 440 m, sh | 445 m, sh | 435 sh |
| ν_9 | b_{3u} | IR | 180 vs | 182 mw | 173 mw |

^aR = Raman, IR = infrared, vs = very strong, s = strong, m = medium, w = weak, sh = shoulder. ^bData from ref 16. ^cSee text for discussion of the assignment of these peaks.

were cooled by using a Cryodyne Model 22C cryocooler fitted with a Palm Beach Cryophysics Model 4025 thermometer/temperature controller. Molar extinction coefficients were estimated by measuring crystal thicknesses with a polarizing microscope fitted with a graduated eyepiece and are estimated to be accurate to ~10%.

The compound $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ was prepared as large, dark blue, chunky crystals by the method of Makanova et al.¹¹ with the (001), (100), and (102) crystal faces being well developed. Several attempts were made to grow crystals of the analogous deuterated complex by a method using D_2O , and $\text{C}_2\text{H}_5\text{OD}$ as solvent, but these were never entirely successful. Usually an orange-red compound, thought to be $\text{Cu}_4\text{OCl}_6(\text{Ph}_3\text{PO})_2$,¹² or yellow crystals of the complex $\text{Cu}(\text{Ph}_3\text{PO})_2\text{Cl}_2$ ¹³ were formed. However, one such preparation did yield blue crystals of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ that were partially deuterated, and these were used for the spectroscopic measurements described below. From the areas of the bands due to the overtones of the infrared OH and OD stretching vibrations, it is estimated that ~60% of the hydrogen atoms were replaced by deuterium atoms in these crystals. The compound $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$

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$O_2Br_2 \cdot 4(C_6H_5)_3PO$, required as an aid in the assignment of the vibrational spectrum, was made by the method of Mikanova et al.¹¹ The complex $Cu(4-picO)_2Cl_2$ was prepared as light green needles by the method described by Johnson and Watson,¹⁴ using ethanol to which a few drops of water had been added as a solvent. The (011) crystal face was found to be well developed. A small number of yellow crystals also formed, and these are thought to be the dimeric complex $[CuCl_2(4-picO)]_2$ reported by Johnson and Watson.¹⁴

Crystal morphologies were identified by measuring interfacial crystal angles with a stereoscopic polarizing microscope and confirmed by analysis of the single-crystal EPR spectrum of the complexes. The compounds had satisfactory analyses. Anal. Calcd for $[Cu(H_2O)_2Cl_2] \cdot 4Ph_3PO$ ($C_{72}H_{64}O_6Cl_2P_4Cu$): C, 66.43; H, 4.92. Found: C, 66.82; H, 5.13. Calcd for $[Cu(H_2O)_2Br_2] \cdot 4(C_6H_5)_3PO$ ($C_{72}H_{64}O_6Cl_2P_4Br_2Cu$): C, 62.95; H, 4.70. Found: C, 63.01; H, 4.70. Calcd for $Cu(4-picO)_2Cl_2$ ($C_{12}H_{14}O_2N_2Cl_2Cu$): C, 40.87; H, 4.00; N, 7.94. Found: C, 41.04; H, 4.08; N, 7.64.

Results and Discussion

Vibrational Spectra. Comparison of the infrared and Raman spectra of $[Cu(H_2O)_2Cl_2] \cdot 4Ph_3PO$ with those of the analogous bromide and with those of triphenylphosphine oxide was used to identify the peaks due to metal-ligand vibrations as listed in Table I. Here, the peaks above 200 cm^{-1} have energies very similar to those reported previously by Mikanova et al.¹¹ The peaks due to the metal-ligand vibrations of $Cu(4-picO)_2Cl_2$ listed in Table I were identified in a similar fashion, with those above 300 cm^{-1} being reported previously by Malek and Fresco.¹⁵ The band assignments for both complexes are generally similar to those reported for the analogous vibrations in $K_2CuCl_4 \cdot 2H_2O$,¹⁶ $CuCl_2(\text{dimethyl sulfoxide})_2$,¹⁷ and various aromatic amine *N*-oxide complexes,^{14,18} and the energies of the peaks reported for the first of these compounds are also given for comparison. It should be noted that in $K_2CuCl_4 \cdot 2H_2O$ the ligand coordination geometry is similar to that in $[Cu(H_2O)_2Cl_2] \cdot 4Ph_3PO$ except for the presence of weakly coordinated axial chloride ligands.¹⁹ For the assignments in Table I the form of the normal vibrations is identical with that described previously for the analogous complexes CuL_2Cl_2 , where L is a heterocyclic amine,²⁰ with each oxygen donor ligand being treated as a single group.

The high energy (444 cm^{-1}) of the ν_1 mode of a_g symmetry in $Cu(H_2O)_2Cl_2$, which is predominantly a Cu-O stretch, is presumably a result of the very short copper-oxygen bond (1.904 \AA , compared with 1.97 \AA in $K_2CuCl_4 \cdot 2H_2O$). Because of the large ligand mass, the corresponding vibration in $Cu(4-picO)_2Cl_2$, which involves motion of the whole amine oxide ligand, is expected to occur at rather low energy, and the intense band at 137 cm^{-1} in the Raman spectrum of the complex is tentatively assigned to this mode. This assignment receives some support from the progression frequency resolved in the low-temperature optical spectrum of the compound (see following section). The M-N stretch for complexes of pyridine and related donors has been assigned to peaks between ~ 125 and 155 cm^{-1} ,^{20,21} considerably lower than the 370 – 525 cm^{-1} for the M-NH₃ stretch in four-coordinate divalent metal amine complexes.²² A weak peak at 413 cm^{-1} in the spectrum of $Cu(4-picO)_2Cl_2$ may also be due to a Cu-O stretch of a_g symmetry, being similar in energy to the band assigned to this mode in the hydrate complex. The metal-oxygen symmetric stretch has been assigned to peaks of about this energy for $M(\text{pyridine } N\text{-oxide})_6^{2+}$ complexes, $M = Co, Ni$.^{23,24} For the amine oxide complexes, coupling with ligand N-O

Table II. Molecular Projections Associated with the Extinction Directions of the (102) and (100) Crystal Faces of $[Cu(H_2O)_2Cl_2] \cdot 4Ph_3PO$ and the (011) Crystal Face of $Cu(4-picO)_2Cl_2$

| direction | x^2 | y^2 | z^2 |
|----------------------------------|-------|-------|-------|
| $[Cu(H_2O)_2Cl_2] \cdot 4Ph_3PO$ | | | |
| [102] | 0.90 | 0.07 | 0.02 |
| [010] | 0.04 | 0.01 | 0.94 |
| [001] | 0.07 | 0.93 | 0.01 |
| $Cu(4-picO)_2Cl_2$ | | | |
| 35° to [100] | 0.32 | 0.13 | 0.55 |
| -55° to [100] | 0.46 | 0.39 | 0.15 |

Table III. Symmetries of the Vibrations Inducing Intensity for the Electronic Transitions of a Copper(II) Complex of D_{2h} Symmetry

| transition | polarization | | |
|--|--------------|----------|----------|
| | x | y | z |
| ${}^2B_{1g}(xy) \leftarrow {}^2A_g(x^2 - y^2)$ | b_{2u} | b_{3u} | a |
| ${}^2B_{2g}(xz) \leftarrow$ | b_{1u} | a | b_{3u} |
| ${}^2B_{3g}(yz) \leftarrow$ | a | b_{1u} | b_{2u} |
| ${}^2A_g(z^2) \leftarrow$ | b_{3u} | b_{2u} | b_{1u} |

^aNo vibration available.

stretching vibrations may occur, so that the peaks at $\sim 400\text{ cm}^{-1}$ could be due to a_g vibrations, which predominantly involve motion of the ligand oxygen atoms. The modes of a_g symmetry in which the motion predominantly involves the chloride ligands have energies quite similar to the corresponding vibration² in planar $CuCl_4^{2-}$, $\sim 275\text{ cm}^{-1}$. Presumably, the somewhat lower energy of this vibration in $K_2CuCl_4 \cdot 2H_2O$, 224 cm^{-1} , reflects the longer Cu-Cl bond length in this six-coordinate complex¹⁹ (2.285 \AA compared with $\sim 2.23\text{ \AA}$ for the four-coordinate complexes).

The ν_5 mode of b_{1u} symmetry involving an out-of-plane bending motion of the chloride ligands could not be identified with certainty. Weak peaks at 86 and 71 cm^{-1} were observed in the far-infrared spectrum of $[Cu(H_2O)_2Cl_2] \cdot 4Ph_3PO$, one of which could possibly be due to this vibration. A normal-coordinate analysis yielded an estimate of $\sim 70\text{ cm}^{-1}$ for the mode.²⁵ The absorption due to this vibration is expected to be very weak, as it corresponds to the infrared- and Raman-inactive out-of-plane bend of b_{2u} symmetry of a complex of D_{4h} symmetry involving four identical ligands. In planar $CuCl_4^{2-}$ the temperature dependence of the electronic spectrum suggests an energy of $\sim 65\text{ cm}^{-1}$ for this mode,^{2,3,6} and a similar analysis of the electronic spectrum of the $Cu(H_2O)_2Cl_2$ complex implies a comparable energy for the ν_5 mode (see following section).

Electronic Spectra. The temperature dependence of the electronic spectra of $[Cu(H_2O)_2Cl_2] \cdot 4Ph_3PO$, measured on the (102) and (100) crystal faces with the electric vector parallel to the [102], [001], and [010] directions, is shown in Figure 1. The squares of the molecular projections associated with these spectra are given in Table II; here, x is parallel to the Cu-O vector, z is normal to x and the Cu-Cl vector, and y is normal to x and z . It may be seen that to a good approximation the above three spectra correspond to the x , y , and z molecular spectra, respectively. The low-temperature molecular spectra, after correction for the small misalignments inherent in the above crystal spectra by a procedure described in detail elsewhere,¹⁰ are shown in Figure 2.

The spectra of $Cu(4-picO)_2Cl_2$ measured between 10 and 290 K with the electric vector along the two extinction directions of the (011) crystal face are shown in Figure 3. The molecular projections associated with these spectra are given in Table II, the coordinate system being analogous to that defined for $[Cu(H_2O)_2Cl_2] \cdot 4Ph_3PO$.

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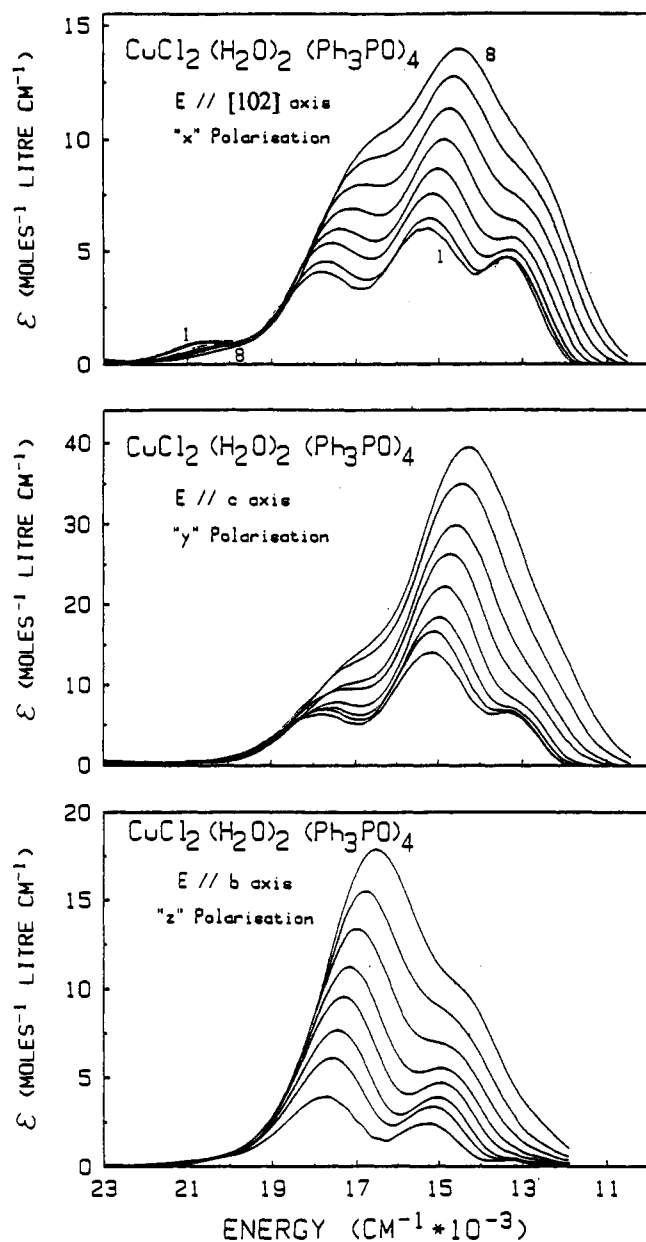


Figure 1. Variation as a function of temperature of the spectra of single crystals of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\text{Ph}_3\text{PO}$ with the electric vector parallel to the [102], [001], and [010] crystal directions, measured at 10, 50, 90, 130, 170, 210, 250, and 290 K. The spectrum at 10 K is labeled by 1 and that at 290 K by 8.

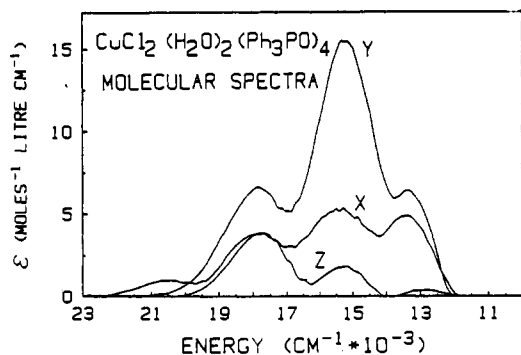


Figure 2. Molecular spectra of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\text{Ph}_3\text{PO}$ at 10 K.

Assignment of the "d-d" Transitions. Neglecting the hydrogen atoms of the water molecules, the $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$ complex in $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\text{Ph}_3\text{PO}$ approximates closely to D_{2h} symmetry, being rigorously centrosymmetric, with OCuCl angles of 90.9° . Although the hydrogen positions were not located in the crystal

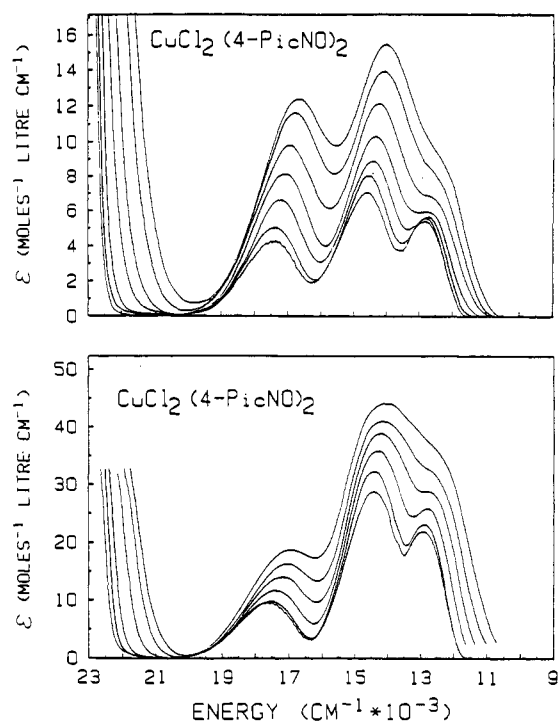


Figure 3. Spectra of the (011) crystal face of $\text{Cu}(\text{4-picO})_2\text{Cl}_2$ measured at 10, 50, 100, 150, 200, and 250 K with the electric vector at an angle of 35° (top) and -55° (bottom) to the [100] crystal axis. The spectra increase progressively in intensity as the temperature is raised.

structure determination,⁹ it seems likely that the oxygen atoms of the triphenylphosphine oxide molecules are hydrogen-bonded to the water molecules. The plane formed by the water oxygen atom and the two closest phosphine oxide oxygen atoms makes an angle of 34° with the plane of the CuO_2Cl_2 group, and if the hydrogen atoms lie in the former plane, this lowers the symmetry of the $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$ chromophore to $C_{2h}(x)$.

The intensity of the d-d transitions in a centrosymmetric complex is induced by coupling with ungerade vibrational modes,^{10,26} and assuming effective D_{2h} symmetry, the nature of the vibrations inducing intensity into each electronic transition of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\text{Ph}_3\text{PO}$ is given in Table III. It may be seen that transitions to the ${}^2B_{1g}(xy)$, ${}^2B_{2g}(xz)$, and ${}^2B_{3g}(yz)$ excited states are vibronically forbidden in z, y, and x polarization, respectively. In the $C_{2h}(x)$ point group each transition would be allowed in every polarization. The molecular spectrum of the complex (Figure 2) consists of three bands of moderate intensity centered at 13 200, ~ 15 200, and 17 700 cm^{-1} , which are clearly due to d-d transitions. A weak band also occurs at ~ 20 600 cm^{-1} in x polarization, but this is ascribed to coupling of the highest energy d-d transition with internal O-H stretching vibrations of the water molecules. This assignment, which is discussed below, is confirmed by the fact that no such high-energy band is observed in the spectrum of $\text{Cu}(\text{4-picO})_2\text{Cl}_2$ (Figure 3).

The fact that the band at 13 200 cm^{-1} is virtually absent in z polarization suggests that this may be assigned to the ${}^2B_{1g}(xy) \leftarrow {}^2A_g(x^2 - y^2)$ transition and that the effective point group is D_{2h} . Gaussian analysis indicates that the middle band is centered at 15 310 cm^{-1} in x polarization and 15 150 cm^{-1} in y polarization; the former peak is ascribed to the transition to the ${}^2B_{2g}(xz)$ state; the latter to the ${}^2B_{3g}(yz)$ state. In z polarization, transitions to both these states are vibronically allowed and the band occurs at an intermediate energy, 15 210 cm^{-1} , as expected. The band at 17 700 cm^{-1} , which occurs with approximately equal intensity in all three polarizations, is assigned to the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition.

The spectrum of $\text{Cu}(\text{4-picO})_2\text{Cl}_2$ shows three peaks, centered at 12 750, ~ 14 500, and 17 450 cm^{-1} , which may be assigned by analogy with those of $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$. The first and last peaks are due to transitions to the ${}^2B_{1g}(xy)$ and ${}^2A_g(z^2)$ excited states, respectively. The middle band maximizes at 14 400 and 14 600

Table IV. "Average" Energies (cm^{-1}) of the Vibrations Inducing the Intensity of the "d-d" Transitions of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ Derived from the Temperature Dependence of the Band Intensities

| excited state | polarization ^a | | |
|-------------------------|---------------------------|----------|----------|
| | x | y | z |
| ${}^2\text{B}_{1g}(xy)$ | 250 (10) | 150 (10) | b |
| ${}^2\text{B}_{2g}(xz)$ | 185 (5) | b | |
| ${}^2\text{B}_{3g}(yz)$ | b | 135 (5) | 120 (10) |
| ${}^2\text{A}_g(z^2)$ | 160 (10) | 240 (20) | 70 (4) |

^a Estimated uncertainties are given in parentheses. ^b No vibration available.

cm^{-1} when the electric vector makes angles of -55 and 35° with the $[100]$ direction, respectively, and the relative changes in the projections upon the x and y molecular axes (Table II) suggest that these peaks correspond to transitions to the ${}^2\text{B}_{3g}(yz)$ and ${}^2\text{B}_{2g}(xz)$ excited states, although their resolution is by no means complete.

Temperature Dependence of the Spectra. For centrosymmetric complexes, the variation of the oscillator strength as a function of temperature may be used to estimate the energies of the u modes inducing intensity.^{10,26} Studies of several compounds containing planar CuCl_4^{2-} have provided generally reasonable agreement between the energies of these u vibrations and the vibrational frequencies derived from infrared spectroscopy and calculated by normal-coordinate analysis.¹⁻³ The theory of vibronic intensity stealing^{26,27} suggests that the oscillator strength $f(T)$ at temperature T is related to that at 0 K, $f(0)$, by the expression

$$f(T) = f(0) \coth(h\nu/2kT) \quad (1)$$

where h and k are the Planck and Boltzmann constants, respectively, and ν is the frequency of the vibration inducing intensity.

The variation of the band intensities of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ as a function of temperature, estimated by Gaussian analysis using a procedure described previously,² are shown in Figure 4. Here, different symbols have been used for measurements made on different crystals, and uncertainties in the intensities are denoted by vertical error bars when these are larger than the symbol size. Spectra such as those shown in Figure 1 were used in the analysis, with the appropriate simultaneous equations¹⁰ being solved to transform the data into pure molecular spectra. Intensity variations calculated by using eq 1, optimized by a least-squares fitting procedure, are also shown in Figure 4 for each transition, and the estimated "best-fit" average energies of the vibrations inducing intensity are given in Table IV.

The transitions to the ${}^2\text{B}_{1g}(xy)$ and ${}^2\text{A}_g(z^2)$ excited states have intensity induced by modes of b_{2u} symmetry in x and y polarization, respectively, and the analysis suggests that these have "average" energies of ~ 250 and $\sim 240 \text{ cm}^{-1}$, implying that most of the intensity derives from the δ (O-Cu-O) in-plane deformation assigned to the peak at 277 cm^{-1} in the infrared spectrum (Table I). Transitions to the above states in y and x polarization are allowed by vibrations of b_{3u} symmetry, and energies of ~ 150 and $\sim 160 \text{ cm}^{-1}$ were deduced for the "average" energies of these modes, respectively, suggesting that the corresponding in-plane deformation involving the Cl^- ligands with an energy of 182 cm^{-1} is responsible for the bulk of the intensity. It therefore appears that the higher energy stretching vibrations of b_{2u} and b_{3u} symmetries are inactive in inducing intensity. This was also found to be the case for planar CuCl_4^{2-} for the analogous modes of e_u symmetry.² The transitions to the ${}^2\text{B}_{3g}(yz)$ and ${}^2\text{B}_{2g}(xz)$ excited states in z polarization cannot be resolved, and the intensity of the composite band is induced by modes of both b_{2u} and b_{3u} symmetries. As was also observed² for the corresponding ${}^2\text{E}_g^-(yz,xz) \leftarrow {}^2\text{B}_{1g}(x^2-y^2)$ transition of the D_{4h} CuCl_4^{2-} ion, the "average" energy of the inducing vibrations, $\sim 120 \text{ cm}^{-1}$, is significantly lower than that of the active deformation modes, possibly due to coupling with low-energy lattice vibrations.

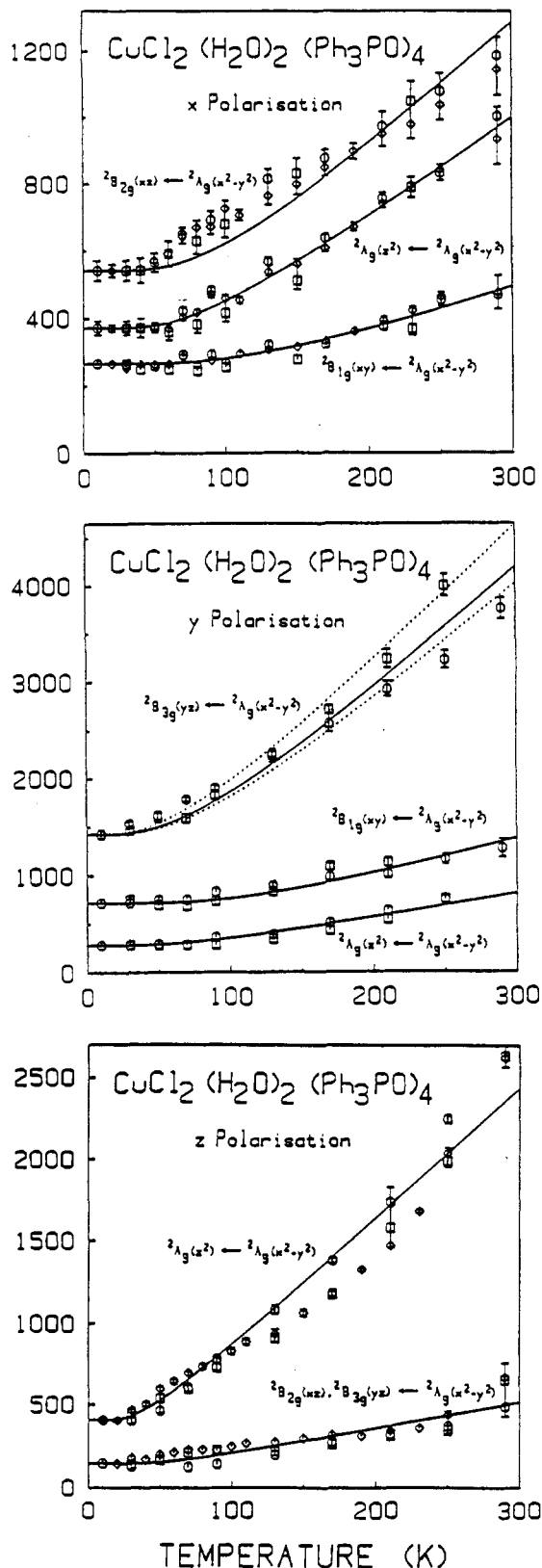


Figure 4. Variation of the intensities of the "d-d" transitions of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ as a function of temperature. The data for independent measurements are shown by different symbols, and the uncertainties derived from the Gaussian analysis are indicated by error bars. The solid lines represent the best-fit variations in intensity derived from eq 1 by using the "average" vibrational energies given in Table IV.

Vibrations of b_{1u} symmetry are active in inducing intensity into transitions to the ${}^2\text{B}_{2g}(xz)$, ${}^2\text{B}_{3g}(yz)$, and ${}^2\text{A}_g(z^2)$ excited states in x , y , and z polarization, respectively. The energy deduced from the temperature dependence of the first of these transitions, 185 cm^{-1} , is quite similar to that obtained from infrared spectroscopy

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for the ν_4 $\delta(\text{O}-\text{Cu}-\text{O})$ out-of-plane bending vibration of this symmetry, 167 cm⁻¹, suggesting that the bulk of the intensity is derived from this mode. The average energy for the mode inducing intensity into the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition is 70 cm⁻¹. This is the energy expected for the ν_5 b_{1u} out-of-plane bending vibration involving the chloride ligands, the analogous vibration^{2,3,6} having an energy of ~ 65 cm⁻¹ in planar CuCl₄²⁻. In each of these cases just one mode apparently dominates the intensity-stealing process. For the transition to the ${}^2B_{3g}(yz)$ state in y polarization, however, the intensity variation implies an "average" energy, 135 cm⁻¹, intermediate between the energies of the two b_{1u} vibrations (70 and 167 cm⁻¹). The best-fit calculated intensity variation indicated in Figure 4 for this transition was obtained by assuming that 86% of the intensity at 0 K is induced by the higher energy mode, the remainder being induced by the lower energy vibration. Again, similar behavior was observed for the ${}^2E_g(yz, xz) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition of the D_{4h} CuCl₄²⁻ ion in xy polarization, where $\sim 85\%$ of the intensity is due to coupling with the out-of-plane bend of a_{2u} symmetry, the remainder being derived from the lower energy mode of b_{2u} symmetry.²

As insufficient data were available to resolve the spectra of Cu(4-picO)₂Cl₂ into their molecular components, a quantitative analysis of their temperature dependence was not possible. However, it is apparent that a significant increase in intensity occurs on raising the temperature, particularly for the highest energy band when the electric vector lies closest to the z molecular axis (Figure 3, Table II). This behavior is very similar to that observed for Cu(H₂O)₂Cl₂ and CuCl₄²⁻ and suggests that, for Cu(4-picO)₂Cl₂ also, the b_{1u} out-of-plane bending vibration involving the chloride ligands is active in inducing intensity and has a very low energy.

A particularly novel feature of the electronic spectrum of planar CuCl₄²⁻ is the unusual red shifts of the band maxima that occur on warming from 10 K to room temperature.^{2,3} These shifts, which range from about 600 cm⁻¹ to 900 cm⁻¹, are much larger than expected on the basis of the theory of vibronic intensity stealing in its simple form,²⁶ implying that the equilibrium nuclear geometry of the CuCl₄²⁻ ion in each excited electronic state is distorted from planarity toward the pseudotetrahedral stereochemistry observed in the ground state for most compounds containing this complex.³

Gaussian analysis also suggests substantial shifts in the band maxima of the d-d transitions of [Cu(H₂O)₂Cl₂]-4Ph₃PO as the temperature is raised from 10 to 290 K: 1150 \pm 60, 1060 \pm 50, 920 \pm 50, and 890 \pm 50 cm⁻¹ for the transitions to the ${}^2A_g(z^2)$, ${}^2B_{2g}(xz)$, ${}^2B_{3g}(yz)$, and ${}^2B_{1g}(xy)$ states, respectively. Because of the complexity of the Cu(H₂O)₂Cl₂ molecule, a quantitative analysis of the nature of the excited-state potential surface has not been attempted. However, for planar CuCl₄²⁻ it has been shown⁶ that the more the complex is distorted toward a tetrahedral geometry in the excited electronic state, the greater is the red shift in the band maximum—a shift of ~ 900 cm⁻¹ implies that each Cu-Cl bond is distorted by more than $\sim 7^\circ$ from the plane of the complex, while one of ~ 600 cm⁻¹ is associated with an angular distortion of only $\sim 4-5^\circ$. The large red shifts observed for [Cu(H₂O)₂Cl₂]-4Ph₃PO, 890–1150 cm⁻¹, suggest a substantial distortion of the Cu(H₂O)₂Cl₂ molecule in the excited states of this compound. This seems reasonable, in view of the fact that the ν_5 $\delta(\text{Cl}-\text{Cu}-\text{Cl})$ out-of-plane bending vibration has a very low energy, ~ 70 cm⁻¹; moreover, other similar complexes involving two oxygen and two chloride ligands, such as CuCl₂(Ph₃PO)₂, are known to adopt pseudotetrahedral geometries in the ground state.¹³

Although the precise mechanism by which the potential surfaces of these complexes become distorted in the excited state has not yet been investigated, it has been proposed that this probably involves a pseudo-Jahn-Teller coupling between the excited d states and metal-ligand charge-transfer states.^{3,6} These are quite close in energy in planar chlorocuprates (the lowest charge-transfer state in these complexes lies only ~ 6000 cm⁻¹ above the ${}^2A_g(z^2)$ state).²⁸

This proposal gains support from the fact that for both planar CuCl₄²⁻ and [Cu(H₂O)₂Cl₂]-4Ph₃PO the red shift increases linearly with the energy of the excited d state. Vibronic coupling between the charge-transfer and d states is expected to vary in just this manner, increasing approximately linearly as these states approach one another in energy.

Vibrational Fine Structure. The middle and highest energy d-d transitions of [Cu(H₂O)₂Cl₂]-4Ph₃PO exhibit moderately well resolved fine structure at low temperature (Figure 2). This is caused by the excitation of multiple vibrational quanta in addition to the single quantum jump of each electronic transition, and to a first approximation, only vibrational modes of a_g symmetry may couple in this way.¹⁰ In principle, the present situation is complicated by the fact that each excited-state potential surface is apparently distorted in the b_{1u} out-of-plane bending mode (see preceding section), so that progressions in this vibration are also expected. However, analysis of the electronic spectrum of planar CuCl₄²⁻ has suggested that in practice, provided the distortion in this low-energy mode is substantial, as seems to be the case for [Cu(H₂O)₂Cl₂]-4Ph₃PO, multiple transitions involving the bending vibration will not be resolved^{3,6} and only the effects of displacements in normal coordinates of a_g symmetry in the potential surfaces of the upper state compared with the ground state will therefore be considered.

Previous studies of the vibrational fine structure observed in the electronic spectrum of planar CuCl₄²⁻ have provided estimates of the increase in Cu-Cl bond length that accompanies each electronic transition.^{2,3,6} A similar analysis of the spectrum of [Cu(H₂O)₂Cl₂]-4Ph₃PO is more complicated, as two modes of a_g symmetry occur for this complex, one involving motion predominantly of the water ligands, ν_1 , and the other motion of the chloride ions, ν_2 . Displacement of the upper potential surfaces in both these normal coordinates will occur, and interference between these may give rise to a progression with an energy interval that differs from both a_g vibrations. Because this appears to originate from a single vibration that does not correspond to a normal mode of the complex, it has been termed the "missing mode", or MIME, effect.²⁹ In several cases, Zink and co-workers²⁹⁻³² have analyzed such fine structure using a method involving time-dependent perturbation theory to obtain the magnitudes of the displacements in the various a_g coordinates.^{32,33}

Recently, we described a variational method of calculating the band shapes of electronic transitions³⁻⁶ that provides an alternative to that reported by Zink and co-workers²⁹⁻³² for interpreting the band shape expected for an electronic transition coupled to two modes of a_g symmetry. In the present case, considering only the vibrations of a_g symmetry, the ground- and excited-state potential functions were defined by applying a Hamiltonian of the form

$$H = -0.5\delta^2/\delta\xi^2 + V(\xi) \quad V(\xi) = c_1\xi + c_2\xi^2 \quad (2)$$

to a basis of harmonic oscillator wave functions characterized by a harmonic energy $h\nu$. Here, ξ is a dimensionless coordinate related to the symmetry coordinate S by

$$\xi = S\sqrt{4\pi^2c\nu/h} \quad (3)$$

where h is Planck's constant, c is the velocity of light, and $h\nu$ is in cm⁻¹. The matrix elements of (2) are easily evaluated by published methods,³⁴ it being assumed that no rotation of the normal coordinates occurs in the excited state (i.e. that the Duschinsky effect³⁵ can be ignored).

In the present case, the relevant basis functions are the ν_1 and ν_2 vibrations in the ground and excited electronic states. In the ground state, these are defined by the energies 444 and 252 cm⁻¹,

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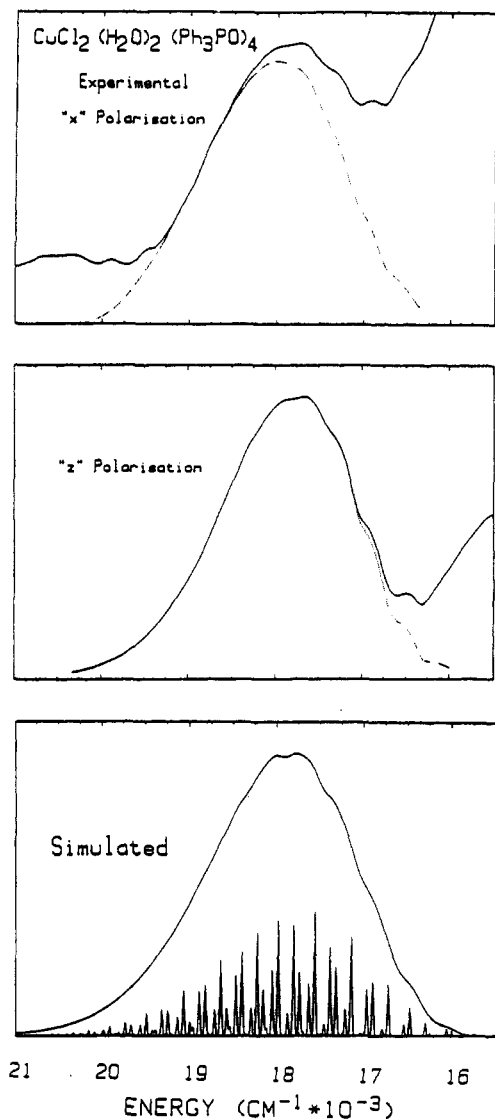


Figure 5. Experimental spectra of the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\text{Ph}_3\text{PO}$ with the electric vector along the [102] and [010] directions (x and z , respectively). The dashed lines indicate the appearance of the bands when the absorption due to neighboring transitions is subtracted. The simulated spectrum was calculated by the variational method described in the text, assuming displacements in the ν_1 and ν_2 modes defined by $V(\xi) = 0.447\xi^2 - 2.4641\xi$ [$\Delta S(\text{Cu}-\text{O}) = 16$ pm, $\delta r(\text{Cu}-\text{O}) = 11.3$ pm] and $V(\xi) = 0.472\xi^2 - 1.7904\xi$ [$\Delta S(\text{Cu}-\text{Cl}) = 11$ pm, $\delta r(\text{Cu}-\text{Cl}) = 7.8$ pm]. The potential functions of the two a_g modes correspond to harmonic oscillators having ground- and excited-state energies of 444 and 420 cm^{-1} and of 252 and 244 cm^{-1} , respectively. A half-width of 115 cm^{-1} for both progressions was used in the simulation, and the underlying structure is illustrated by showing the pattern obtained for a half-width of 10 cm^{-1} .

respectively (Table I). It is expected that these energies will be reduced slightly in the excited electronic states, and for the ν_2 mode a reduction equal to the average observed² for the a_{1g} mode of planar CuCl_4^{2-} was used, 3%. For the ν_1 mode an upper-state energy of 420 cm^{-1} was assumed (test simulations were also carried out by using an energy equal to that in the ground state, but this had relatively little effect on the band shapes). The experimental band shapes observed at 10 K for the ${}^2A_g(z^2) \leftarrow A_g(x^2 - y^2)$ transition of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\text{Ph}_3\text{PO}$ with the electric vector along the [010] and [102] directions (i.e. approximately along z and x , respectively) are shown in Figure 5. It can be seen that the form of the vibrational structure is essentially independent of the polarization direction, confirming that the nature of the vibration inducing intensity has little influence on this aspect of the spectra. Simulations of the band were generated for a wide range of displacements of the upper potential surface in both a_g modes, and that giving optimum agreement with experiment is also shown

in Figure 5 (the equation defining this surface is given in the caption to the figure). The basic half-width of the component peaks for the optimum simulation was 115 cm^{-1} , and to show the complex nature of the structure underlying the band, the positions and relative intensities of the components are also indicated by showing the spectrum obtained by using a half-width of 10 cm^{-1} .

In order to obtain approximate estimates of the individual changes in bond length accompanying the electronic transition, it was assumed that the normal and symmetry coordinates are identical, that is, that the higher energy mode involves motion of just the water molecules and the lower motion involves that of just the chloride ions. The normal-coordinate analysis carried out on the complex²⁵ suggested that this is a good approximation. Under these circumstances, the change in bond length δr is related to the displacement in the symmetry coordinate ΔS by

$$\delta r = \Delta S / \sqrt{2} \quad (4)$$

Here, ΔS is related to the dimensionless coordinate ξ by eq 3. Substitution of the appropriate masses, 18 for water and 35.5 for chlorine, yields estimates of the change in Cu-O and Cu-Cl bond lengths of 11.3 and 7.8 pm, respectively, which are quite similar to those derived by analysis of the band shapes observed for planar CuCl_4^{2-} , ~ 9 pm for the transitions to the ${}^2A_g(z^2)$ and ${}^2B_{2g}(xy)$ excited states.²

The spectrum of $\text{Cu}(4\text{-picO})_2\text{Cl}_2$ also exhibits vibrational fine structure at low temperature (Figure 3), this being best resolved in the highest energy peak. As molecular spectra could not be derived for this complex, a quantitative interpretation of this feature was not attempted. However, it is noteworthy that the observed progressional interval, ~ 140 cm^{-1} , is much lower than the value of ~ 400 cm^{-1} observed for $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\text{Ph}_3\text{PO}$, being quite close to the energy proposed for the ν_1 Cu-O stretching mode of $\text{Cu}(4\text{-picO})_2\text{Cl}_2$, in which the whole amine oxide ligand is involved in the vibration (137 cm^{-1} , Table I). This seems reasonable, as in the excited electronic state the lengthening of each Cu-O bond must involve displacement of the whole ligand, rather than just the oxygen atoms. The progressional frequency observed in the electronic spectrum of $\text{Cu}(4\text{-picO})_2\text{Cl}_2$ thus apparently lies between those of the ν_2 and lower energy ν_1 vibrations, but close to that of the Cu-O stretching mode, as was also observed for $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\text{Ph}_3\text{PO}$, suggesting that the bond length changes accompanying the electronic transitions in the two complexes are quite similar.

Assignment of the High-Energy Band in the Spectrum of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\text{Ph}_3\text{PO}$. At low temperature, a weak band centered at $\sim 20\,600$ cm^{-1} is observed in the electronic spectrum of $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2] \cdot 4\text{Ph}_3\text{PO}$ in x polarization (Figure 2). The vibrational fine structure on this mirrors that on the ${}^2A_g(z^2)$ transition centered ~ 3000 cm^{-1} lower in energy, suggesting that the weak band may be due to a transition to this d state coupled to what is formally an O-H stretching mode of the water ligands. Bands of this kind have been reported for a number of other hydrate complexes.³⁶⁻³⁹ To test this hypothesis, attempts were made to prepare the complex in which the H_2O ligands were replaced by D_2O , but the highest levels of deuteration that could be achieved were only $\sim 60\%$. In the electronic spectrum of such a crystal with the electric vector along the [102] direction (approximately along the x axis) the anomalous high-energy band was observed to be significantly weaker for the partially deuterated crystal, confirming that this is probably due to the d-d transition coupling with one or more internal water vibrations.

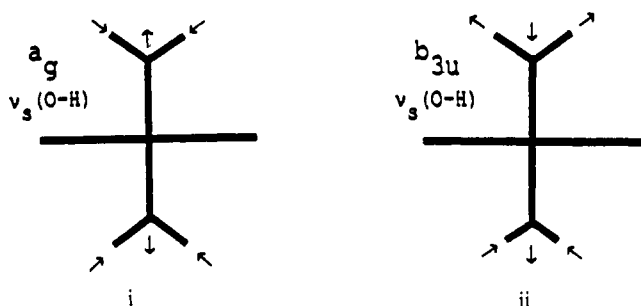
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Table V. Observed and Calculated Transition Energies and Metal–Ligand Bonding Parameters of [Cu(H₂O)₂Cl₂]₂·4Ph₃PO and Cu(4-picO)₂Cl₂ Compared with Those of Planar CuCl₄²⁻

| | transition energy, cm ⁻¹ | | | | AOM bonding parameter, cm ⁻¹ | | | | | |
|------------------------|--|--------|--------|----------------|---|---------------------|--------------------|---------------------|---------------------|-----------------|
| | xy | xz | yz | z ² | e _σ (Cl) | e _π (Cl) | e _σ (O) | e _{πx} (O) | e _{πy} (O) | e _{ds} |
| | CuCl ₄ ²⁻ | | | | | | | | | |
| obs | 12 155 | 13 960 | | 16 560 | | | | | | |
| calc ^a | 12 160 | 13 855 | 14 085 | 16 560 | 5250 | 885 | | | | 1450 |
| | [Cu(H ₂ O) ₂ Cl ₂] ₂ ·4Ph ₃ PO | | | | | | | | | |
| obs | 13 240 | 15 410 | 15 180 | 17 710 | | | | | | |
| calc (I) ^b | 13 240 | 15 415 | 15 175 | 17 710 | 5560 | 940 | 5880 | 1060 | 830 | 1485 |
| calc (II) ^b | 13 240 | 15 445 | 15 170 | 17 710 | 5560 | 1150 | 6145 | 820 | 1250 | 1415 |
| | Cu(4-picO) ₂ Cl ₂ | | | | | | | | | |
| obs | 12 760 | 14 400 | 14 600 | 17 470 | | | | | | |
| calc ^a | 12 770 | 14 420 | 14 800 | 17 470 | 5750 | 970 | 5225 | 850 | 760 | 1550 |

^a Calculated by using an effective spin–orbit coupling constant of -580 cm^{-1} . ^b Calculated by using an effective spin–orbit coupling constant of -620 cm^{-1} .

There are two ways in which combinations of the internal stretching vibrations of the water molecules might act to produce the observed band. One quantum of the a_g combination of the symmetric O–H stretching modes, illustrated in diagram i, could



add to the “normal” d–d excitation. In effect, this would make this “anomalous” band the second member of a progression in this vibration, analogous to those in the metal–ligand modes of a_g symmetry discussed in the previous section. However, it is difficult to see why this mechanism should not induce the same band shape in every polarization, which conflicts with the observation that the band is polarized along the copper–oxygen bond direction (Figure 2). It has been noted that a similar band in the spectra of the complexes $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$ and $\text{V}(\text{H}_2\text{O})_4\text{Cl}_2^+$ is similarly polarized along the xy molecular axes.^{37,38}

The second plausible mechanism by which the anomalous band might occur involves combinations of the internal water vibrations that destroy the inversion symmetry of the complex. The combination of the symmetric O–H stretches shown in diagram ii has the same symmetry as the metal–ligand vibration of b_{3u} symmetry and would hence induce intensity in the ${}^2A_g(z^2) \leftarrow {}^2A_g(x^2 - y^2)$ transition in x polarization. However, this motion of the oxygen atoms is similar to the higher energy b_{3u} metal–ligand mode, ν_8 , which is apparently ineffective in inducing intensity (see earlier section). It thus appears that neither of the above mechanisms provides an entirely satisfactory explanation of all of the properties of the anomalous band at $\sim 20\,600\text{ cm}^{-1}$, and we are currently attempting more detailed normal-coordinate calculations in an attempt to better understand the nature of this transition. A further observation that requires consideration is the fact that the band apparently broadens and decreases in intensity upon increase in temperature (Figure 4), a feature that has been noted for other transitions of this type.^{37,38} Both of the above mechanisms depend upon the internal vibrations of the two water molecules acting coherently. Possibly, the increase in thermal motion of the lattice as the temperature rises causes loss of this coherence, hence decreasing the coupling of the d–d transition with the water vibrations.

Metal–Ligand Bonding Parameters. The angular overlap model (AOM), developed originally by Schäffer and Jørgensen,⁴⁰ pro-

vides a convenient way of interpreting the d-orbital energies in transition-metal complexes in terms of metal–ligand bonding parameters. This method and the related cellular ligand field (CLF) approach⁴¹ have recently been applied to a range of copper(II) complexes involving chloride^{1,42–44} and oxygen donor^{39,43,45,46} ligands. In the present study, the computer program CAMMAG, developed by Gerloch and co-workers,⁴⁷ was used to determine the AOM bonding parameters in optimum agreement with the observed transition energies of the complexes.

This program calculates the energy levels of a complex of known geometry, taking as input the bonding parameters e_σ , $e_{\pi x}$, and $e_{\pi y}$ of each ligand and the information provided by the crystal structure determination of the compound. To fully define the d orbitals of either [Cu(H₂O)₂Cl₂]₂·4Ph₃PO or Cu(4-picO)₂Cl₂, five metal–ligand parameters are necessary, one σ and one π parameter for the chloride (assuming the π bonding to be isotropic about the Cu–Cl bond axis) and one σ and two π parameters for the oxygen donor ligands (here $e_{\pi x}$ refers to the π interaction parallel to the plane defined by the water hydrogen atoms for the former complex and the aromatic ring system of the amine oxide for the latter). In addition, for planar complexes it has been found that the d_{z^2} orbital lies at anomalously low energy.¹⁰ This effect has been ascribed to configuration interaction with the empty metal 4s orbital⁷ and is taken into account in the present model by an additional parameter e_{ds} , with the d_{z^2} orbital being lowered in energy by an amount $4e_{ds}$.⁴²

As only four transition energies are observed for each of the above two compounds, it is impossible to determine all six metal–ligand bonding parameters uniquely. The chloride parameters were therefore set equal to those observed in the planar CuCl₄²⁻ ion, with slight corrections being made for the minor differences in Cu–Cl bond length. Here (calculation 1 in Table V), it was assumed that the bonding parameters vary inversely as approximately the fifth power of the bond distance, as suggested both by the pressure dependence of d–d transition energies of various octahedral complexes⁴⁷ and by theoretical considerations.⁴⁸ It has been found that the transition energies observed for a wide range of tetrachlorocuprates with distorted tetrahedral geometries can be reproduced satisfactorily in this way.⁴ The bonding pa-

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rameters for the oxygen donor ligands in $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ and $\text{Cu}(4\text{-picO})_2\text{Cl}_2$ derived by using these approximations are given in Table V, together with those of planar CuCl_4^{2-} for comparison. Effective spin-orbit coupling constants of -580 cm^{-1} for the tetrachloride and pyridine *N*-oxide complexes and -620 cm^{-1} for the hydrate complex were used in these calculations.

It may be seen that the water ligands are found to have a somewhat stronger σ -bonding power than the chloride ions in the $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$ complex ($e_\sigma = 5880\text{ cm}^{-1}$ compared with $e_\sigma = 5560\text{ cm}^{-1}$), though, considering the approximations in the present treatment, it is doubtful that the difference is significant. However, a recent analysis of the temperature dependence of the EPR spectrum of the $\text{CuCl}_4(\text{H}_2\text{O})_2^{2-}$ complex present in copper(II)-doped NH_4Cl shows that here also the water ligand is a slightly stronger σ donor than chloride.⁵⁰ The unusual dynamic behavior of this complex is ascribed to the difference in σ -bonding power of the chloride and water ligands, and the analysis provides an estimate, $e_\sigma(\text{H}_2\text{O}) - e_\sigma(\text{Cl}^-) = \sim 200\text{ cm}^{-1}$, which agrees quite well with that of the present study ($\sim 300\text{ cm}^{-1}$). The above value also agrees well with estimates³⁸ derived from the electronic spectrum of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (here, e_σ was found to range from ~ 5800 to 4500 cm^{-1} for Cu-O bond lengths ranging from 1.932 to 1.971 Å; the Cu-O distance in $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$, 1.904 Å, is shorter than these). A surprising feature of the analysis is the significant value (1060 cm^{-1}) deduced for $e_{\pi x}$, the π interaction parallel to the H-H vector of the water hydrogen atoms—a simple covalent picture of the bonding in a metal hydrate complex would suggest that this parameter should be close to zero. This anomaly, which has also been noted in the analysis of the optical spectra of other hydrate complexes,^{38,51} may possibly be due to the effects of so-called “misdirected valency”.⁵² If a higher value was taken for the π -bonding parameter of the chloride ligands (calculation 2 of Table V) this would imply a lower value of $e_{\pi x}$ for the water ligands.

The σ -bonding parameter of the pyridine *N*-oxide ligand was determined to be somewhat lower than that of both water and chloride, possibly reflecting the long Cu-O bond distance in this complex compared with $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$ (an inverse dependence on the fifth power of the bond length would in fact predict a decrease in e_σ from 5880 to 5230 cm^{-1} as the Cu-O bonds lengthen from 1.904 Å in $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ to 1.949 Å in $\text{Cu}(4\text{-picO})_2\text{Cl}_2$, in excellent agreement with the value of 5225 cm^{-1} estimated for the latter compound). The π -bonding parameters deduced for the *N*-oxide ligand are quite small and effectively isotropic about the Cu-O bond axis ($e_{\pi x} = 850\text{ cm}^{-1}$, $e_{\pi y} = 760\text{ cm}^{-1}$). However, here, σ - π cross terms should be included in any rigorous inter-

pretation of the interactions with the metal orbitals of π symmetry.⁵² These were not investigated in the present study so that the π -bonding parameters given in Table V should be considered quite approximate estimates.

The values of the parameter e_{ds} for $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ and $\text{Cu}(4\text{-picO})_2\text{Cl}_2$, 1485 and 1550 cm^{-1} , respectively, are quite similar to that derived for planar CuCl_4^{2-} , 1450 cm^{-1} . Simple theory^{7,42} suggests that e_{ds} reflects the depression in energy of the $a_g(d_{z^2})$ orbital caused by configuration interaction with the empty metal $a_g(4s)$ orbital and that the magnitude of this interaction should be proportional to the difference in metal-ligand interaction along the *z* and *xy* axes.⁴² The high values of these parameters are thus consistent with the planar, four-coordinate nature of the complexes.

Conclusions

The electronic spectra of the $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$ and $\text{Cu}(4\text{-picO})_2\text{Cl}_2$ complexes are quite similar to that of planar CuCl_4^{2-} , except that the former complex exhibits an anomalous band $\sim 3000\text{ cm}^{-1}$ higher in energy than the highest d-d transition. This band, which is polarized along the Cu-O bond vectors, is thought to be caused by coupling of the d-d transition with internal O-H stretching vibrations of the water molecules, though the precise mechanism by which this takes place remains unclear. For $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$ the variation of the band intensities as a function of temperature is generally consistent with the assignments of the *u* vibrations deduced from the infrared spectrum of the complex. As with planar CuCl_4^{2-} , the out-of-plane bending vibration, which carries the complex toward a tetrahedral geometry, is inferred to have a very low energy, $\sim 70\text{ cm}^{-1}$. Although this was not investigated quantitatively, the large red shifts observed for the band maxima on raising the temperature from 10 to 295 K suggest that the equilibrium geometry of the $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$ complex is substantially distorted toward a tetrahedron in the excited electronic states. The vibrational fine structure observed at low temperature in the spectrum of $\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2$ implies displacements in both totally symmetric normal vibrations of the complex, consistent with expansions in both the Cu-O and Cu-Cl bond lengths in the excited electronic states, and similar conclusions can be drawn from the structure seen in the spectrum of $\text{Cu}(4\text{-picO})_2\text{Cl}_2$. The water ligands in $[\text{Cu}(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 4\text{Ph}_3\text{PO}$ are slightly stronger σ donors than the chloride ions, while the amine oxide ligands in $\text{Cu}(4\text{-picO})_2\text{Cl}_2$ are marginally weaker. In both compounds, the oxygen ligands act as π donors, with the anisotropy of this interaction being uncertain.

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