# Electronic Spectra and Bonding Parameters of Three Planar Complexes *trans*-CuCl$_2$N$_2$ Where N Is a Heterocyclic Amine

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The electronic spectra of single crystals of the planar, four-coordinate complexes CuCl$_2$L$_2$, L = 1-phenyl-3,5-dimethylpyrazole (pdmp), 2,6-dimethylpyridine (2,6-lut), and 2,3-dimethylpyridine (2,3-lut) and the molecular *g* values of CuCl$_2$(2,6-lut)$_2$ are reported. The temperature dependence of the band shape of the lowest energy transition of CuCl$_2$(pdmp)$_2$ suggests that a low-energy vibrational mode of a$_g$ symmetry couples with the electronic transition, and this is also suggested by the spacing between the peaks comprising the fine structure observed in the low-temperature spectrum of CuCl$_2$(2,6-lut)$_2$. This latter spacing differs from the energy of both a$_g$ vibrational modes contributing to the band shape, which is in effect an interference pattern resulting from the addition of several progressions. The d-orbital energy sequence in the complexes is d$_{z^2}$ < d$_{xz}$ < d$_{yz}$ < d$_{xy}$ ≪ d$_{x^2-y^2}$, and an analysis using the angular overlap model suggests similar σ-bonding parameters for the amine ligands, with these being significantly higher than that of the chloride ion. The amines act as weak π-donors and, in agreement with simple theory, the metal–ligand π-interaction in the plane of these ligands is negligible. As with other planar complexes, the d$_{z^2}$ orbital is much lower in energy than simple theory predicts, probably because of configuration interaction with the higher energy metal 4s orbital.

## 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 in both the ground and excited electronic states of this complex.[1-6] The transition energies have been used to deduce angular overlap metal–ligand bonding parameters for chloride toward Cu$^{2+}$, and it was inferred that the $^2$A$_{1g}$(z$^2$) excited state is considerably higher in energy than is predicted by simple bonding schemes.[1] This feature has since been confirmed in a range of other planar complexes.[7] Analysis of the temperature dependence of the band intensities provided a means of probing the energies of the ungerade vibrations, and the out-of-plane bending mode of b$_{2u}$ symmetry, which is both infrared and Raman inactive, was found to be of very low energy.[1,2,6] 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 has also allowed the deduction of the extent to which the Cu–Cl bonds lengthen in each excited state,[1,2] providing a useful test of simple models relating bond length to the d-electron configuration of a transition-metal complex.[8]

In view of the above, analysis of 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 *trans*-CuCl$_2$X$_2$, where X is a nitrogen or oxygen donor ligand. We present here results on three compounds involving heterocyclic amines: CuCl$_2$(2,3-lut)$_2$, CuCl$_2$(2,6-lut)$_2$, and CuCl$_2$(pdmp)$_2$ (2,3-lut = 2,3-dimethylpyridine, 2,6-lut = 2,6-dimethylpyridine, pdmp = 1-phenyl-3,5-dimethylpyrazole). In addition, the EPR spectrum has been used to derive the molecular *g* values for CuCl$_2$(2,6-lut)$_2$. The bonding characteristics of these amines should be of particular interest, both because of their similarity to ligands of biological importance and because the π-bonding capacity of heterocyclic amines has been the subject of some controversy.[9,10]

## Experiment Section

The three complexes were prepared by following methods described previously,[11-13] and all had satisfactory analyses. Anal. Calcd for CuCl$_2$(2,3-lut)$_2$ (C$_{14}$H$_{18}$N$_2$CuCl$_2$): C, 48.22; H, 5.20; N, 8.03. Found: C, 47.94; H, 5.19; N, 7.90. Anal. Calcd for CuCl$_2$(2,6-lut)$_2$ (C$_{14}$H$_{18}$N$_2$CuCl$_2$): C, 48.22; H, 5.20; N, 8.03. Found: C, 48.22; H, 5.11; N, 7.91. Anal. Calcd for CuCl$_2$(pdmp)$_2$ (C$_{20}$H$_{24}$N$_4$CuCl$_2$): C, 55.17; H, 5.05; N, 11.70. Found: C, 54.86; H, 5.01; N, 11.69. The compound CuCl$_2$(2,3-lut)$_2$ crystallized from ethanol as chunky plates

**Table I.** Molecular Projections for the Extinction Directions of the Complexes

| complex | direction | $x^2$ | $y^2$ | $z^2$ |
|---|---|---|---|---|
| CuCl$_2$(pdmp)$_2$ | [100] | 0.072 | 0.043 | 0.886 |
| | [010] | 0.802 | 0.169 | 0.027 |
| | [101] | 0.086 | 0.687 | 0.227 |
| CuCl$_2$(2,3-lut)$_2$ | (010)$^a$ | 0.850 | 0.006 | 0.144 |
| | (010)$^b$ | 0.036 | 0.583 | 0.381 |
| CuCl$_2$(2,6-lut)$_2$ | (001)$^c$ | 0.090 | 0.894 | 0.016 |
| | (001)$^d$ | 0.083 | 0.001 | 0.916 |
| | $e$ | 0.55 | 0.15 | 0.30 |
| | $e$ | 0.16 | 0.16 | 0.68 |

$^a$76° to the [001] axis. $^b$-14° to the [001] axis. $^c$-35° to the [100] axis. $^d$55° to the [100] axis. $^e$Molecular projections for the (1̄11) crystal face derived by measuring the *g* values from the EPR spectrum of the complex.

with the (010), (011), and (01̄1) faces well developed, while CuCl$_2$(2,6-lut)$_2$ crystallized from methanol with the (1̄11) and to a lesser extent the (001) and (010) faces of the triclinic unit cell well developed. The compound CuCl$_2$(pdmp)$_2$ formed with the (001) and (101̄) faces well developed upon being recrystallized from ethanol and methyl cyanide, respectively.

Electron paramagnetic resonance (EPR) spectra were measured by using a JEOL FE3X spectrometer operating at X-band (~9 GHz) frequency with the crystals being rotated with the standard JEOL accessory. Electronic spectra were measured on a Cary 17 spectrophotometer using polarized light with the crystals mounted by a technique described previously.[2,14] The samples were cooled with 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%. Crystal

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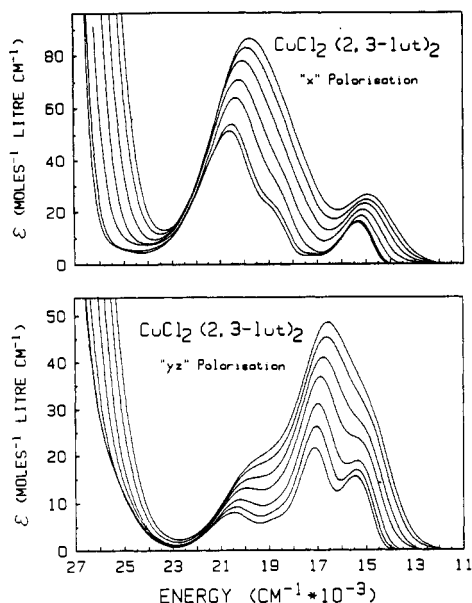
**Figure 1.** Electronic spectra of the (010) crystal face of $CuCl_2(2,3\text{-lut})_2$ with the electric vector at 76° ("x") and −14° ("yz") to the [001] direction measured at 10, 50, 100, 150, 200, 250, and 290 K. The intensity increases progressively with temperature.
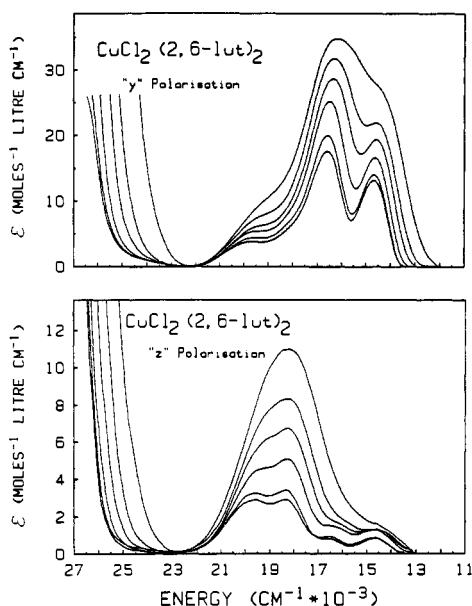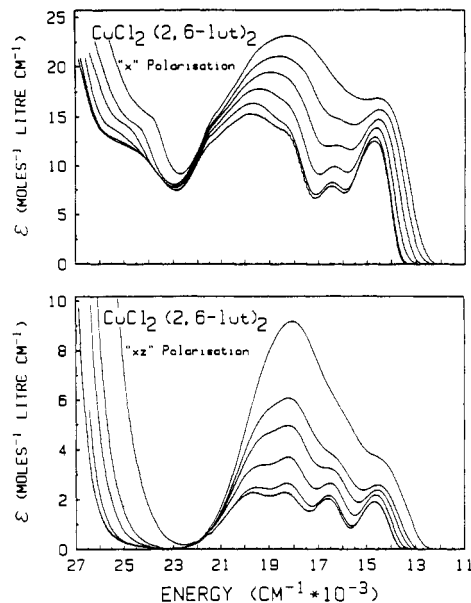


**Figure 2.** Electronic spectra of the (001) crystal face of $CuCl_2(2,6\text{-lut})_2$ with the electric vector at −35° ("y") and 55° ("z") to the [100] direction measured at 10, 50, 100, 150, 200, and 290 K. The intensity increases progressively with temperature.

morphologies were identified by measuring interfacial crystal angles with a stereoscopic polarizing microscope and were confirmed where necessary by analysis of the single-crystal EPR spectrum of the complexes.

## Results and Discussion

**Geometry of the Complexes.** The basic stereochemistry of the three complexes is very similar. Each lies on a crystallographic inversion center and is thus rigorously centrosymmetric, with a planar, four-coordinate geometry. In every case, the in-plane bond angles are very close to 90° and the plane of the amine ring is approximately orthogonal to the plane of the primary coordination sphere, the dihedral angles being 79.8, 86.4, and 88.4° for $CuCl_2(pdmp)_2$,[11] $CuCl_2(2,6\text{-lut})_2$,[15] and $CuCl_2(2,3\text{-lut})_2$,[16] respectively.

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**Figure 3.** Electronic spectra of the (1̄11) crystal face of $CuCl_2(2,6\text{-lut})_2$. See Table I for the appropriate molecular projections for each spectrum. In order of increasing intensity, the five lowest spectra were recorded at 10, 50, 100, 150, and 200 K, with the most intense spectra being measured at 250 and 290 K for polarizations "x" and "xz", respectively.
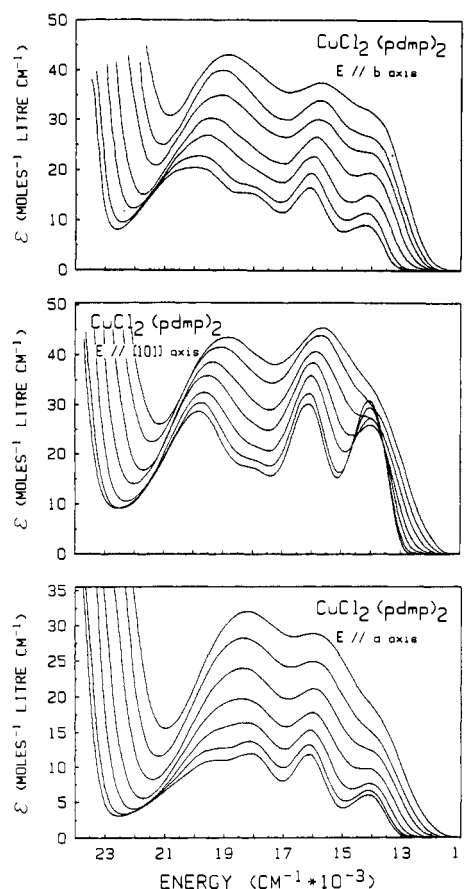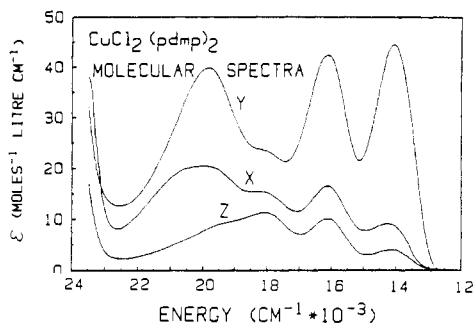


**Figure 4.** Electronic spectra of $CuCl_2(pdmp)_2$ with the electric vector parallel to the [010], [101], and [100] directions measured at 10, 50, 100, 150, 200, 250, and 290 K. The intensity increases progressively with temperature.

**Electronic Spectra.** The temperature dependence of the electronic spectra of $CuCl_2(2,3\text{-lut})_2$, with the electric vector parallel to the extinction directions of the (010) crystal face, is shown in Figure 1. Similar spectra for the (001) and (1̄11) crystal faces of $CuCl_2(2,6\text{-lut})_2$ and the (001) and (101̄) faces of $CuCl_2(pdmp)_2$ are shown in Figures 2–4. The squares of the molecular pro-

**Figure 5.** Molecular electronic spectra of $CuCl_2(pdmp)_2$ calculated from the [010], [101], and [100] crystal spectra measured at 10 K.

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

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

jections associated with each of these spectra are given in Table I; here, $x$ is parallel to the Cu–N vector, $z$ is normal to x and the Cu–Cl vector, and $y$ is normal to $x$ and $z$. For the ($\bar{1}11$) face of $CuCl_2(2,6\text{-lut})_2$, the angles between the extinction directions and the crystal axes could not be measured accurately, so the molecular projections were deduced by measuring the $g$ values with the magnetic field along each extinction direction, and comparing these with the molecular $g$ values of the complex. In the case of $CuCl_2(pdmp)_2$, it may be seen that the three crystal spectra correspond quite closely to the molecular spectra, and these are shown in Figure 5, after correction of the low-temperature spectra for the minor misalignments inherent in the crystal spectra by a procedure described in detail elsewhere.[14]

**Assignment of the Bands.** Each complex is centrosymmetric, so that the intensity of the "d–d" transitions is gained by coupling with ungerade vibrations. The complexes $CuCl_2(2,3\text{-lut})_2$ and $CuCl_2(2,6\text{-lut})_2$ both deviate very little from the point group $D_{2h}$, and the vibronic selection rules for a copper(II) complex of this symmetry are shown in Table II. It may be seen that in this point group the 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.

Four bands are observed at low temperature in the electronic spectra of $CuCl_2(2,3\text{-lut})_2$, centered at 15 370, 17 100, 19 050, and 20 550 cm$^{-1}$. The band at 17 100 cm$^{-1}$ is absent when the electric vector is approximately along the $x$ axis (Figure 1, Table I), so that this can confidently be assigned to the transition $^2B_{3g}(yz) \leftarrow {}^2A_g(x^2 - y^2)$. The band at 19 050 cm$^{-1}$ decreases substantially in intensity when the spectrum obtained with the electric vector at $-14°$ to the [001] direction is compared with that at 76° (Figure 1). This coincides with a large increase in the $y$ molecular projection (Table I), making it highly likely that this band is due to the transition $^2B_{2g}(xz) \leftarrow {}^2A_g(x^2 - y^2)$.

The low-temperature spectra of the (001) crystal face of $CuCl_2(2,6\text{-lut})_2$ also show four bands at energies of 14 720, 16 630, 18 330, and 19 670 cm$^{-1}$. These are similar to those of the analogous $CuCl_2(2,3\text{-lut})_2$ complex except for a small shift to lower energy, which is probably related to the slightly longer metal–ligand bond lengths in the former complex. The peak at 18 330 cm$^{-1}$ is virtually absent in $y$ polarization (Figure 2, Table I) and hence must be due to the transition $^2B_{2g}(xz) \leftarrow {}^2A_g(x^2 - y^2)$. The two lowest energy bands are both very weak in $z$ polarization, so that on this basis either could be assigned to the transition $^2B_{1g}(xy) \leftarrow {}^2A_g(x^2 - y^2)$, which is forbidden in this polarization. However, the band at 16 630 cm$^{-1}$ is by far the weakest peak in the ($\bar{1}11$) spectrum having the greatest $x$ contribution (Figure 3, Table I), when the transition to the $^2B_{2g}(yz)$ state is forbidden, so that it is likely that this band is due to the transition to this excited state.

The lowest energy band is then assigned to the $^2B_{1g}(xy) \leftarrow {}^2A_g(x^2 - y^2)$ transition, leaving that at 19 670 cm$^{-1}$ as being due to the transition to the $^2A_g(z^2)$ excited state.

In addition to these four bands, which must account for all the possible "d–d" transitions, the spectrum of the ($\bar{1}11$) face of $CuCl_2(2,6\text{-lut})_2$ shows weak bands centered at $\sim$21 500 cm$^{-1}$ and $\sim$24 500 cm$^{-1}$ when the electric vector makes a projection of 0.55 with the $x$ axis (Figure 3). The band at $\sim$24 500 cm$^{-1}$ was also observed by Ludwig and Gasser[17] in the reflection spectrum of $CuCl_2(2,6\text{-lut})_2$ and other similar planar complexes, and was assigned as a parity-forbidden chloride → metal charge-transfer transition. If this assignment is correct, it is surprising that the analogous peak is not resolved in the $x$ spectrum of $CuCl_2(2,3\text{-lut})_2$ (Figure 1). The weak shoulder at $\sim$21 500 cm$^{-1}$ is similar to a band at $\sim$20 300 cm$^{-1}$ observed by Desjardins et al.[18] in the single-crystal spectra of bis(methadonium)$CuCl_4$, $(metH)_2CuCl_4$, which was assigned to trace amounts of the complex $CuCl_3(OH)^{2-}$. Possibly the band at $\sim$21 500 cm$^{-1}$ in the spectrum of $CuCl_2(2,6\text{-lut})_2$ is due to a charge-transfer transition associated with trace amounts of an impurity such as $CuCl(OH)(2,6\text{-lut})_2$.

The electronic spectrum of $CuCl_2(pdmp)_2$ shows four bands centered at 13 970, 16 070, 18 100, and 19 540 cm$^{-1}$, these energies being quite similar to the "d–d" bands of $CuCl_2(2,6\text{-lut})_2$. The complex $CuCl_2(pdmp)_2$ deviates somewhat from $D_{2h}$ symmetry, first because of the asymmetry of the pyrazole ligand (the uncoordinated nitrogen atom is only 298 pm from the copper ion) and second because the plane of the amine is not strictly orthogonal to that of the primary coordination sphere (the dihedral angle is 79.8°). The strict point group of $CuCl_2(pdmp)_2$ is $C_i$, in which an ungerade vibration is available to induce intensity into every "d–d" transition. This may explain why each band is observed in every polarization in the molecular spectrum of this complex (Figure 5). However, it is noteworthy that the bands at 18 100 and 13 970 cm$^{-1}$ are rather weak in $y$ and $z$ polarization, respectively, which is consistent with the $D_{2h}$ selection rules if these are due to transitions to the $^2B_{2g}(xz)$ and $^2B_{1g}(xy)$ excited states. It seems highly probable that the bands at 16 070 and 19 540 cm$^{-1}$ have similar assignments to the analogous peaks in the other complexes, being due to transitions to the $^2B_{3g}(yz)$ and $^2A_g(z^2)$ excited states, respectively, using $D_{2h}$ notation. It may be seen that the band at 19 540 cm$^{-1}$ is asymmetric to higher energy in $x$ polarization (Figure 5), possibly indicating the presence of a very weak absorption at $\sim$21 500 cm$^{-1}$ similar to that discussed above for $CuCl_2(2,6\text{-lut})_2$.

The spectra of all three complexes thus suggest a similar energy sequence of the d orbitals, $d_{z^2} < d_{xz} < d_{yz} < d_{xy} \ll d_{x^2-y^2}$, which is identical with that derived recently[19] for the analogous, planar complexes $CuCl_2(H_2O)_2$ and $CuCl_2(4\text{-methylpyridine } N\text{-oxide})_2$, $CuCl_2(4\text{-PicNO})_2$.

**Temperature Dependence of the Spectra.** Previous studies[2,19] of the variation as a function of temperature of the band intensities of planar $CuCl_4^{2-}$ and $CuCl_2(H_2O)_2$ have provided estimates of the energies of the ungerade vibrations inducing intensity into the "d–d" transitions. The comparatively poor resolution of the bands at higher temperature (Figures 1–4) precludes a similar quantitative study for the present complexes. However, it is noteworthy that a large increase in intensity is observed for the highest energy bands of $CuCl_2(2,6\text{-lut})_2$ and $CuCl_2(pdmp)_2$ in $z$ polarization as the temperature is raised from 10 to 290 K (Figures 2 and 4). For the former complex, assuming the simple theory of vibronic intensity stealing,[20] an estimate of the approximate band areas suggests an average effective energy of $\sim$100 cm$^{-1}$ for the vi-

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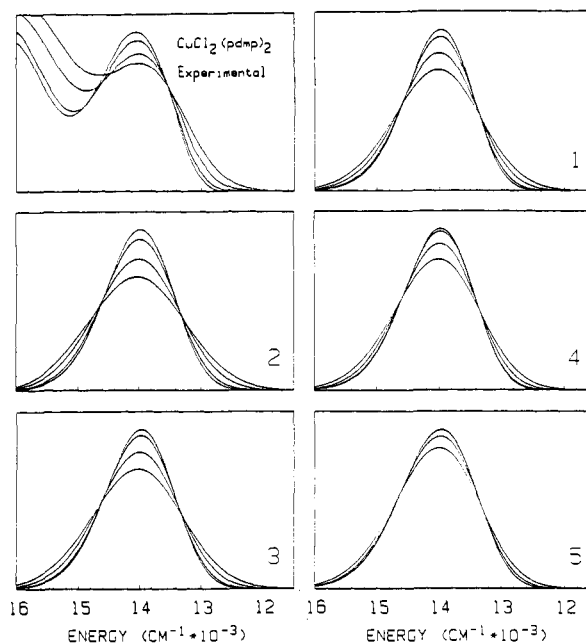(19) McDonald, R. G.; Hitchman, M. A. *Inorg. Chem.*, in press.
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brations inducing intensity. This is quite similar to the energies deduced for the corresponding transitions in the planar CuCl$_4^{2-}$ and CuCl$_2$(H$_2$O)$_2$ complexes. For these two complexes it was inferred[2,19] that much of the intensity is induced by coupling with the out-of-plane bending mode, which carries the complex from a planar toward a tetrahedral geometry, this having an energy of ~70 cm$^{-1}$, and it would seem that this mode also has a low energy for the CuCl$_2$N$_2$ complexes of the present study. This is not unreasonable, as it is known[13,17] that CuCl$_2$(2,6-lut)$_2$ and similar complexes adopt a pseudotetrahedral geometry when dissolved in noncoordinating solvents, suggesting that the planar and tetrahedral stereochemistries are almost equal in energy. Indeed, the (ClCuCl) out-of-plane bending mode of b$_{1u}$ symmetry has been assigned to a peak of energy 94 cm$^{-1}$ in the infrared spectrum of the CuCl$_2$(2,6-lut)$_2$ complex,[12] while the similar mode involving the amine ligands has been assigned[22] to a peak at 68 cm$^{-1}$.

A particularly unusual feature of the electronic spectra of the planar complexes CuCl$_4^{2-}$ and CuCl$_2$(H$_2$O)$_2$ is the red-shift of the band maxima, which occurs on warming from 10 to 290 K.[2,3] The simple theory of vibronic coupling predicts a shift of no more than the energy of the inducing intensity vibration,[14,20] typically ~200 cm$^{-1}$, and the much larger shifts observed for these two complexes, 500–1000 cm$^{-1}$, were ascribed to a distortion from the planar toward a tetrahedral geometry in the equilibrium nuclear geometry of the excited electronic states.[3] In the case of planar CuCl$_4^{2-}$ such a distortion was confirmed by detailed analysis of the vibrational fine structure observed at low temperature for one compound,[6] and the way in which the band shape alters as a function of temperature[3,5] for another. While the poor resolution of the spectra precludes an accurate estimate of the positions of the band maxima at high temperature in the electronic spectra of the CuCl$_2$N$_2$ complexes of the present study, it is clear that the red-shifts occurring on warming from 10 to 290 K are comparatively modest, perhaps 400–500 cm$^{-1}$ in the best resolved transitions of CuCl$_2$(2,3-lut)$_2$ and CuCl$_2$(2,6-lut)$_2$ (Figures 1 and 2). This suggests that if a distortion toward a tetrahedral geometry does occur in the excited electronic states of the planar CuCl$_2$N$_2$ complexes, this is much less pronounced than is the case for planar CuCl$_4^{2-}$ and CuCl$_2$(H$_2$O)$_2$.

The temperature dependence of the lowest energy transition of CuCl$_2$(pdmp)$_2$ in *y* polarization is unusual, as the height of the band actually *decreases* as the temperature is raised (Figures 4 and 6). This is caused by the that the band broadens as the temperature rises, with the area remaining essentially constant. Behavior of this kind is well established for parity-allowed electronic transitions, where the intensity is independent of temperature. The band broadening is associated with the thermal population of higher levels of vibrations of a$_g$ symmetry, and several studies of the phenomenum have been carried out previously.[21] For parity-forbidden transitions, such as those of the present complex, the change in band shape caused by alterations in the population distribution of the a$_g$ levels cannot normally be investigated because the "hot" bands associated with the thermal population of higher levels of the ungerade vibrations inducing intensity also serve to broaden the peaks.[20] However, for the above transition of CuCl$_2$(pdmp)$_2$, no detectable change in intensity occurs as the temperature rises from 10 to 150 K, as over this temperature range the spectral curves pass through two clear isosbestic points (Figures 4 and 6). This implies that the intensity-inducing vibration must be of rather high energy. Assuming the complex to conform to the D$_{2h}$ point group, this vibration is of b$_{3u}$ symmetry. The b$_{3u}$ stretch is indeed expected to be of high energy, and a peak at 240 cm$^{-1}$ in the infrared spectrum of CuCl$_2$(pdmp)$_2$ has been assigned to this mode.[22] It would thus seem that this vibration is responsible for the intensity of the $^2$B$_{1g}$(*xy*) ← $^2$A$_g$(*x*$^2$ − *y*$^2$) transition of CuCl$_2$(pdmp)$_2$ in *y* polarization. However, it is not clear why in this complex the lower

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**Figure 6.** Comparison of simulated and observed band shapes for the lowest energy transition of CuCl$_2$(pdmp)$_2$ in *y* polarization at 10, 50, 100, and 150 K. The constants defining the $\nu_1$ excited state potential were $c_1$ = −5.5, −7.0, −5.8, −4.5, and −2.5, and the ground-state energies of this mode were 90, 90, 110, 140, and 200 cm$^{-1}$, for curves 1–5, respectively, while for the $\nu_2$ excited-state potential $c_1$ = −2.274 for curve 1 and −1.819 for the remaining curves. In every case, both vibrational energies were reduced by 5% in the excited state and the constant $c_2$ = 0.4513 for all potential surfaces.

energy in-plane bening mode of b$_{3u}$ symmetry is apparently inactive in inducing intensity. In planar CuCl$_4^{2-}$ and CuCl$_2$(H$_2$O)$_2$, the bulk of the intensity of the corresponding electronic transition is induced by coupling with this bending vibration,[2,19] which is of rather low energy, ~150 cm$^{-1}$.

As the band intensity of the $^2$B$_{1g}$(*xy*) ← $^2$A$_g$(*x*$^2$ − *y*$^2$) transition of CuCl$_2$(pdmp)$_2$ in *y* polarization is unaffected by ungerade vibrations between 10 and 150 K, it is feasible to investigate only the effects of the a$_g$ vibrations upon the band shape. Symmetry arguments dictate that only progressions in a$_g$ modes will contribute to the band envelope, and raising the temperature thermally populates higher levels of these vibrations. It is the larger amplitudes of these upper levels that cause the intensity of the outer progressional members to increase, broadening the band as the temperature rises. Previous studies, by Day and co-workers, of the way in which bands due to charge-transfer transitions broaden as the temperature increases, made use of analytic expressions relating the half-width to temperature.[21] These expressions, which are analogous to those used to explain the way in which the intensity of parity-forbidden electronic transitions varies with temperature, provided an estimate of the totally symmetric a$_g$ mode in good agreement with that from the Raman spectra of each complex. A similar treatment of the temperature dependence of the bandwidth of the $^2$B$_{1g}$(*xy*) ← $^2$A$_g$(*x*$^2$ − *y*$^2$) transition of CuCl$_2$(pdmp)$_2$ is complicated by the fact that, even if the amine ligands are considered as single units as far as the vibrations of the complex are concerned, progressions in two modes of a$_g$ symmetry are expected to contribute to the band structure.

For this reason, it was decided to investigate the variation of the band shape as a function of temperature by using the variational method developed recently[3-6] to study the effects of vibronic coupling upon various aspects of the electronic spectrum of the planar CuCl$_4^{2-}$ ion. The procedure for simulating the band shapes has been described in detail elsewhere.[3] In the present case, considering that the progressions involve just vibrations of a$_g$ symmetry, this consists of applying a vibrational Hamiltonian of the form

$$H = -0.5\delta^2/\delta\xi^2 + V(\xi) \qquad V(\xi) = c_1\xi + c_2\xi^2 \qquad (1)$$
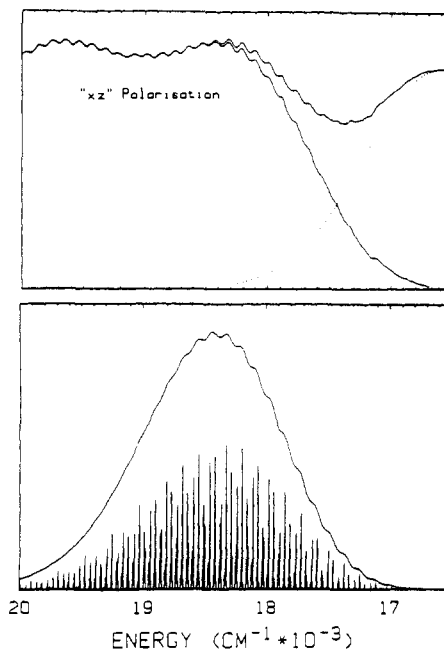
to a basis of harmonic oscillator wave functions characterized by a harmonic energy $h\nu$ to derive the relevant ground- and excited-state potential functions. Here, $\xi$ is a dimensionless coordinate related to the normal coordinate $S$ by

$$\xi = 1.722 \times 10^{-3}(Mh\nu)^{1/2}S \qquad (2)$$

where $M$ is the inverse of the element of the G matrix in amu appropriate to the normal coordinate, $h\nu$ is in cm$^{-1}$, and S is in pm. The matrix elements of (1) are easily evaluated by published methods.[50] Diagonalization of the secular equation yields the energies of the vibrational levels in (nonintegral) units of $h\nu$, and the wave functions as linear combinations of the harmonic basis functions. The overlaps between the components of the ground- and excited-state vibrational wave functions are then calculated and used to estimate the desired Franck–Condon factors. In this procedure, it is assumed that no rotation of the normal coordinates occurs in the excited state (i.e. the Duschinsky effect[23] can be ignored). The band shape at any temperature is obtained by calculating the Boltzmann population distribution over the ground-state energy levels and weighting the transition probabilities accordingly.

In the present case, the relevant basis functions are the two $a_g$ vibrations, $\nu_1$ and $\nu_2$, where $\nu_1$ largely involves motion of the amine ligands and $\nu_2$ involves motion of the chloride ions. In the ground state, the Raman spectrum of $CuCl_2(pdmp)_2$ suggests an energy of 246 cm$^{-1}$ for the latter mode,[22] this being quite similar to the energy of the totally symmetric stretch[2] in planar $CuCl_4^{2-}$, $\sim$275 cm$^{-1}$, and to the energies of the peaks assigned[22] to the $\nu_2$ mode in $CuCl_2(2,3\text{-lut})_2$ and $CuCl_2(2,6\text{-lut})_2$, 251 and 245 cm$^{-1}$, respectively. The energy of the $\nu_1$ mode is uncertain, though it is expected to be quite low because of the large effective mass of the amines. On the basis of a force-field calculation, Suzuki and Orville-Thomas[24] estimated the energy of the metal–amine totally symmetric stretch as $\sim$146 cm$^{-1}$ for $CuCl_2(py)_2$, and similar values have been suggested by other workers.[25] An even lower energy is expected for $CuCl_2(pdmp)_2$, because of the greater mass of the amine, and band-shape simulations were carried out by assuming energies of 90, 110, 140, and 200 cm$^{-1}$ for the $\nu_1$ mode. It is expected that the vibrational energies will be reduced slightly in the excited electronic states, and a 5% reduction was assumed for both the $\nu_1$ and $\nu_2$ modes, this being similar to that deduced from the vibrational structure observed in the electronic spectra of a range of complexes.[8,14]

The bandwidth of an electronic transition depends upon the extent to which the excited state is displaced from the ground state in the $a_g$ coordinates.[14] In the present simulations, a displacement in $\nu_2$ corresponding to a lengthening $\Delta S = 11.3$ pm was used. Assuming this mode to involve motion of the chloride ions only, this corresponds to a change $\delta r \approx \Delta S/\sqrt{2} \approx 8$ pm in each Cu–Cl bond, this being equal to that deduced previously[2] for the lowest energy "d–d" transition of planar $CuCl_4^{2-}$. The displacement in the $\nu_1$ mode was then chosen to produce optimum agreement with the low-temperature band shape. The simulated band shapes and the way in which these change as the temperature is raised from 10 to 150 K are shown in Figure 6 for ground-state energies of the $\nu_1$ mode ranging from 90 to 200 cm$^{-1}$. The constants defining each potential surface are given in the caption to Figure 6. For the calculation giving curve 1, a change in the Cu–Cl bond length $\delta r \approx 10$ pm was used, but it can be seen that this has little effect on the resulting simulations. If it is assumed that the reduced mass of the $\nu_1$ vibration is $1/m_L$, where $m_L$ is the mass of the ligand, this yields estimates of the lengthening of the Cu–N bonds in the range $\delta r \approx 17$–23 pm. These seem too large by a factor of $\sim$2, possibly because this simple approach ignores both the weak Cu···N axial interactions and the coupling with internal ligand vibrations. Simulations (curves 2–5) show that the tem-

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**Figure 7.** Comparison of the simulated band shape of the transition to the $^2B_{2g}(xz)$ state with that observed experimentally at 10 K for the ($\bar{1}11$) crystal face of $CuCl_2(2,6\text{-lut})_2$. For the simulations, the ground-state vibrational energies were 140 and 244 cm$^{-1}$ for the $\nu_1$ and $\nu_2$ modes, respectively, with these being reduced to 130 and 220 cm$^{-1}$ in the excited state. The constants $c_1$ defining the displacements in the excited-state potential surfaces were $-4.0$ for the $\nu_1$ mode and $-2.2696$ for the $\nu_2$ mode. A basic half-width of 38 cm$^{-1}$ was used for the components, with the complexity of the underlying structure being illustrated by also presenting the curves derived by using a half-width of 2 cm$^{-1}$.

perature dependence of the band shape is quite sensitive to the energy of the $a_g$ modes generating the band. In particular, the temperature at which the band height starts to decrease rises progressively as the energy of the $\nu_1$ vibration increases. Optimum agreement with experiment is obtained for either $\nu_1 = 90$ or 110 cm$^{-1}$, suggesting that $\nu_1 \approx 100$ cm$^{-1}$ in the complex. The Raman spectrum of $CuCl_2(pdmp)_2$ does indeed show a strong peak at 109 cm$^{-1}$, which may possibly be due to this mode.[22] The low energy of the $\nu_1$ vibration is confirmed by the analysis of the vibrational fine structure observed in the spectrum of $CuCl_2(2,6\text{-lut})_2$ (see following section).

**Vibrational Fine Structure.** At low temperature, the electronic spectrum of $CuCl_2(2,6\text{-lut})_2$ exhibits vibrational fine structure on the two highest energy transitions, this being best resolved in the spectra of the ($\bar{1}11$) face (Figures 3 and 7). Previous studies[1,2,4,5] of similar structure observed in the spectrum of planar $CuCl_4^{2-}$ have shown that, in agreement with theory, the progressions occur in the $a_{1g}$ symmetric stretching mode. For $CuCl_2(2,6\text{-lut})_2$ the situation is complicated by the fact that, even making the simplifying assumption that the amine ligands behave as single units, two modes of $a_g$ symmetry occur. In order to simulate the spectra, the energies of these $\nu_1$ and $\nu_2$ modes are required. The $\nu_2$ mode is readily assigned to an intense band at 245 cm$^{-1}$ in the Raman spectrum[22] of $CuCl_2(2,6\text{-lut})_2$, but the assignment of the $\nu_1$ metal–amine stretch is less certain. This vibration has been assigned at $\sim$145 cm$^{-1}$ in $CuCl_2(py)_2$ and similar complexes,[24,25] and a somewhat lower energy seems likely in $CuCl_2(2,6\text{-lut})_2$, because of the greater mass of the amine. The Raman spectrum of the complex[22] shows bands at 140 and 125 cm$^{-1}$, and both of these possibilities were explored in the simulations. Optimum agreement was obtained by assuming the former assignment (Figure 7), with the energies of the $\nu_1$ and $\nu_2$ modes reduced to 130 and 220 cm$^{-1}$, respectively, in the excited state. The energy separation between the members of the progression in the simulated spectrum, 108 cm$^{-1}$, is in excellent agreement with that observed experimentally, $\sim$110 cm$^{-1}$. A half-width of 38 cm$^{-1}$ was used for the component peaks of the optimum simulations, but the complex nature of the underlying band structure is also

illustrated by using a component half-width of 2 cm$^{-1}$. The constants defining the form of the potential surfaces of the excited state are given in the figure caption. The displacement with respect to the ground state in the $\nu_2$ mode, $\Delta S = 14.1$ pm, $\delta r \approx \Delta S/\sqrt{2} \approx 10$ pm is identical with that deduced[2,3] for the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition of planar CuCl$_4^{2-}$. Assuming that the reduced mass of the $\nu_1$ mode equals that of the whole ligand, the change in this normal coordinate, $\delta\xi = 4$, corresponds to a displacement of 13 pm in each Cu–N bond, which also seems reasonable.

As was also the case[19] in the similar planar complexes with oxygen donor ligands, CuCl$_2$(H$_2$O)$_2$ and CuCl$_2$(4-PicNO)$_2$, the progressional interval observed in the electronic spectrum of CuCl$_2$(2,6-lut)$_2$, 110 cm$^{-1}$, apparently does not correspond to the energy of either a$_g$ mode, $\sim$130 and $\sim$220 cm$^{-1}$ in the excited state. Similar behavior has been observed in the spectra of several other complexes,[19,26–30] and it has been shown that this effect (termed by Zink and co-workers the "missing mode", or MIME effect[26]) is caused by interference between the contributing progressions. It is noteworthy that in this example of the MIME effect, the observed energy separation is actually outside the range spanned by the two contributing a$_g$ vibrations, an unusual but not unknown situation.[29] For all three complexes, the spacing observed in the spectrum is closer to the energy of the $\nu_1$ mode than to that of the $\nu_2$ mode: spacings of 110, 140, and 400 cm$^{-1}$ were observed for CuCl$_2$(2,6-lut)$_2$, CuCl$_2$(4-PicNO)$_2$, and CuCl$_2$(H$_2$O)$_2$, respectively, compared with estimated excited-state energies of $\sim$130, $\sim$130, and $\sim$420 cm$^{-1}$ for the $\nu_1$ modes involving motion of the whole ligand and $\sim$220, $\sim$275, and $\sim$244 cm$^{-1}$ for the $\nu_2$ modes. This implies that in each case the difference in bond distance between the ground and excited state is greater for the oxygen or nitrogen ligands than for the chloride ions.

**$g$ Values of CuCl$_2$(2,6-lut)$_2$.** The EPR spectrum of a representative complex, CuCl$_2$(2,6-lut)$_2$, was studied at room temperature. A single, relatively broad signal was observed for all orientations of the magnetic field, consistent with the fact that the triclinic unit cell contains a single molecule. The crystal $g$ values for different magnetic field directions are available on request from the authors, and these were used to derive the magnitudes and directions of the principal molecular $g$ values by a method described previously:[31]

| principal $g$ values (standard deviation) | eigenvectors in molecular coordinates | | |
|---|---|---|---|
| | $x$ | $y$ | $z$ |
| 2.0297 (0.0003) | 0.998 | −0.065 | 0.003 |
| 2.0506 (0.0003) | 0.065 | 0.996 | 0.055 |
| 2.2095 (0.0003) | −0.01 | −0.055 | 0.998 |

As expected, within experimental error the principal in-plane directions of the g tensor are parallel to the Cu–N and Cu–Cl bond directions. The molecular $g$ values are quite similar to those reported for CuCl$_2$(2-methylpyridine)$_2$ ($g_x = 2.0328$, $g_y = 2.0622$, and $g_z = 2.2220$).[32] The latter complex has a structure that is basically similar to that of CuCl$_2$(2,6-lut)$_2$, except that the molecules are linked into loose dimers via long axial Cu–Cl bonds.[33]

For a complex of $D_{2h}$ symmetry, it has been shown that the in-plane g anisotropy is expected to be dominated by admixture of the $^2A_g(z^2)$ excited state into the $^2A_g(x^2 - y^2)$ ground state.[34] This admixture is caused by the difference in $\sigma$-bonding along the $x$ and $y$ axes, and the lowest g value should be associated with the strongest $\sigma$-interaction.[34] In the present case, the lowest g

value is parallel to the Cu–N bonds, which is consistent with the view[35] that amines are stronger $\sigma$-donors than chloride, as is also confirmed by the ligand field analysis presented below.

**Metal–Ligand Bonding Parameters.** The angular overlap model (AOM), developed originally by Schäffer and Jørgensen,[36] provides 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) approach[37] have recently been applied to a range of copper(II) complexes involving chloride[1,4,38,39] and nitrogen[38,40–43] donor ligands. In the present study, the computer program CAMMAG, developed by Gerloch and co-workers,[44] 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 $e_\sigma$, $e_{xx}$, and $e_{xy}$ of each ligand and the information provided by the crystal structure determination of the compound. To fully define the metal–ligand interaction in each of the present complexes, five metal–ligand parameters are necessary, one $\sigma$- and one $\pi$-parameter for the chloride (assuming the $\pi$-bonding to be isotropic about the Cu–Cl bond axis), and one $\sigma$-parameter and two $\pi$-parameters for the nitrogen donor ligands (here $e_{xx}$ refers to the $\pi$-interaction in the plane of the amine ring system). In addition, for planar complexes, it has been found that the d$_{z^2}$ orbital lies at anomalously low energy.[1,7] In the CLF model, this effect has been related to the effects of the ligand "voids" in the axial positions of a planar complex.[37,41] Alternatively, the depression has been ascribed to configuration interaction with the empty metal 4s orbital and has been treated within the framework of the AOM by an additional parameter $e_{ds}$, with the d$_{z^2}$ orbital being lowered in energy by an amount $4e_{ds}$.[7,45] The latter approach has been followed in the present work.

It is clearly impossible to determine all six bonding parameters uniquely from the four "d–d" transition energies observed for each complex. The chloride parameters were therefore set equal to those observed in the planar CuCl$_4^{2-}$ ion, with slight corrections being made for the minor differences in Cu–Cl bond length where appropriate (the Cu–Cl bond distances in CuCl$_2$(pdmp)$_2$, 226.8 pm, are identical with those in (metH)$_2$CuCl$_4$, while those in CuCl$_2$(2,3-lut)$_2$ and CuCl$_2$(2,6-lut)$_2$ are marginally shorter, 225.4 and 226.4 pm). These corrections, were made by assuming that the bonding parameters vary inversely as the fifth power of the bond distance, as suggested both by the pressure dependence of "d–d" transition energies of various octahedral complexes[46] and by theoretical considerations.[47] 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 parameters for the amine ligands derived using these approximations are given in Table III, together with those of planar CuCl$_4^{2-}$ for comparison. An effective

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**Table III.** Observed and Calculated Transition Energies and Metal–Ligand Bonding Parameters of the Complexes, All in cm⁻¹

| | transition energy | | | | AOM bonding parameters | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $xy$ | $yz$ | $xz$ | $z^2$ | $e_\sigma(Cl)$ | $e_\pi(Cl)$ | $e_\sigma(N)$ | $e_{\pi x}(N)$ | $e_{xy}(N)$ | $e_{ds}$ |
| | | | | | $CuCl_4^{2-}$ | | | | | |
| obs | 12155 | 13960 | | 16560 | | | | | | |
| calc | 12160 | 14085 | 13855 | 16560 | 5250 | 885 | | | | 1450 |
| | | | | | $CuCl_2(2,3\text{-lut})_2$ | | | | | |
| obs | 15370 | 17100 | 19050 | 20550 | | | | | | |
| calc | 15375 | 17100 | 19040 | 20550 | 5415 | 915 | 7140 | −110 | 855 | 1865 |
| | | | | | $CuCl_2(2,6\text{-lut})_2$ | | | | | |
| obs | 14720 | 16630 | 18330 | 19670 | | | | | | |
| calc | 14715 | 16630 | 18320 | 19670 | 5300 | 895 | 6930 | −15 | 960 | 1715 |
| | | | | | $CuCl_2(pdmp)_2$ | | | | | |
| obs | 13970 | 16070 | 18100 | 19540 | | | | | | |
| calc | 13970 | 16075 | 18095 | 19535 | 5250 | 885 | 6610 | −200 | 1070 | 1800 |

spin–orbit coupling constant of −580 cm⁻¹ was used in the calculations.

It may be seen that in all three complexes the amine ligands are considerably stronger $\sigma$-donors than the chloride ions and the $e_\sigma$ values are generally consistent with those reported for amines toward $Cu^{2+}$ in other studies.[38,40–43] These have generally involved saturated amines; for instance, Deeth and Gerloch have reported[38] values of $e_\sigma$ ranging from 5100 to 6500 cm⁻¹ for aliphatic amines with Cu–N bond lengths varying from 208 to 202 pm, while Hitchman et al. have deduced values between 6050 and 6730 cm⁻¹ for the amine groups in several copper(II) amino acid complexes with somewhat shorter Cu–N bond distances ($\sim$198 pm).[42] The molecular $g$ values $g_x = 2.033$, $g_y = 2.051$, and $g_z = 2.212$ calculated for $CuCl_2(2,6\text{-lut})_2$ by CAMMAG using an isotropic orbital reduction parameter $k = 0.69$ are in excellent agreement with those measured experimentally, $g_x = 2.030$, $g_y = 2.051$, and $g_z = 2.210$.

The $\pi$-bonding parameters of the three amines are quite similar, with $e_{xy}$ being $\sim$1000 cm⁻¹ and $e_{\pi x}$ taking a small negative value. In view of the uncertainty in the chloride parameters, the amine bonding parameters cannot be considered accurate to better than $\sim$200 cm⁻¹, so that the in-plane $\pi$-bonding in every complex does not differ significantly from zero. This is to be expected, as the nitrogen p orbitals in the plane of each amine are already involved in $\sigma$-bonds, and so are unavailable for $\pi$-bond formation. Indeed, in several studies of transition-metal complexes of heterocyclic amines, the in-plane $\pi$-bonding of the amines has been set equal to zero in order to derive the remaining bonding parameters,[35,48] and it is gratifying to obtain confirmation that this procedure is valid. The out-of-plane $\pi$-bonding parameters of heterocyclic amines have been the subject of controversy. Negative values of $e_{xy}$ have been deduced for a range of $Cr^{3+}$ pyridine complexes by Schäffer and co-workers,[9] corresponding to $\pi$-acceptance by the amines, though this conclusion has been questioned by Smith.[10] The quinoline ligands in several cobalt(II) and nickel(II) complexes have also been found to act as $\pi$-acceptors.[49] The modest positive values of the present study suggest weak $\pi$-donor character for the amines and are similar to those derived recently for a number of $Ni^{2+}$ complexes with heterocyclic amines.[48] It seems possible

that under different circumstances this type of ligand may function either as a $\pi$-donor or $\pi$-acceptor.

Similar values of the parameter $e_{ds}$ are obtained for all three compounds, $\sim$1800 cm⁻¹, these being somewhat higher than that derived for planar $CuCl_4^{2-}$, 1450 cm⁻¹. Simple theory 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,[45] and that the magnitude of this interaction should be proportional to the difference in metal–ligand interaction along the $z$ and $xy$ axes. A higher value of this parameter is therefore to be expected for the amine complexes, because of the stronger $\sigma$-bonding power of the nitrogen ligands compared with chloride.

### Conclusions

The temperature dependence of the band shape of the lowest energy transition of $CuCl_2(pdmp)_2$ suggests that the metal–ligand $a_g$ vibrational mode involving motion of the bulky amine is of low energy, $\sim$110 cm⁻¹. A similar conclusion can be drawn from the analysis of the vibrational structure observed at low temperature in the electronic spectrum of $CuCl_2(2,6\text{-lut})_2$, which suggests that this mode has an energy of $\sim$130 cm⁻¹ in the excited state. The spacing of the peaks in this fine structure does not equal the energy of either of the $a_g$ vibrational modes contributing to the band shape, the pattern resulting from the interference between the progressions in these two modes.

The d-orbital energy sequence in all three complexes is $d_{z^2} < d_{xz} < d_{yz} < d_{xy} \ll d_{x^2-y^2}$, and an analysis using the angular overlap model and the molecular $g$ values of $CuCl_2(2,6\text{-lut})_2$ suggests that the $\sigma$-bonding strength of the amine ligands are similar and significantly higher than that of the chloride ion. The amines act as weak $\pi$-donors, and in agreement with simple theory, the metal–ligand $\pi$-interaction in the plane of these ligands is negligible. As with other planar complexes, the $d_{z^2}$ orbital is much lower in energy than simple theory predicts, the effect being even more pronounced than in the analogous $CuCl_4^{2-}$ complex.

**Registry No.** $CuCl_2(pdmp)_2$, 75324-55-9; $CuCl_2(2,3\text{-lut})_2$, 34777-64-5; $CuCl_2(2,6\text{-lut})_2$, 54053-59-7.

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