$[Fe(bt)_2(NCS)_2]$ were found to be equal within 3% and 4%, respectively.[18,19] It is conceivable that the spin-state transitions in these systems may take place by the formation of independent domains whereas interacting domains appear to be present in $[Fe(bpp)_2](BF_4)_2$ (and may occur in other systems). The conditions defining this difference in behavior would, nevertheless, still need to be specified.

The difference may be illusory rather than real, however. The nature of the distribution of areas shown in Figure 4 may provide an alternative explanation for the apparent difference in the behavior of $[Fe(phy)_2](ClO_4)_2$ and $[Fe(bt)_2(NCS)_2]$ on the one hand and $[Fe(bpp)_2](BF_4)_2$ on the other. Thus, scanning curves situated close to the maximum of one of the parabolic curves, or being disposed symmetrically with respect to that maximum, will have similar (but not identical) areas, whereas the areas of scanning curves located on the slope of one of the parabolas will be significantly different. The observation of almost equal areas could thus be fortuitous and the result of the range of μ_{eff}^2 chosen for study. The applicability of the independent domain model is thus not necessarily established by the behavior of only a small number of scanning curves. A more detailed study of the hysteresis by construction of an extended series of curves within the same temperature limits is required to determine if the behavior of $[Fe(phy)_2](ClO_4)_2$ and $[Fe(bt)_2(NCS_2)]$ is in fact different from that of $[Fe(bpp)_2](BF_4)_2$, and work along these lines is currently in progress in our laboratories.

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Electronic, EPR, and Vibrational Spectra of the $CuCl_6^{4-}$ Ion

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The electronic, EPR, and vibrational spectra of $(cyclamH_4)CuCl_6$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) are reported and interpreted in terms of the elongated tetragonal geometry of the isolated $CuCl_6^{4-}$ ions present in this compound. Comparisons have been made with chlorocuprates having other geometries. It is inferred from the electronic spectrum that the axial chloride ligands have a small but significant effect on the energy levels of $(cyclamH_4)CuCl_6$, despite their long distance from the metal ion (317.5 pm), and this interaction leads to the near degeneracy of the d_{z^2} and $d_{xz,yz}$ orbitals in the $CuCl_6^{4-}$ complex. Angular overlap metal-ligand-bonding parameters have been derived and compared with those of other complexes with differing degrees of tetragonal distortion.

Introduction

Because chlorocuprates are comparatively simple and exhibit a wide range of stereochemistries, they have often been used to probe the ways in which various spectroscopic and bonding properties change as a function of geometric distortion.[1] Particular attention has been paid to the electronic, EPR, and vibrational spectra of the four-coordinate $CuCl_4^{2-}$ ion as this changes between a square-planar and a tetrahedral geometry.[2-7] The five-coordinate $CuCl_5^{3-}$ complex is unusual, since although the most stable configuration is apparently a square-based pyramid, vibronic coupling induces a dynamic equilibrium that produces a time-averaged trigonal-bipyramidal geometry.[8] Considerable interest has also been shown in the spectroscopic changes accompanying axial ligation of planar $CuCl_4^{2-}$ to produce a tetragonally elongated six-coordinate $CuCl_6^{4-}$ complex.[9-11] However, until now, the latter studies have involved compounds of the form $(cation)_2CuCl_4$, with axial coordination occurring by the linkage of neighboring complexes to form infinite polymers. Despite several attempts to produce compounds containing isolated $CuCl_6^{4-}$ groups,[12,13] it is only recently that this has been achieved in the compound $(cyclamH_4)CuCl_6$ (cyclam = 1,4,8,11-tetraazacyclotetradecane).[14] The present paper reports the spectral properties and bonding characteristics of this compound and compares these with the behavior of chlorocuprates having other stereochemistries.

Experimental Section

The preparation and characterization of $(cyclamH_4)CuCl_6$ has been described previously.[14] Infrared spectra were measured as polythene disks by using a Digilab FTS 20E Fourier transform spectrometer using a 6.25-μm beam splitter. Raman spectra were recorded with a Cary 82 spectrophotometer fitted with an argon laser using the 488-nm excitation line. A powdered sample pressed into a disk was used, with this being rotated in a spinning cell to minimize overheating. Electronic spectra of single crystals were measured upon a Cary 17 spectrophotometer using polarized light by a method described previously.[15,16] The crystals were cooled by using a Cryodyne Model 22C cryocooler. EPR spectra were recorded at room temperature by using a JEOL JES-FE X-band spectrometer.

Results and Discussion

Geometry of the $CuCl_6^{4-}$ Ion. The triclinic unit cell of $(cyclamH_4)CuCl_6$ contains a single formula unit.[14] The $CuCl_6^{4-}$ ion lies on an inversion center, with the elongated tetragonal stereochemistry so often observed for Cu(II) complexes. The in-plane bonds are almost equal (229.1 and 230.2 pm) and are much shorter than the axial bonds (317.5 pm), and the ClCuCl angles involving the in-plane ligands differ from 90° by less than a degree. The

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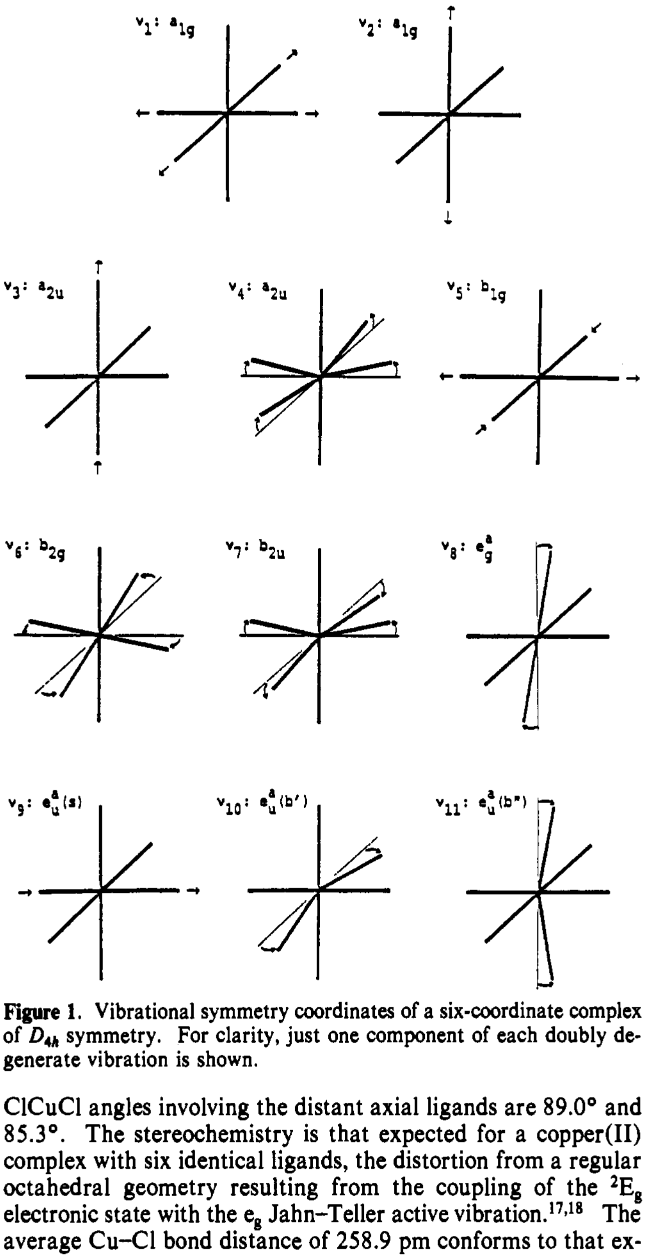

Figure 1. Vibrational symmetry coordinates of a six-coordinate complex of D_{4h} symmetry. For clarity, just one component of each doubly degenerate vibration is shown.

ClCuCl angles involving the distant axial ligands are 89.0° and 85.3°. The stereochemistry is that expected for a copper(II) complex with six identical ligands, the distortion from a regular octahedral geometry resulting from the coupling of the ^2E_g electronic state with the e_g Jahn–Teller active vibration.[17,18] The average Cu–Cl bond distance of 258.9 pm conforms to that expected when the metal–chloride bond lengths of the divalent transition ions are plotted as a function of atomic number.[19] On the other hand, the Jahn–Teller displacement Q, which may be defined as[17]

$$Q = \sqrt{2(\delta x)^2 + 2(\delta y)^2 + 2(\delta z)^2}$$

is considerably larger (100 pm) than that usually observed for ligands such as NO_2^- and H_2O (typically, 30–40 pm).[17,21] Here, δx, δy, and δz are the displacements from the average bond length along each axis. The cause of the discrepancy is not clear, though it may merely be a reflection of the fact that Cu–Cl bonds are inherently longer than those to oxygen and nitrogen. The value of Q for linked $CuCl_6^{4-}$ polyhedra, for instance in $(C_2H_5NH_3)_2CuCl_4$, is also high (80 pm).[20] It must also be noted that Q is quite sensitive to lattice perturbations, particularly those due to hydrogen bonding. For instance, the $Cu(H_2O)_6^{2+}$ ion exhibits a range of distortions in various lattices[21] compared with that observed in aqueous solution.[22]

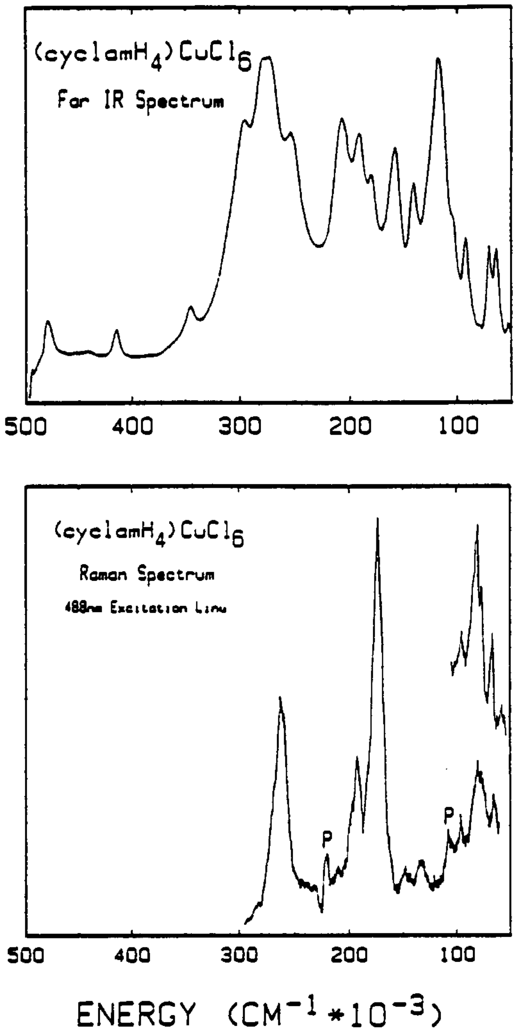

Figure 2. Far-infrared and Raman spectra of $(cyclamH_4)CuCl_6$ The latter is expanded at higher resolution below 100 cm^{-1}. Laser emissions are marked by the symbol P.

Table I. Vibrational Assignments for the $CuCl_6^{4-}$ Ion in $(cyclamH_4)CuCl_6$ Compared with Those Reported[15] for the Planar $CuCl_4^{2-}$ Ion in $(metH)_2CuCl_4$

		energy, cm^{-1}	
mode	symmetry	$(cyclamH_4)CuCl_6$	$(metH)_2CuCl_4$
ν_1	a_{1g}	262	275
ν_2	a_{1g}	101, 80?	
ν_3	a_{2u}	118	
ν_4	a_{2u}	141	158
ν_5	b_{1g}	191	195
ν_6	b_{2g}	170	182
ν_7	b_{2u}	*a*	*a*
ν_8	e_g	80, 72, 62?	
ν_9	e_u	278, 273	303, 285
ν_{10}	e_u	180	179, 177
ν_{11}	e_u	69, 62	

[a] Raman and infrared inactive; normal-coordinate analysis suggests values of ~85 and ~90 cm^{-1} for this mode for $(metH)_2CuCl_4$ and $(cyclamH_4)CuCl_6$, respectively,[28] while analysis of the temperature dependence of the electronic spectrum of the former complex suggests an energy of ~65 cm^{-1}.

Vibrational Spectra. If the slight differences in the in-plane bond lengths and the out-of-plane bond angles are neglected, the $CuCl_6^{4-}$ ion in $(cyclamH_4)CuCl_6$ belongs to the point group D_{4h}, and the ligand motion of the normal modes of the complex are shown schematically in Figure 1. The infrared and Raman

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spectra of the compound in the low-energy region are shown in Figure 2. The assignments of the peaks attributed to metal–ligand vibrations are listed in Table I. Seven of the modes involve motion of the four strongly bound in-plane chlorides (Figure 1), thus corresponding to vibrations of the planar $CuCl_4^{2-}$ ion, and the energies of these observed in bis(methadonium) tetrachlorocuprate, $(metH)_2CuCl_4$,[15] are given in Table I for comparison. The remaining vibrations, which involve the long axial Cu–Cl bonds, are expected to occur at low energy, so the assignments of these are tentative. To aid in these assignments, the infrared and Raman spectra of the cation hydrochloride, $cyclamH_4Cl_4$, were also measured in the region above 100 cm^{-1}. The Raman spectrum showed only a single very weak peak at $\sim$170 cm^{-1}. The infrared spectrum of $cyclamH_4Cl_4$ in this region is dominated by an intense peak at 164 cm^{-1}, and for this reason the a_{2u} vibration of $(cyclamH_4)CuCl_6$ was tentatively assigned to the peak observed at 141 cm^{-1} for this compound (Figure 2), rather than that at 158 cm^{-1}, despite the fact that the analogous mode occurs at 158 cm^{-1} in planar $CuCl_4^{2-}$.[15]

The assignments for $CuCl_6^{4-}$ are consistent with those reported for a range of hydrated chlorocuprates.[23-25] The most extensive data are those reported for $K_2CuCl_4(H_2O)_2$,[24,25] which contains short bonds to the two water molecules and short and long bonds to the chloride ions.[26] This complex is reported[25] to have infrared-active peaks at 139 and 108 cm^{-1}, which may correlate with those at 118 and $\sim$66 cm^{-1} assigned to modes of a_{2u} and e_u symmetry in $(cyclamH_4)CuCl_6$, and Raman-active peaks[24] at 133 and 110 cm^{-1}, which are assigned to stretching and bending modes of the axial chloride ligands analogous to those at $\sim$90 and $\sim$70 cm^{-1} in $(cyclamH_4)CuCl_6$. Agreement between the vibrational energies is good, considering the fact that the terminal Cu–Cl bond lengths in $K_2CuCl_4(H_2O)_2$ are considerably shorter than those in $(cyclamH_4)CuCl_6$ (289.5 pm compared with 317.5 pm). It can be noted that the splittings of the peaks assigned to the out-of-plane deformations of e_u (62 and 69 cm^{-1}) and e_g (62 and 72 or 72 and 80 cm^{-1}) symmetry may be attributed to the difference between the out-of-plane bond angles, $\sim 4°$.

The out-of-plane bending mode of b_{2u} symmetry is both infrared and Raman inactive. Considerable interest has been shown in the energy of this vibration for four-coordinate $CuCl_4^{2-}$, since it carries the complex from a planar toward a tetrahedral geometry.[15,27] Moreover, it strongly influences the electronic spectrum of planar $CuCl_4^{2-}$. Analysis of the temperature dependence of the electronic spectrum of several salts containing this complex suggests an energy of $\sim$65 cm^{-1} for the mode,[15] in reasonable agreement with an estimate of $\sim$85 cm^{-1} obtained by normal-coordinate analysis.[15,28] A similar normal-coordinate analysis for the $CuCl_6^{4-}$ ion in $(cyclamH_4)CuCl_6$ yields an estimate[28] of $\sim$90 cm^{-1} for the energy of the b_{2u} mode. This rise in energy seems reasonable, as for an out-of-plane bending vibration the addition of axial chloride ligands will increase ligand–ligand repulsions. As discussed below, the temperature dependence of the electronic spectrum of $(cyclamH_4)CuCl_6$ is consistent with these conclusions.

The $CuCl_6^{4-}$ ion has two, totally symmetric stretching modes of a_{1g} symmetry, as opposed to the single vibration of this type that occurs for planar $CuCl_4^{2-}$. The ν_1 mode involves motion of the in-plane ligands and correlates directly with the totally symmetric stretch of the planar complex (Figure 1), though the energy is somewhat lower because of the longer Cu–Cl bond lengths. It is interesting to observe that, as has been noted elsewhere,[15] the energy of the ν_1 mode is inversely proportional to about the fifth power of the bond distance for these complexes. The average Cu–Cl bond lengths are 225.1 and 226.5 pm for the planar complexes in $(creatininium)_2CuCl_4$ and $(metH)_2CuCl_4$[15] and 229.7 pm in $(cyclamH_4)CuCl_6$;[14] such a dependence predicts that the ν_1 mode should decrease from the value of 290 cm^{-1} in the first compound to 275 and 262 cm^{-1} in the latter two, respectively, in exact agreement with experiment (Table I). The lower energy ν_2 mode largely involves motion of the weakly bound axial chlorides (Figure 1), and a similar extrapolation to a bond length of 317.5 pm predicts an energy of $\sim$52 cm^{-1} for this vibration. This is rather lower than the energy of the peaks tentatively assigned to this mode, 80–100 cm^{-1} (Table I), though it is not really to be expected that a relationship of this kind would work quantitatively over such a wide range of bond distances.

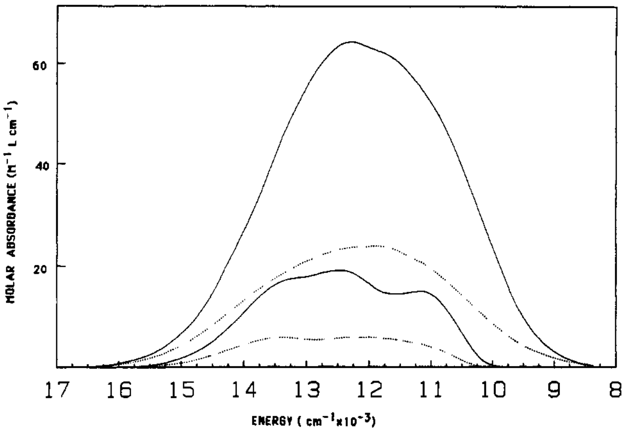

Figure 3. Electronic spectrum of an arbitrary section of a single crystal of $(cyclamH_4)CuCl_6$ with the electric vector in the *xy* molecular plane (full line) and approximately along the *z* axis (dashed line) measured at 290 and 10 K. The more intense spectra are those measured at higher temperatures.

Electronic Spectrum. The compound $(cyclamH_4)CuCl_6$ crystallizes as chunky plates with the (100) crystal face well developed. The *z* molecular axis makes a large angle with this face, but it was possible to cleave a section approximately normal to (100) that was highly pleochroic. Analysis of the variation of the *g* anisotropy within this section showed that one extinction direction was almost parallel to *z* (coinciding with a *g* value of 2.246, which is close to the value g_z = 2.266 suggested by the EPR analysis described below). The electronic spectra of the section measured at 290 and 10 K with the electric vector in the *xy* plane and approximately along *z* are shown in Figure 3. The molar absorbance of the bands was estimated by measuring the thickness of the section (0.10 mm) using the calibrated graticule of a microscope eyepiece.

Assignment of the Spectrum. Three electronic "d–d" transitions are expected for a copper(II) complex of D_{4h} symmetry[16,27] and the vibronic selection rules predict that each of these may be observed in *xy* polarization. In agreement with this, three bands are resolved at low temperature in this polarization, centered at 13 400, 12 400, and 11 100 cm^{-1} (Figure 3). In *z* polarization, however, the transition $^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2 - y^2)$ should not be observed, as it is vibronically forbidden. Although the highest energy peak is clearly observed at low temperature in the spectrum which is predominantly *z* polarized, the lower energy region is poorly resolved (Figure 3). However, in the more intense spectrum measured at 290 K in this polarization, the band maximum occurs just below 12 000 cm^{-1}, and given the fact that a slight red-shift is expected on going from 10 to 290 K,[16] this implies that the band centered at 11 100 cm^{-1} at low temperature is absent in *z* polarization, and hence is due to the $^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition. This assignment agrees with the ligand-field analysis presented below, and is similar to that proposed for the planar $CuCl_4^{2-}$ ion.[15,27] In the latter complex, the $^2E_g(xz, yz) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition occurs $\sim$1800 cm^{-1} higher in energy than the $^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition.[15] The presence of the axial ligands should decrease this separation somewhat in $(cyclamH_4)CuCl_6$, making it likely that the band at 12 400 cm^{-1} is due

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to $^2E_g(xz, yz) \leftarrow {}^2B_{1g}(x^2 - y^2)$, with that at 13 400 cm^{-1} being caused by the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$ transition. However, as discussed below, the close proximity of these two transitions means that they are significantly mixed by spin–orbit coupling.

Band Intensities and Temperature Dependence of the Spectra. The spectrum of the $CuCl_6^{4-}$ ion in (cyclamH_4)$CuCl_6$ is considerably more intense in *xy* than in *z* polarization. This anisotropy is similar to that observed for the planar $CuCl_4^{2-}$ ion, where it has been rationalized[4] in terms of the low intensity of the charge-transfer transition from which the *z*-polarized intensity is "stolen". Interestingly, it appears that no such anisotropy occurs in the spectrum of bis(ethylammonium) tetrachlorocuprate, $(EtNH_3)_2CuCl_4$.[10,29] Possibly, the polymeric nature of the $CuCl_6^{4-}$ units present in the latter compound influences the mechanism by which the "d–d" transitions gain intensity.

The overall intensity of the spectrum of (cyclamH_4)$CuCl_6$ is also quite similar to that of planar $CuCl_4^{2-}$, at both 10 and 290 K. A detailed analysis of the temperature dependence of the spectrum of (cyclamH_4)$CuCl_6$ is not feasible, as the close proximity of the bands means that these overlap too much to allow their resolution by Gaussian analysis at higher temperatures. Clearly, the spectra intensify substantially on warming from 10 to 290 K (Figure 3) and an approximate estimate of the total areas of the spectra suggests an overall increase of ~3.7 in *xy* polarization and ~4.6 in *z* polarization. Assuming that the simple theory of vibronic intensity stealing applies,[16] this implies average energies of the ungerade vibrations inducing intensity of ~100 and ~80 cm^{-1}, respectively, which is consistent with the low energy proposed for several of these vibrations (Table I).

An important feature of the spectrum of (cyclamH_4)$CuCl_6$, which differs from that of compounds containing planar $CuCl_4^{2-}$, is the temperature dependence of the band maxima. For planar $CuCl_4^{2-}$, these shifts to lower energy by between 600 and 1000 cm^{-1} on warming from 10 to 290 K,[15,27] and this has been interpreted as indicating that the complex has a distorted tetrahedral equilibrium geometry in the excited electronic states.[30] The spectrum of the $CuCl_6^{4-}$ ion in (cyclamH_4)$CuCl_6$ shows a red-shift of only 100–300 cm^{-1} over this temperature range (Figure 3), which is quite consistent with the conventional theory of vibronic intensity stealing,[16] implying that this complex does not undergo a pseudotetrahedral distortion in the excited electronic state. This seems reasonable, as the presence of axial ligands, albeit very distant ones, should destabilize an out-of-plane motion of the chloride ions, as is also suggested by the higher energy estimated for the b_{2u} out-of-plane bending mode for the $CuCl_6^{4-}$ compared with the $CuCl_4^{2-}$ complex (i.e. ~90 cm^{-1} compared with ~65 cm^{-1}).

It is also noteworthy that the low-temperature spectrum of (cyclamH_4)$CuCl_6$ shows no evidence of vibrational fine structure. To date, the spectrum of planar $CuCl_4^{2-}$ in four different compounds has been reported,[15,27,31] and three of these exhibit vibrational structure. The absence of such structure in the spectrum of (cyclamH_4)$CuCl_6$ may simply be due to lattice effects or the greater number of ungerade vibrations that are available to induce intensity for the six-coordinate complex. In addition, the $CuCl_6^{4-}$ complex has two modes of a_{1g} symmetry, rather than the single mode of the planar $CuCl_4^{2-}$ ion, and as the progressions are in the a_{1g} vibrations, the additional congestion caused by a second band-generating mode may serve to "wash out" the structure. This may also explain why no vibrational structure has been observed in the low-temperature "d–d" spectrum of four-coordinated $CuCl_4^{2-}$ in lattices where this has a pseudotetrahedral geometry of D_{2d} symmetry[5,32]—two vibrational modes of a_1 symmetry also occur in this point group.

EPR Spectrum. The EPR spectrum of a single crystal of (cyclamH_4)$CuCl_6$ was recorded for rotations of the magnetic field at 10° intervals in the (100) crystal plane and two planes orthogonal to this. A single broad signal was observed for all orientations of the magnetic field. A least-squares analysis of the *g* values, measured by a procedure described in detail elsewhere,[33] yielded the following estimates of the molecular *g* values:

$$g_x = 2.053 \qquad g_y = 2.050 \qquad g_z = 2.260$$

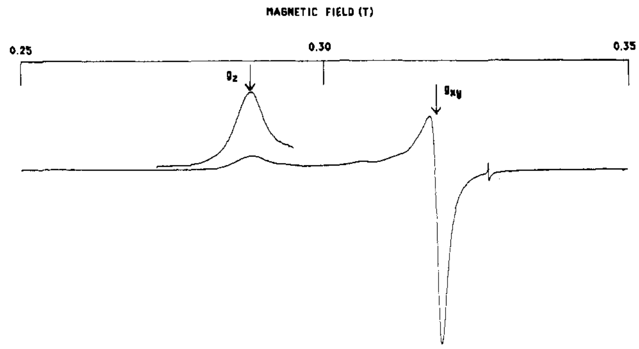

Figure 4. Electron paramagnetic resonance spectrum of a powdered sample of (cyclamH_4)$CuCl_6$ recorded at room temperature. A similar spectrum was obtained at 110 K. The magnetic fields that were taken to correspond to the molecular *g* values are indicated by arrows. The small resonance at high field is due to a speck of powdered α,α'-diphenyl-β-picrylhydrazyl (DPPH) that was used as an internal standard of known *g* value (2.0036).

The spectrum of a powdered sample (Figure 4) suggested similar values:

$$g_{xy} = 2.057 \qquad g_z = 2.272$$

There has been considerable theoretical interest in the *g* values of chlorocuprates, and the way in which these change as a function of stereochemistry.[1,34] In particular, it has been noted that the simple expressions that interpret the *g* shifts from the free electron value just in terms of the admixture of excited d states by spin–orbit coupling, with covalency being taken into account by an orbital reduction parameter *k*, are inadequate.[35] Substitution of the average values $g_{xy} = 2.054$ and $g_z = 2.266$ for (cyclamH_4)$CuCl_6$ into the expressions

$$g_{xy} = 2.0023 - 2\lambda k_{xy}^2/E_{xz,yz} \qquad g_z = 2.0023 - 8\lambda k_z^2/E_{xy}$$

together with the free ion spin–orbit coupling constant $\lambda = -829$ cm^{-1} and excited-state energies $E_{xz,yz} = 12\,400$ cm^{-1} and $E_{xy} = 11\,100$ cm^{-1} produces the values $k_{xy} = 0.62$ and $k_z = 0.66$. These fall between the values estimated from the *g* values of planar, four-coordinate $CuCl_4^{2-}$, $k_{xy} = 0.57$ and $k_z = 0.64$, and those calculated for the polymeric, six-coordinate $CuCl_6^{4-}$ units present in $(EtNH_3)_2CuCl_4$, $k_{xy} = 0.64$ and $k_z = 0.71$.[35] Presumably, this is because the tetragonal distortion in (cyclamH_4)$CuCl_6$ (in-plane and axial bond lengths 229.7 and 317.5 pm) lies between that of planar $CuCl_4^{2-}$ (in-plane bond lengths 226.1 pm) and the groups in $(EtNH_3)_2CuCl_4$ (in-plane and axial bond lengths 228 and 298 pm).[21] The orbital reduction parameters of (cyclamH_4)$CuCl_6$ agree well with recent estimates of the unpaired spin density on the metal in chlorocuprates (~65% from photoelectron spectroscopy and the analysis of the chlorine hyperfine coupling parameters),[36] but it seems likely that this is little more than coincidence, as in these compounds contributions to the *g* values from various ligand-based sources are thought to be substantial.[35] This may be seen from the orbital reduction parameters, which can be derived from the *g* values of the pseudotetrahedral $CuCl_4^{2-}$ ion,[37]

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$k_{xy} = 0.53$ and $k_z = 0.67$. The low value of k_{xy} is quite incompatible with the fact that the transfer of unpaired spin to the ligands is expected to be less pronounced than is the case for planar $CuCl_4^{2-}$.[4] It has been pointed out[38] that the deviation of the g_{xy} value of pseudotetrahedral $CuCl_4^{2-}$ from the estimate obtained by assuming ligand field theory has contributed to the poor correlation of the metal hyperfine parameters of this complex with simple theoretical predictions.

Metal–Ligand Bonding Parameters. Chlorocuprates have been the subject of numerous theoretical studies, ranging from simple crystal field to sophisticated molecular orbital calculations.[39] Special attention has often been paid to the changes that accompany variations in stereochemistry, and those studies[9-11] that have looked at the effects of axial ligation upon the energy levels of planar $CuCl_4^{2-}$ are of particular relevance to the present investigation. Of special interest is the fact that the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2-y^2)$ electronic transition occurs at very high energy in planar, four-coordinate $CuCl_4^{2-}$.[15,26] This is thought to be due to configuration interaction between the $a_{1g}(z^2)$ and $a_{1g}(4s)$ metal orbitals,[9,40] an effect that is expected to diminish progressively as ligands approach the metal along the *z* molecular axis. The influence of the long axial bonds in (cyclamH_4)$CuCl_6$ is of interest in this context.

The angular overlap model (AOM)[41] and the closely related cellular ligand field (CLF) approach[42] to the bonding in metal complexes have been particularly fruitful methods of parametrizing the metal–ligand interactions in transition-metal complexes. For a complex of D_{4h} symmetry, the AOM relates the d-orbital energies *E* to the metal–ligand σ- and π-bonding parameters e_σ and e_π of the ligands along the *z* and *xy* molecular axes by the expressions[40]

$$E(x^2 - y^2) = 3e_\sigma(xy) \qquad (1a)$$

$$E(z^2) = e_\sigma(xy) + 2e_\sigma(z)' \qquad e_\sigma(z)' = e_\sigma(z) - 2e_{ds} \qquad (1b)$$

$$E(xz, yz) = 2e_\pi(xy) + 2e_\pi(z) \qquad (1c)$$

$$E(xy) = 4e_\pi(xy) \qquad (1d)$$

Here, it is assumed that the π interaction is isotropic about the metal–ligand bond axis, which should be a good approximation for a ligand such as chloride. The overall *effective* metal–ligand interaction along the *z* axis is represented by $e_\sigma(z)'$; this may be broken down, as shown, into the normal σ-interaction of the ligands along *z*, $e_\sigma(z)$, plus a contribution due to d–s mixing, e_{ds}.

The three transition energies observed for (cyclamH_4)$CuCl_6$ provide insufficient information to determine unique values for all of the metal–ligand-bonding parameters of the $CuCl_6^{4-}$ ion. However, the parameters deduced for planar, four-coordinate $CuCl_4^{2-}$ should provide a fairly accurate estimate of the values for the in-plane ligands of the six-coordinate complex. Quite similar transition energies were observed for the planar species in three different lattices,[15] and if the minor effect of spin–orbit coupling is neglected, the average energies of the $^2B_{2g}(xy) \leftarrow 2B_{1g}(x^2-y^2)$ and $^2E_g(xz, yz) \leftarrow {}^2B_{1g}(x^2-y^2)$ transitions, 12 315 and 14 095 cm^{-1}, yield the estimates $e_\sigma(xy) = {\sim}5285\ cm^{-1}$ and $e_\pi(xy) = {\sim}885\ cm^{-1}$ (eq 1a, 1c, and 1d). The average energy of the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2-y^2)$ transition, 16 680 cm^{-1}, implies that $e_\sigma(z)' = -3055\ cm^{-1}$ in this complex, and as $e_\sigma(z) = 0$, this yields the estimate $e_{ds} = {\sim}1530\ cm^{-1}$ for the d–s mixing coefficient in the planar complex.

Optimum agreement with the transition energies observed for (cyclamH_4)$CuCl_6$ was obtained by using similar bonding parameters for the in-plane ligands to those of planar $CuCl_4^{2-}$, but an effective bonding parameter for the axial ligands has a magnitude about half that for the planar complex. The optimum values for (cyclamH_4)$CuCl_6$ are

$$e_\sigma(xy) = 4800\ cm^{-1} \qquad e_\pi(xy) = 820\ cm^{-1}$$
$$e_\pi(z) = 75\ cm^{-1} \qquad e_\sigma(z)' = -1650\ cm^{-1}$$

The computer program CAMMAG developed by Gerloch and coworkers[43] was used to calculate the "d–d" transition energies in (cyclamH_4)$CuCl_6$. A value of $-540\ cm^{-1}$ was used for the effective spin–orbit coupling constant in the complex, corresponding to the unpaired electron spending 65% in the metal orbitals, as suggested by recent studies.[36] The calculated values in cm^{-1} obtained by using the above bonding parameters are 11 062 (11 100), 12 265, 12 508 (12 400), 13 588 (13 400) cm^{-1}, with the energies observed experimentally shown in parentheses. Interestingly, the wave functions associated with the transitions calculated at 12 265 and 13 588 cm^{-1} each consist of an approximately equal admixture of the d_{z^2} and $d_{xz,yz}$ orbitals; i.e., in the absence of spin–orbit coupling, these orbitals are almost equal in energy.

The fact that the bonding parameters in the in-plane ligands in (cyclamH_4)$CuCl_6$ are slightly smaller than those in planar $CuCl_4^{2-}$ is consistent with the longer bond lengths in the six-coordinate complex (229.7 pm, compared with an average of 226.1 pm).[14,15] Assuming that the bonding parameters vary inversely as about the fifth power of the bond distance, which is consistent both with theory[44] and experimental observation[45] for small bond length changes, implies that the bonding parameters $e_\sigma(xy) = {\sim}5285\ cm^{-1}$ and $e_\pi(xy) = {\sim}885\ cm^{-1}$ of planar $CuCl_4^{2-}$ should decrease to $e_\sigma(xy) = {\sim}4885\ cm^{-1}$ and $e_\pi(xy) = {\sim}820\ cm^{-1}$ for the in-plane ligands of the $CuCl_6^{4-}$ ion, in good agreement with the above optimum values.

The effective axial ligand field interaction in (cyclamH_4)$CuCl_6$, $e_\sigma(z)' = -1650\ cm^{-1}$, is considerably smaller in magnitude than that in planar $CuCl_4^{2-}$, ${\sim}{-3055}\ cm^{-1}$, suggesting that the axial ligands do significantly affect the energy levels of the Cu^{2+} ion, despite the very long bond distance. In fact, the above value of $e_\sigma(z)'$ deduced for the isolated $CuCl_6^{4-}$ ion correlates very well with recent estimates of this parameter derived by Deeth and Gerloch[11] for a range of complexes containing polymeric $CuCl_6^{4-}$ units of varying tetragonality. The axial bond length of 317.5 pm in (cyclamH_4)$CuCl_6$ falls between that of 326 pm in $[Pt(NH_3)_4][CuCl_4]$[46] and 304 pm in $(n\text{-}C_3H_7NH_3)_2CuCl_4$,[47] and the value of $e_\sigma(z)' = -1650\ cm^{-1}$ lies between the estimates of -2050 and $-750\ cm^{-1}$ deduced for the latter compounds.[11] The above conclusion that the d_{z^2} and $d_{xz,yz}$ orbitals are almost equal in energy in (cyclamH_4)$CuCl_6$ also agrees with the preferred assignments proposed by Deeth and Gerloch[11] of the "d–d" spectra of $[Pt(NH_3)_4][CuCl_4]$ and $(n\text{-}C_3H_7NH_3)_2CuCl_4$, namely that in the former compound the $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2-y^2)$ transition gives rise to the highest energy peak, while in the latter, and other complexes with even shorter axial Cu–Cl bond lengths, it is responsible for the lowest energy band. It therefore seems that as a Cl^- ligand approaches a Cu^{2+} ion, significant metal–ligand interactions commence at a bond distance of ~320–330 pm.

The effective parameter $e_\sigma(z)'$ includes two contributions, a direct σ-interaction from the axial ligands, $e_\sigma(z)$, and a lowering in energy that has been ascribed to configuration interaction between the metal 4s and the $3d_{z^2}$ orbitals,[9,40] parametrized in the present scheme by e_{ds}. Using the above estimates of the bonding parameters of the in-plane ligands and assuming that these parameters vary inversely as the fifth power of the bond length yield

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the estimates $e_\sigma(z) = \sim 970$ cm^{-1} and $e_\pi(z) = \sim 162.5$ cm^{-1} for the axial ligands in (cyclamH_4)$CuCl_6$. However, it has been suggested that a dependence of this kind probably overestimates the bonding interactions of distant ligands[48] and that their effects may be better approximated by assuming that the bonding parameters are proportional to the square of the metal–ligand diatomic overlap integrals. The relevant overlap integrals have been estimated[49] as ~0.076 and ~0.025 (σ overlaps) and ~0.035 and ~0.009 (π overlaps) at 229 and 317.5 pm, respectively, implying the values $e_\sigma(z) = \sim 530$ cm^{-1} and $e_\pi(z) = \sim 55$ cm^{-1} for the axial ligands. Taking both these approaches into consideration, the very approximate estimates $e_\sigma(z) = \sim 700$ cm^{-1} and $e_\pi(z) = \sim 75$ cm^{-1} may be made for the axial chlorides in (cyclamH_4)$CuCl_6$. Substitution into eq 1b yields the value $e_{ds} \simeq 1175$ cm^{-1} for the $CuCl_6^{4-}$ ion in this complex.

The parameter e_{ds} describes the energy by which the $^2A_{1g}(z^2)$ state is depressed by d–s mixing, this being $4e_{ds}$.[9] Simple perturbation theory implies that the fractional occupancy of the 4s orbital in this state is $4e_{ds}/E_{4s}$. Here, E_{4s} is the energy separation between the 3d and 4s orbitals, which may be estimated[50] as ~80 000 cm^{-1}. These values thus imply ~5.8% occupancy of the 4s orbital in the $^2A_{1g}(z^2)$ state of (cyclamH_4)$CuCl_6$. This is somewhat less than the value of ~7.6% obtained from the above average data of the planar $CuCl_4^{2-}$ ion, which is as expected, since the degree of mixing depends upon the difference between the interaction of the ligands in the *xy* plane and along the *z* axis.[40] These estimates may be compared with those obtained from the analysis of the metal hyperfine parameters derived from the EPR spectra of copper(II) complexes having $^2A_{1g}(z^2)$ ground states. It has been deduced[51] that the unpaired electron spends ~3.2% of its time in the metal 4s orbital in the compressed tetragonal complex CuF_6^{4-}, which compares quite favorably with the above estimate of ~5.8% for the $CuCl_6^{4-}$ ion when it is remembered that the fluoro complex departs much less from a regular octahedral geometry[52] than is the case for the chloro complex. In the linear CuF_2 molecule, which is the limiting complex formed by tetragonally compressing an octahedral copper(II) complex, the 4s occupancy apparently rises to ~33% in the ground state.[51,53] This very high value presumably results from the extremely short Cu–F bonds, which means that the ligand-field anisotropy is much greater than in the limiting complex formed by axial elongation, planar $CuCl_4^{2-}$. The general self-consistency of this picture is confirmed by a recent analysis of the "d–d" spectrum of the linear NiO_2^{2-} ion,[54] which implied ~25% contribution of the 4s orbital to the $a_{1g}(z^2)$ orbital.

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Infrared Spectra of As_4–Ozone Reaction and Photolysis Products in Solid Argon

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As_4 and O_3 codeposited with excess argon at 14–17 K produced new sharp weak bands at 921.7, 590.3, and 565.4 cm^{-1} that increased with red-light photolysis. In the early stages of 630–1000-nm irradiation, the upper band was favored, but in later stages the upper band decreased while the lower bands increased. These single O atom species are assigned to AsO complex and bridge-bonded As_4O formed by decomposition of excited terminally bound As_4O. New bands in the 700–810-cm^{-1} region below As_4O_6 that were favored on UV photolysis are assigned to bridge-bonded As_4O_x (x = 2–5) species; As_4O_6 was also formed on codeposition and increased by UV photolysis. As_4 is more reactive with O_3 than P_4 under the conditions of these experiments.

Introduction

Although spectroscopy of the smallest arsenic oxide, AsO, and the largest arsenic oxides, As_4O_6 and As_4O_{10}, have been extensive,[1-6] there has been no characterization of smaller intermediate arsenic oxide species. However, the larger As_4O_x (x = 6–10) species evaporating from the solid oxides have been examined by matrix infrared methods.[7] Several new lower oxides of phosphorus have been identified and characterized in this laboratory from matrix reactions of P_4 with oxygen atoms,[8] and this approach has been applied to the arsenic–oxygen system. The tetrahedral As_4 vapor species has been characterized,[9-12] and the controlled reaction of As_4 with O atoms is the subject of this matrix investigation.

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