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EPR, Electronic, and Vibrational Spectra of the $CuCl_6^{4-}$ Anion in [tris(2-aminoethyl)amineH_4]$_2$[$CuCl_6$]Cl_4·2H_2O and Crystal Structure of the Complex

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The synthesis and crystal structure of [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·2$H_2O$, $C_{12}H_{48}Cl_{10}CuN_8O_2$, are reported. Crystals of the compound are triclinic, $P\bar{1}$, with $a = 8.317(1)$ Å, $b = 9.506(1)$ Å, $c = 11.450(1)$ Å, $\alpha = 94.43(1)°$, $\beta = 103.29(1)°$, and $\gamma = 114.04(1)°$ ($Z = 1$). The structure contains isolated $CuCl_6^{4-}$ anions, with Cu−Cl(1) = 2.251(1), Cu−Cl(2) = 2.361(1), and Cu−Cl(3) = 3.105(1)Å. The g values obtained from the EPR spectrum of the powder are $g_1 = 2.05$, $g_2 = 2.08$, and $g_3 = 2.29$. These values are consistent with an elongated octahedral symmetry with a slightly rhombic distortion. The vibrational spectra of the $CuCl_6^{4-}$ anion are assigned in D_{2h} symmetry.

Introduction

The chlorocuprates(II) are rather interesting both experimentally and theoretically. This arises in large part because a wide range of stereochemistries has been observed. The isolated monomeric chlorocuprate(II) anions are ideal candidates for the study of the restrictions imposed by the Jahn−Teller or pseudo-Jahn−Teller effect, since the copper(II) ion is subjected to a comparatively simple isotropic ligand field. The most common monomeric species is the four-coordinate $CuCl_4^{2-}$ anion, which generally has geometries ranging from slightly compressed tetrahedral to square planar.[1] A few crystallographic studies are reported in which ions with tetrahedral or nearly tetrahedral geometry are found.[2] However, large anisotropic displacement parameters for the Cl atoms are indicative of disorder. Monomeric five- or six-coordinated $CuCl_{2+n}^{n-}$ anions are much rarer. They have been found in only six compounds: four containing $CuCl_5^{3-}$ anions[3,4] and two containing the $CuCl_6^{4-}$ anion.[5] However, they exhibit very interesting properties in view of the Jahn−Teller effect. For the isolated $CuCl_5^{3-}$ anion, a distorted square pyramidal geometry is found in [N(2amet)pipzH_3]$CuCl_5$·2H_2O and in (pipzH_2)$_2$$CuCl_6$·MeOH.[3] In contrast, trigonal bipyramidal geometry is observed in the room-temperature form of M(NH_3)$_6$$CuCl_5$ (M = Cr, Co).[4] However, a structural phase transition is observed below room temperature, and the coordination geometry changes to distorted square pyramidal.[4] The most stable configuration is apparently the one with square pyramidal geometry, and it is argued that the trigonal bipyramidal geometry may be the dynamic average of three square pyramidal orientations.[6] The first isolated $CuCl_6^{4-}$ anion was found in the compound (cyclamH_4)$CuCl_6$.[5a] The stereochemistry is a tetragonally elongated octahedron, which is expected for a copper(II) complex with six identical ligands. The other example of an isolated $CuCl_6^{4-}$ anion was reported[5b] in (3-chloroanilinium)$_8$$CuCl_{10}$. The crystal structure analysis showed that the $CuCl_6^{4-}$ ion has an unusual compressed tetragonal distortion; however, it can be interpreted as the an "antiferrodistortive" order pattern, which is two almost equally weighted elongated rhombic octahedra misaligned by 90°.[7−9]

In this paper, we report the crystal structure and the EPR, electronic, and vibrational spectra of the title compound and compare these with the behavior of the other reported $CuCl_6^{4-}$ ions.

Experimental Section

Synthesis. To 0.01 mol of tris(2-aminoethyl)amine and 0.01 mol of copper(II) chloride were added approximately 20 mL of distilled water and 20 mL of concentrated hydrochloric acid. After a few minutes, orange crystals began to precipitate. The solution was continuously evaporated at room temperature. Two days later, green crystals started to grow. Crystals of the green compound were picked from the solution and air-dried.

The compounds tris(2-aminoethyl)amine(HCl)$_4$·$x$$H_2O$ and tris(2-aminoethyl)amine(HBr)$_4$·$x$$H_2O$ were prepared for IR and Raman spectroscopic measurements by simply crystallizing tris(2-aminoethyl)amine from dilute hydrochloric acid and hydrobromic acid, respectively.

X-ray Crystallographic Studies. The structure was determined for the green crystals. A prismatic crystal (0.3 × 0.5 × 0.5 mm) was selected for data collection on a Syntex P2$_1$ spectrometer upgraded to Siemens P4 specifications using graphite-monochromated molydenum radiation (λ(Kα) = 0.710 73 Å). Crystallographic data are reported in Table 1. The unit cell parameters and final orientation matrices were obtained from least-squares refinement of machine-centered reflections. During the data collection, the intensities of three standard reflections, monitored every 97 reflections, remained constant. Data collection and data reduction were performed by utilizing the XSCANS program.[10]

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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Table 1. Parameters for the Data Collection and Structure Refinement for [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·$2H_2O$

empirical formula	$C_{12}H_{46}N_8OCl_2Cu$	fw	754.6
a, Å	8.317(1)	crystal system	triclinic
b, Å	9.506(1)	space group	$P\bar{1}$
c, Å	11.450(1)	temp	23 °C
α, deg	94.43(1)	λ(Mo Kα), Å	0.710 73
β, deg	103.29(1)	ρ_{calcd}, g cm^{-3}	1.587
γ, deg	114.04(1)	μ(Mo Kα), cm^{-1}	15.64
V, Å^3	789.6(2)	*R*,^{a} %	3.55
Z	1	R_w,^{b}%	6.75

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å × 10^2) for [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·$2H_2O$

	x	*y*	*z*	U_{eq}^{a}
Cu(1)	0	0	5000	29(1)
Cl(1)	2602(1)	671(1)	6512(1)	27(1)
Cl(2)	982(1)	2620(1)	4712(1)	25(1)
Cl(3)	1828(1)	−827(1)	3145(1)	44(1)
Cl(4)	6047(1)	5105(1)	7041(1)	34(1)
Cl(5)	−7019(1)	1862(1)	50(1)	32(1)
N(1)	−2142(3)	2767(2)	2606(2)	21(1)
N(2)	338(3)	1413(3)	1675(2)	31(1)
C(1)	−790(4)	2113(3)	980(2)	27(1)
C(2)	−2509(3)	1818(3)	1372(2)	24(1)
N(3)	−5201(3)	2564(3)	4620(2)	33(1)
C(3)	−3462(4)	2799(3)	4347(2)	32(1)
C(4)	−3890(3)	2287(3)	2978(2)	24(1)
N(4)	−2307(3)	6484(3)	2119(2)	34(1)
C(5)	−2173(4)	5063(3)	1634(2)	32(1)
C(6)	−1184(3)	4514(3)	2655(2)	27(1)
O(1)	7669(5)	3257(4)	8774(3)	82(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The intensity data were corrected for Lorenz and polarization effects, and an empirical absorption correction, based on ψ-scan data, was applied. The structure was solved *via* direct methods, completed by a subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures. The structure refinement was performed with the SHELXTL-PLUS crystallographic package.[11] Table 2 gives the positional and thermal parameters for [tris(2-aminoethyl)amineH_4]$_2$-$CuCl_{10}$·$2H_2O$. All non-hydrogen atoms were refined with anisotropic displacement parameters to $R = 3.55\%$. Hydrogen atoms were treated as idealized contributions.

EPR Measurement. Electron paramagnetic resonance spectra were measured at room temperature and at 78 K on a Varian E-3 X-band spectrometer. The finely powdered sample was packed in a quartz tube. The magnetic field strength was calibrated by reference to a DPPH sample. Simulation of the EPR spectrum was performed using the POWFIT program.[12]

Electronic Spectrum. The diffuse reflectance spectrum was recorded on a Perkin-Elmer 330 spectrophotometer at room temperature. An integrating sphere (supplied by Perkin-Elmer) and a $MgSO_4$ reference were used in conjunction with a powdered sample pressed between UV grade quartz plates.

IR Spectroscopy. Infrared absorption spectra were obtained in the 100−550 cm^{-1} range using a Bruker 113 vacuum bench FT-IR. A glowbar source, 6 μm Mylar beam splitter, and TGS detector with a polyethylene window were used. The samples were ground with polyethylene powder in an agate mortar and pestle to form uniform powders of 4%−8% by weight of sample. These powders were pressed into 7 mm diameter disks using a hand press. Each resulting pellet was then studied in standard transmission configuration. The transmission data were converted to absorbance and plotted. In some cases, a low-order polynomial function was used to flatten the background. Data were taken at 4 cm^{-1} resolution.

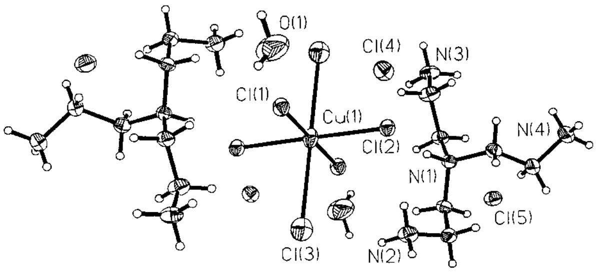

Figure 1. ORTEP drawing of the [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·$2H_2O$ molecule showing the labeling scheme. The thermal ellipsoids for non-hydrogen atoms are drawn at the 50% probability level. Atoms related by the inversion center are not labeled.

Table 3. Bond Lengths (Å) and Bond Angles (deg) for the $CuCl_6^{4-}$ Anion in [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·$2H_2O$, (cyclam$H_4$)$CuCl_6$, and (3-chloroanilinium)$_8$$CuCl_{10}$

	trisCuCl$_6$	(cyclamH_4)-$CuCl_6$^{5b}	(3-chloroanilinium)$_8$-$CuCl_{10}$	
			ref 9	ref 7
Cu(1)−Cl(1)	2.251(1)	2.291	2.278(1)	2.28(1)
Cu(1)−Cl(2)	2.361(1)	2.302	2.39(2)	2.38(1)
Cu(1)−Cl(3)	3.105(1)	3.175	2.82(3)	2.83(5)
Cl(1)−Cu(1)−Cl(2)	88.9(1)	89.9(>0.1)	90.4(3)	
Cl(1)−Cu(1)−Cl(3)	89.4(1)	94.7(>0.1)	90.3(4)	
Cl(2)−Cu(1)−Cl(3)	93.1(1)	91.0(>0.1)	90.2(4)	

Raman Spectroscopy. Spectra were measured of neat powders in a capillary tube using 20 mW of 514.5 nm radiation from a Spectra-Physics argon ion laser. Laser radiation was filtered and passed through a Pellin-Brocha prism monochromator before impinging on the samples. Raman scattered radiation was dispersed in a double 1-m monochromator (Jobin Yvon) equipped with holographic gratings. The resulting signal was converted to pulses by a photomultiplier followed by a discriminator−amplifier. Pulses were counted by a Stanford Instruments pulse counter, and the resulting counts were read by a data acquisition program running on a PC. The entire data collection process was controlled by the PC, and typically 8−16 scans were coadded. Each scan was run at 1 cm^{-1}/s, and the total of counts in each 2 cm^{-1} interval was the intensity-stored. Final spectra were converted to counts per second. The slit width used was typically 1 mm, providing an overall instrumental resolution of about ±3 cm^{-1}.

Results and Discussion

Structure of [tris(2-aminoethyl)amineH_4]$_2$[$CuCl_6$]Cl_4·$2H_2O$. The structure of [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·$2H_2O$ contains tris(2-aminoethyl)amine$H_4$$^{4+}$ cations, an isolated $CuCl_6^{4-}$ anion, lattice Cl^- ions, and lattice water molecules. The ORTEP drawing of the molecular structure of [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·$2H_2O$ with its labeling scheme is shown in Figure 1. Bond distances and bond angles for the $CuCl_6^{4-}$ ions in [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·$2H_2O$ and in other reported isolated $CuCl_6^{4-}$ ions are given in Table 3. The $CuCl_6^{4-}$ ion lies on an inversion center, with three distinguished Cu−Cl distances (2.251(1), 2.361(1), and 3.105(1) Å). The distances are correlated with the hydrogen-bonding interactions in which they are involved, as discussed below. The in-plane Cl−Cu−Cl angles differ from 90° by about 1°, and the out-plane angles differ from 90° by about 3°. Thus, the geometry of the $CuCl_6^{4-}$ anion is approximately an elongated rhombic octahedron. The tris(2-aminoethyl)amine cation shows the usual saturated conformation with expected values for bond distances (1.477−1.522 Å) and angles (108.1−114.1°), which are listed in Table 4. There are extensive hydrogen bonds among the $CuCl_6^{4-}$ anion, the ammonium groups, water

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(11) Sheldrick, G. M. *SHELXTL-PLUS*, Release 4.0; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990.

(12) POWFIT EPR simulation software distributed by the Laboratory of Molecular Biophysics, National Institute of Environmental Health Sciences.

Table 4. Bond Lengths (Å) and Bond Angles (deg) for the tris(2-aminoethyl)amineH_4 Cation in [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·$2H_2O$

N(1)−C(2)	1.511(3)	C(2)−N(1)−C(4)	110.5(2)
N(1)−C(4)	1.509(4)	C(2)−N(1)−C(6)	112.5(2)
N(1)−C(6)	1.510(3)	C(4)−N(1)−C(6)	112.5(2)
N(2)−C(1)	1.483(4)	N(2)−C(1)−C(2)	112.8(2)
C(1)−C(2)	1.520(4)	N(1)−C(2)−C(1)	114.1(2)
N(3)−C(3)	1.481(4)	N(3)−C(3)−C(4)	108.1(2)
C(3)−C(4)	1.519(4)	N(1)−C(4)−C(3)	110.7(2)
N(4)−C(5)	1.477(4)	N(4)−C(5)−C(6)	110.8(2)
C(5)−C(6)	1.522(4)	N(1)−C(6)−C(5)	113.2(2)

molecules, and lattice chloride ions. In the $CuCl_6^{4-}$ anion are formed two strong hydrogen bonds to Cl(3), only one moderately strong hydrogen bond to Cl(2), and only weak bifurcated hydrogen bond to Cl(1). Thus the longest Cu···Cl is involved in the strongest hydrogen bond while the shortest is involved in the weakest. All lattice chloride ions are involved a relatively strong Cl···N contact (Cl···N distances ~3.1 Å) and several weaker contacts (Cl···N distances 3.2−3.4 Å).

Comparison of the Geometries of $CuCl_6^{4-}$ Anions in Different Compounds. A six-coordinate Cu(II) complex with O_h symmetry has a ^2E_g electronic ground state. The degeneracy of the ^2E_g electronic ground state is lifted by the coupling between electronic E_g and vibrational e_g modes. This leads to a potential surface which is well-known as the "Mexican hat" potential surface. There are three equivalent minima in the warped Mexican hat potential surface which correspond to three tetragonal elongated octahedra. If the potential surface is further subject to strain effects, the elongated rhombic distortion occurs.

The geometry of the $CuCl_6^{4-}$ anion in the title compound is an elongated rhombic octahedron with approximately D_{2h} symmetry. Qualitatively, the stereochemistry is as expected for a copper(II) complex subject to a static Jahn−Teller distortion in the presence of a small lattice strain. The rhombic distortion is similar to that in (3-chloroanilinium)$_8$$CuCl_{10}$ (2.287, 2.38, and 2.81 Å)[7,9] and is more apparent than that found in (cyclamH_4)$CuCl_6$ (2.291, 2.302, and 3.175 Å).[5a] The average distance for equatorial bonds is about 2.3 Å for all the isolated $CuCl_6^{4-}$ ions. On the other hand, the axial bond lengths are more sensitive to lattice environments. The static geometries of the two isolated $CuCl_6^{4-}$ ions have substantially longer axial bond lengths, as can be seen by comparison with those in (3-chloroanilinium)$_8$$CuCl_{10}$, for which a dynamic Jahn−Teller effect has been postulated.[7,9] The bond lengths for the isolated $CuCl_6^{4-}$ ions are also compatible with those observed in layer perovskite systems in which the shorter bond lengths vary from 2.27 to 2.36 Å and the longer bond lengths generally range from 2.8 to 3.2 Å.[1]

EPR Spectroscopy. The room-temperature EPR powder spectrum of the $CuCl_6^{4-}$ complex is shown in Figure 2. The 78 K spectrum was qualitatively the same. The simulated spectrum with the optimized *g* values ($g_1 = 2.05$, $g_2 = 2.08$, and $g_3 = 2.29$) is also given in Figure 2. The spectrum is that expected for six-coordinated Cu(II) complexes having a tetragonally elongated geometry. Since the g_1 and g_2 values are very close, the spectrum is an approximately axial type with $g_\perp \sim 2.05-2.08$ and $g_\| = 2.294$. The $g_\perp$ value of 2.05 is in good agreement with those observed for the $CuCl_6$ chromophores in perovskite structures[13] as well as in (cyclamH_4)$CuCl_6$,[14] and in (3-chloroanilinium)$_8$$CuCl_{10}$.[7] However, the $g_\|$ value of 2.294 is significantly larger than the typical $g_\|$ value for $CuCl_6$ chromophores (2.24−2.27).[1] This value is also larger than the reported $g_\|$ value for the (cyclamH_4)$CuCl_6$.[13]

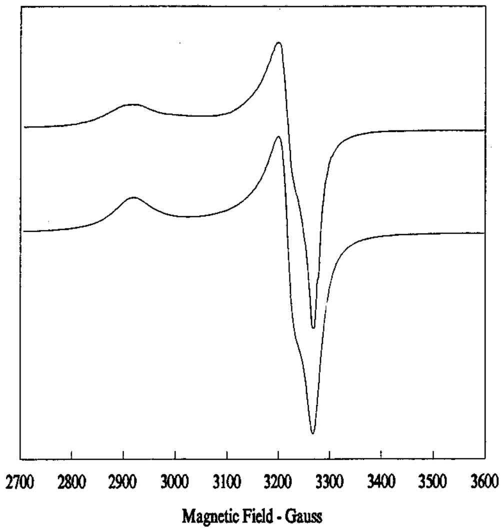

Figure 2. Powder EPR spectrum of [tris(2-aminoethyl)amineH_4]$_2$-$CuCl_{10}$·$2H_2O$ recorded at room temperature (top) along with the simulated spectrum (bottom).

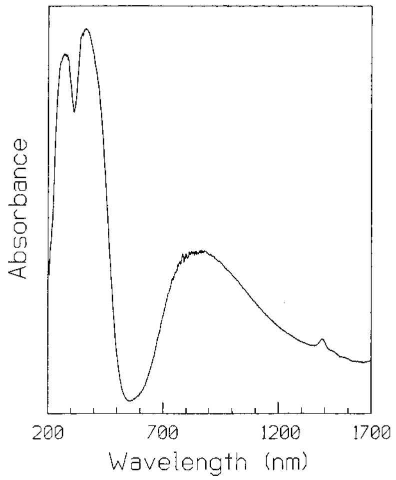

Figure 3. Room-temperature diffuse-reflectance spectrum of [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·$2H_2O$.

Electronic Spectrum. The room-temperature diffuse reflectance spectrum of [tris(2-aminoethyl)amineH_4]$_2$$CuCl_{10}$·$2H_2O$ is shown in Figure 3. There are three bands in the region between 200 and 1700 nm. A broad unresolved band with a maximum at 842 nm is assigned to the d−d transitions. The band position is very similar to those observed in (cyclamH_4)$CuCl_6$[13] and in (3-chloroanilinium)$_8$$CuCl_{10}$.[7] The charge transfer bands are observed in a lower wavelength region (364 and 274 nm). The small peak at 1388 nm is probably due to the quartz plate covering the sample.

Assignment of the Raman Spectrum. Figure 4 contrasts the Raman spectra obtained from [tris(2-aminoethyl)amineH_4]$_2$-$CuCl_{10}$·$2H_2O$ (hereafter called tris$CuCl_6$), tris(2-aminoethyl)-amine$(HCl)_4$·xH_2O (hereafter called tris$(HCl)_4$), and tris(2-aminoethyl)amine$(HBr)_4$·xH_2O (hereafter called tris$(HBr)_4$). The intensities were adjusted to give intensities similar to those of characteristic tris bands in the 600−1600 cm^{-1} region. Table 5 contains the assignments and activities provided by McDonald[13] and others for D_{4h} symmetry hexa- and tetrachlorides. Table 5 also presents the appropriate D_{2h} symmetry labeling and our assignments for the observed modes in tris$CuCl_6$. The tris$CuCl_6$ Raman spectrum is very similar to that reported for (cyclamH_4)$CuCl_6$ by McDonald and Hitchman.[13] Three nondegenerate modes provide a clear pattern that is similar in both the D_{4h} and D_{2h} species. These are the symmetric (in D_{2h}) in-

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(13) McDonald, R. G.; Hitchman, M. A. *Inorg. Chem.* **1989**, *28*, 3996.
(14) McDonald, R. G.; Hitchman, M. A. *Inorg. Chem.* **1986**, *25*, 3273.

Table 5. Vibrational Energies and Assignments

D_{4h} assignments						D_{2h} assignments			
cyclam$H_4(CuCl_6)$[a]				K_2PtCl_4[b]	K_2PdCl_4[c]	[tris(2-aminoethyl)amine$H_4]_2(CuCl_{10}){\cdot}2H_2O$			
ν_1	a_{1g}	R(s)	262	329	308	270	a_g	ν_1	
ν_2	a_{1g}	R(w)	101			112	a_g	ν_3	LA
ν_3	a_{2u}	IR	118			147	b_{1u}	ν_7	LA
ν_4	a_{2u}	IR	141	173	170	172	b_{1u}	ν_8	
ν_5	b_{1g}	R(m)	191	302	274	214	a_g	ν_2	
ν_6	b_{2g}	R(s)	170	194	198	172	b_{1g}	ν_4	
ν_7	b_{2u}	inactive				?	b_{1u}	ν_9	
ν_8	e_g	R(m)	80(?)			95, 56	$b_{2g} + b_{3g}$	$\nu_5 + \nu_6$	LA
ν_9	e_u	IR	278	325	337	316, 274	$b_{2u} + b_{3u}$	$\nu_{10} + \nu_{13}$	
ν_{10}	e_u	IR	180	195	190	201(?)	$b_{2u} + b_{3u}$	$\nu_{11} + \nu_{14}$	
ν_{11}	e_u	IR	65(?)			(?)	$b_{2u} + b_{3u}$	$\nu_{12} + \nu 1_5$	LA

[a] McDonald, R. G.; Hitchman, M. A. *Inorg. Chem.* **1986**, *25*, 3273. [b] McDonald, R. G.; Hitchman, M. A. *Inorg. Chem.* **1989**, 28, 3996. [c] Harrison, T. G.; Patterson, H. H.; Godfrey, J. J. *Inorg. Chem.* **1976**, *15*, 1291. LA signifies motion along the long CuCl axis.

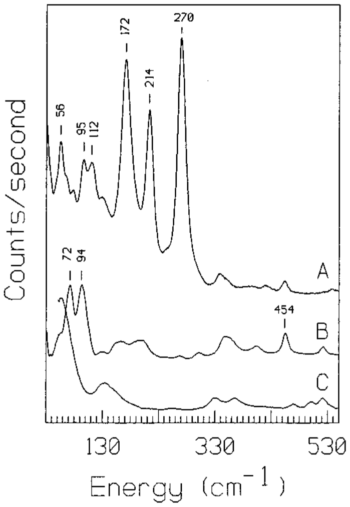

Figure 4. Raman spectra for the 30−530 cm^{-1} region: trisCuCl$_6$ (top); tris(HCl)$_4$ (middle); tris(HBr)$_4$ (bottom).

plane stretches (270 and 214 cm^{-1}) and an in-plane bend at 172 cm^{-1}. These three motions can be assigned with some confidence by comparison with other metal chlorides as seen in Table 5. The remaining Raman fundamentals are more difficult to assign. Accepting McDonald's assignment that the symmetric out-of-plane stretch lies near 101 cm^{-1} in (cyclamH$_4$)-CuCl$_6$, the corresponding motion in trisCuCl$_6$ should lie higher. As indicated by McDonald,[13] the observed vibrational stretching frequencies correlate roughly to the reciprocal bond distance to the fifth power. The out-of-plane Cu−Cl distance in trisCuCl$_6$ is 3.105 Å as compared to 3.175 Å in (cyclamH$_4$)-CuCl$_6$. Thus, the out-of-plane stretches observed at 101 cm^{-1} (Raman) and 118 cm^{-1} (IR) in (cyclamH$_4$)CuCl$_6$ should lie near 114 and 133 cm^{-1}, respectively. We therefore tentatively assign the Raman band at 112 cm^{-1} as the out-of-plane symmetrical stretch. The remaining two medium bands at 95 and 56 cm^{-1} may be the b_{2g} and b_{3g} fundamentals that result from splitting of the e_g mode in D_{4h}. The extreme splitting suggested by the latter assignment may be due to the significant difference in in-plane Cu−Cl distances (2.251 and 2.361 Å), since the b_{2g} and b_{3g} modes represent bending motions oriented along short and long in-plane bonds.

Assignment of the Far-Infrared Spectrum. Far-infrared spectra obtained from trisCuCl$_6$, tris(HCl)$_4$, and tris(HBr)$_4$ are presented in Figure 5. The band near 301 cm^{-1} for tris(HCl)$_4$ is clearly a Cl motion since it is absent in the spectrum of tris-(HBr)$_4$. The bands at 316, 274, 201, 172, and 147 cm^{-1} appear to be associated with the $CuCl_6^{4-}$ moiety. Again referring to the assignments of McDonald and Hitchman,[13,14] and to those of Harrison and co-authors,[15] the highest frequency Cu−Cl stretches are a b_{2u} and b_{3u} pair arising from an e_u motion in D_{4h}. These are the asymmetric in-plane stretches and are expected to be significantly split by the difference in potential as reflected in the differences in in-plane bond distance. The bands at 316 and 274 cm^{-1} are in the expected energy region and are not tris bands. Since these have the best agreement in energy with previous assignments for D_{4h} species, we tentatively assign this pair as the highest frequency b_{2u} and b_{3u} modes. As discussed in the preceding paragraph, the asymmetric out-of-plane stretch is expected to lie in the region of 133 cm^{-1}. The band at 147 cm^{-1} is of significant intensity (as was the corresponding band for (cyclamH$_4$)CuCl$_6$), and there is no other clear band between 150 and 100 cm^{-1}. Thus, we tentatively assign the 147 cm^{-1} band as due to the asymmetric out-of-plane stretch. The remaining assignments presented in Table 5 were made simply by associating the observed IR bands with those having similar positions in the (cyclamH$_4$)CuCl$_6$ spectrum.

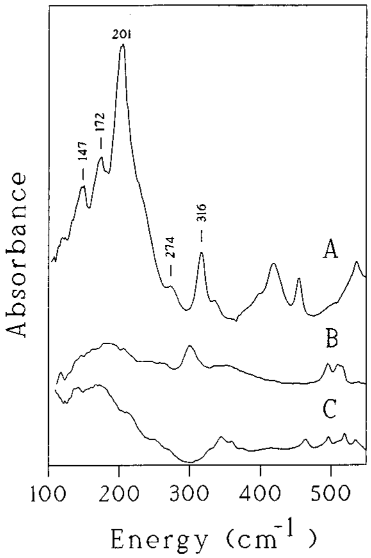

Figure 5. Infrared spectra for the 100−500 cm^{-1} region: trisCuCl$_6$ (top); tris(HCl)$_4$ (middle); tris(HBr)$_4$ (bottom).

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Supporting Information Available: Tables S1−S3, listing structure determination parameters, anisotropic thermal parameters, and H atom positions for [tris(2-aminoethyl)amine$H_4]_2CuCl_{10}{\cdot}2H_2O$ (5 pages). Ordering information is given on any current masthead page.

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(15) Harrison, T. G.; Patterson, H. H.; Godfrey, J. J. *Inorg. Chem.* **1976**, *15*, 1276.