Table I. Assignments of Raman Spectra[a] of $(SBr_3)^+(AsF_6)^-$ and $(SBr_3)^+(SbF_6)^-$

$(SBr_3)^+(AsF_6)^-$ Solid	$(SBr_3)^+(AsF_6)^-$ AsF_3 soln	$(SBr_3)^+(SbF_6)^-$ Solid	$(SBr_3)^+(SbF_6)^-$ SO_2 soln	PBr_3[c] gas	$(SF_3)^+(AsF_6)^-$[d] solid	$CsAsF_6$[e]	$LiSbF_6$[e]	Assignment
	1309[b]							$3\nu(X)$
	872.5		867.5					$2\nu(X)$
685 sh		675 sh			711			$\nu_3{}^f(MF_6)^-$
674	676	642	643.5		686	685	668	$\nu_1(MF_6)$
573 562	560	562.5	560		583 562	576	558	$\}\nu_2(MF_6)^-$
	436 p		434 p					$\nu(X)$
429 414	421 dp	421 410.5	417 dp	400	922			$\}\nu_3{}^g(SBr_3)^+$
391 367.5		277	280[h]		395 360	372	294	$\}\nu_5(MF_6)^-$ or $\nu_4(MF_6)^-$ $\nu_5(MF_6)^-$
375	378.5 p	379	376.5 p	381	942			$\nu_1(SBr_3)^+$
175	174 p	175	175.5 p	161	534			$\nu_2(SBr_3)^+$
128	124 dp	127.5	124 dp	116	403			$\nu_4(SBr_3)^+$

[a] Solvent peaks and Br_2 stretch omitted. These are, however, marked in Figure 1. [b] Frequencies (in cm^{-1}) accurate to ca. ±2 cm^{-1}. [c] See ref 14. [d] See ref 6. [e] See ref 13. [f] Tentative assignment assuming O_h and C_{3v} symmetry for $(MF_6)^-$ (M = As or Sb) and $(SBr_3)^+$. [g] Corresponds to $\nu_3(PBr_3)$ or $\nu_3(SF_3)^+$ in appropriate column. [h] Could be an impurity.

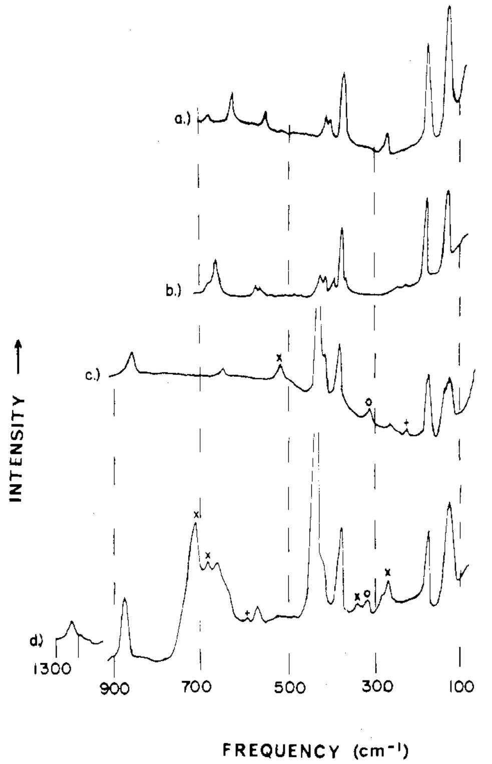

Figure 1. Raman spectra of the $(SBr_3)^+$ cation: (a) solid $(SBr_3)^+(SbF_6)^-$ (6471-Å line); (b) solid $(SBr_3)^+(AsF_6)^-$ (5145-Å line); (c) $(SBr_3)^+(SbF_6)^-$ in SO_2 solution (5145-Å line); (d) $(SBr_3)^+(AsF_6)^-$ in AsF_3 solution (5145-Å line). Slit width 8 cm^{-1} except in (b), which was at 4 cm^{-1}. × indicates solvent peaks. O indicates the Br_2 peak. + indicates impurities.

The spectra support an essentially ionic formulation for the two salts. The peaks attributed to $SBr_3{}^+$ are similar in solution and in the solid state, except ν_3 $(SBr_3{}^+)$, the antisymmetric stretching mode, (e), is split in the solid state. The four Raman active bands (two polarized and two depolarized) expected for $SBr_3{}^+$ are observed, and as expected,[6,18] they are at higher frequencies than the corresponding bands for the isoelectronic molecule PBr_3 except for ν_1 $(SBr_3{}^+)$ which is not significantly different from ν_1 (PBr_3).

The peaks designated $\nu(X)$ in Table I were observed in solution spectra and varied in intensity from sample to sample. The most intense was observed for $(SBr_3)^+(AsF_6)^-$ made in situ in arsenic trifluoride and $(SBr_3)^+(SbF_6)^-$ in dilute sulfur dioxide or arsenic trifluoride solution with the 5145-Å (green) exciting wavelength. The intensity decreased, and the peak broadened in the order 436 > 872 > 1309 cm^{-1} and therefore is likely a resonance Raman spectrum. It was least intense for $(SBr_3)^+(SbF_6)^-$ in sulfur dioxide solution using the 6471-Å (red) exciting frequency and no overtones were observed. We are presently attempting to determine the nature of this species.

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Registry No. $(SBr_3)^+(AsF_6)^-$, 66142-09-4; $(SBr_3)^+(SbF_6)^-$, 66142-10-7.

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Polarized Crystal Electronic Spectrum of Bis(ethylammonium) Tetrachlorocuprate(II) and an Application of the Angular Overlap Model to the Bonding in Chlorocuprate Complexes

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The chlorocuprates exhibit a wide variety of stereochemistries and it is probably for this reason that they have often

Table I. Spectral Transition Energies Calculated by a Least-Squares Procedure for Various Chlorocuprate Complexes Using the Angular Overlap Model[a]

Compd	Type[b]	Bond lengths, A	Ref	Transition	Energies, cm^{-1} × 10^{-3} Calcd	Calcd[f]	Obsd	Ref
$[Cr(NH_3)_6][CuCl_5]$	TB	2.30	17	$d_{x^2-y^2},d_{xy} \rightarrow d_{z^2}$	8.25	7.94	8.70	22
		2.39		$d_{xz},d_{yz} \rightarrow d_{z^2}$	10.23	10.31	10.80	
Cs_2CuCl_4	T	2.24[c]	18	$d_{xz} \rightarrow d_{x^2-y^2}$	5.97	5.70	4.80	3
		2.22[d]		$d_{yz} \rightarrow d_{x^2-y^2}$	6.59	6.33	5.55	
				$d_{xy} \rightarrow d_{x^2-y^2}$	7.83	8.19	7.90	
				$d_{z^2} \rightarrow d_{x^2-y^2}$	9.70	9.41	9.05	
$[C_6H_5N(CH_3)_3]_2CuCl_4$	T	2.256[e]	19	$d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$	6.97	6.68	5.92	4
				$d_{z^2} \rightarrow d_{x^2-y^2}$	9.72	9.35	8.85	
$CsCuCl_3$	TO	2.32	20	$d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$	13.38	12.98	12.93	23
		2.78		$d_{xy} \rightarrow d_{x^2-y^2}$	10.68	10.90	10.00	
				$d_{z^2} \rightarrow d_{x^2-y^2}$	8.07	7.48	8.30	
$(EtNH_3)_2CuCl_4$	TO	2.29	5	$d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$	14.60	14.15	13.30	g
		3.04		$d_{xy} \rightarrow d_{x^2-y^2}$	11.10	11.46	12.39	
				$d_{z^2} \rightarrow d_{x^2-y^2}$	10.53	9.76	11.13	
$(n\text{-}PrNH_3)_2CuCl_4$	TO	2.281	6	$d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$	14.43	13.97	13.50	g
		2.975		$d_{xy} \rightarrow d_{x^2-y^2}$	11.01	11.33	12.30	
				$d_{z^2} \rightarrow d_{x^2-y^2}$	10.72	9.93	11.30	
$(C_6H_5CH_2CH_2NH_2CH_3)_2CuCl_4$	P	2.248	21	$d_{xz} \rightarrow d_{x^2-y^2}$	15.17	14.72	14.15	2
		2.281		$d_{yz} \rightarrow d_{x^2-y^2}$	15.65	15.09	14.40	
				$d_{xy} \rightarrow d_{x^2-y^2}$	11.45	11.86	12.50	
				$d_{z^2} \rightarrow d_{x^2-y^2}$	12.91	11.87[e]	16.90	

[a] See text for the "best fit" ligand field parameters. [b] Complex stereochemistry: TB, trigonal bipyramid; T, distorted tetrahedral; TO, elongated tetragonal octahedral; P, square planar. [c] ClCuCl = 131.2°. [d] ClCuCl = 127.1°. [e] ClCuCl = 132.5°. [f] In this calculation the fitting procedure was carried out without including the $^2B_1(d_{x^2-y^2}) \rightarrow {}^2A_1(d_{z^2})$ transition of $(C_6H_5CH_2CH_2NH_2CH_3)_2CuCl_4$. [g] Present work.

been used to test the application of bonding models of transition-metal complexes.[1] The definite assignment of the excited-state energies of typical complexes with each type of geometry is therefore important, and these have been established for the $CuCl_4^{2-}$ ion in a square-planar[2] and a distorted tetrahedral geometry.[3,4] The present study reports the polarized crystal spectrum of bis(ethylammonium) tetrachlorocuprate [$(EtNH_3)_2CuCl_4$], which contains planar $CuCl_4^{2-}$ groups linked by long axial bonds to produce a centrosymmetric, distorted octahedral coordination geometry.[5] The low-temperature mull spectrum of bis(*n*-propylammonium) tetrachlorocuprate(II) [$(\eta\text{-}PrNH_3)_2CuCl_4$], which has a similar ligand arrangement about the Cu^{2+} ion[6], is also reported.

Experimental Section

The complexes were prepared by the method of Remy and Laves[7] and had satisfactory analyses. $(EtNH_3)_2CuCl_4$ belongs to the orthorhombic space group *Pbca* and crystallized as thick plates with the (100) face best developed. The crystal structure is such[5] that when the electric vector lies in the (100) plane the electronic spectrum is essentially an average of the *xy* and *z* molecular spectra (with *z* defined parallel to the long Cu–Cl bond directions). A section containing the (001) plane was therefore obtained by grinding, and the spectrum was measured at 8 K with the electric vector of light along the *a* and *b* crystal axes using a Cary 17 spectrometer (Figure 1) and an Oxford Instruments cryostat. The *a* spectrum corresponds to the pure *xy* molecular spectrum, while the *b* spectrum corresponds to the proportions 0.53(*xy*) + 0.47 (*z*); the pure *z* spectrum was readily obtained by subtracting out the *xy* component and normalizing to a unit projection of the electric vector along *z*.

Discussion and Comparison with Other Compounds

The spectrum consists of three peaks, the central one being almost absent in *z* polarization. The ligand arrangement approximates closely to D_{4h} symmetry,[5] and the only electric dipole transition forbidden by vibronic selection rules for a copper(II) complex belonging to this point group is $^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2B_{2g}(d_{xy})$ in *z* polarization. The peak at 12 390 cm^{-1} may therefore be assigned as this transition and, as virtually all bonding models require a higher energy for the transition $^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2E_g(d_{xz,yz})$, this may be assigned to the band at 13 300 cm^{-1}, leaving the peak at 11 130 cm^{-1} as $^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2A_{1g}(d_{z^2})$. This overall assignment agrees with that generally assumed for tetragonally distorted octahedral copper chloride complexes,[1] and with the EPR parameters of $(EtNH_3)_2CuCl_4$ and related complexes.[1,2] It is interesting to note that except for the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition, the *z* spectrum of $(EtNH_3)_2CuCl_4$ is somewhat more intense than the *xy* spectrum. This is in contrast to planar $CuCl_4^{2-}$ [2] and most other tetragonally distorted copper(II) complexes.[8] Presumably in $(EtNH_3)_2CuCl_4$ the presence of axial ligands is somehow instrumental in inducing intensity into the *z* spectrum. The spectrum of $(n\text{-}PrNH_3)_2CuCl_4$ (Figure 1) measured as a mull at 77 K closely resembles the *b* spectrum of $(EtNH_3)_2CuCl_4$, and the three bands may be assigned in analogous manner (see Table I).

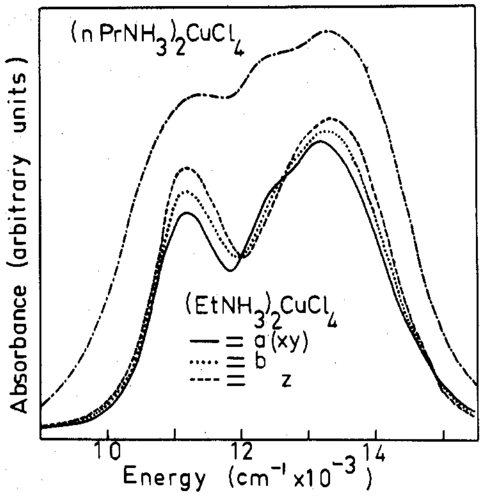

Figure 1. Electronic spectra at 8 K of the (001) crystal face of $(EtNH_3)_2CuCl_4$ with the electric vector parallel to the *a* and *b* crystal axes. The *a* spectrum corresponds to the *xy* molecular spectrum, while the *b* spectrum corresponds to 0.53(*xy*) + 0.47(*z*); the "pure" *z* spectrum is also shown, as is the mull spectrum of $(n\text{-}PrNH_3)_2CuCl_4$ measured at 77 K.

It is interesting to compare the d-orbital energies in the tetragonal octahedral chromophores with those in chlorocuprates having other geometries and to see how well these may be rationalized for the series of complexes using simple bonding models. Several attempts have been made to apply crystal field theory to the chlorocuprates, but more sophisticated calculations suggest that such a model is quite unrealistic.[1] Perhaps the best simple bonding model currently available for metal complexes is the angular overlap model (AOM) of Jorgensen and Schäffer.[9] This has recently been successfully applied to the interpretation of the spectral properties of a variety of metal complexes.[10,11] The AOM suggests that the energy e by which a metal d orbital is raised upon interaction with a ligand orbital is given by $e = S^2K$, where S is the diatomic overlap integral and K is a constant. The total energy of each orbital is obtained by summing the effects of all the ligand orbitals using the angular overlap matrix appropriate to the geometry of the complex. Both σ and π effects are included, and as the Cu (3d) and Cl (3p) overlap integrals have been reported as a function of Cu–Cl bond length[12] the AOM allows the d-orbital energies of a whole series of complexes of different geometries to be expressed as a function of just two parameters, K_σ and K_π. In its simplest form, the AOM predicts that for a spherical ligand such as Cl^- the condition $K_\sigma = K_\pi$ should be satisfied. In practice, it has been proposed that the model may need to be extended in several ways, e.g., by the inclusion of electrostatic effects or ligand–ligand interactions,[10] bonding with ligand s orbitals, or the admixture of metal s or p orbitals with the d functions.[13] The equations relating the d-orbital energies to K_σ and K_π have been given elsewhere for square-planar, tetragonal-octahedral, distorted tetrahedral, and trigonal-bipyramidal ligand coordination.[10,13] These were used to fit the electronic transition energies observed at low temperature for 7 copper(II) complexes of accurately known molecular geometry including all these stereochemistries by a least-squares technique, and the results are shown in Table I. Except for the transition ${}^2B_1(d_{x^2-y^2}) \rightarrow {}^2A_1(d_{z^2})$ in planar $CuCl_4^{2-}$ the calculated and observed energies agree quite well, the "best fit" ligand field parameters being $K_\sigma = 1.01 \times 10^6$ and $K_\pi = 1.21 \times 10^6$ cm^{-1}. Removal of this transition from the calculations gave "best fit" parameters $K_\sigma = 0.94 \times 10^6$ and $K_\pi = 0.93 \times 10^6$ cm^{-1} with the only discrepancies greater than 1000 cm^{-1} occurring for the ${}^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2A_{1g}(d_{z^2})$ transitions of the tetragonal-octahedral chromophores in $(EtNH_3)_2CuCl_4$ and $(n\text{-}PrNH_3)_2CuCl_4$. Considering the wide range of stereochemistries covered, the agreement between the calculated and observed transition energies is remarkably good. Moreover, in agreement with the simple model $K_\sigma \approx K_\pi$. Participation of ligand s orbitals in the bonding or the presence of ligand–ligand interactions should cause K_σ to differ from K_π as well as produce systematic discrepancies in the spectral fits of complexes with differing stereochemistries.[10,13] However, the ${}^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2A_{1g}(d_{z^2})$ transition energy in planar $CuCl_4^{2-}$ is underestimated by ~5000 cm^{-1}. Smith has recently proposed[13] that in this complex the $a_{1g}(d_{z^2})$ orbital is lowered in energy by configuration interaction with the a_{1g}(4s) orbital. In D_{4h} symmetry these two orbitals are mixed by an amount dependent on the difference in ligand interaction along the x and z axes. Because the 4s orbital is so diffuse, its interaction with the ligand orbitals is large even at the long axial bond lengths in the tetragonally distorted octahedral complexes,[13] and it is only in the rigorously planar $CuCl_4^{2-}$ ion that the $a_{1g}(d_{z^2})$ orbital is lowered drastically in energy. The overall spectral fit (see Table I) suggests a depression of ~5000 cm^{-1} in planar $CuCl_4^{2-}$, ~1400 cm^{-1} in $(EtNH_3)_2CuCl_4$ and $(n\text{-}PrNH_3)_2CuCl_4$ (axial bond lengths ~3 Å), and ~800 cm^{-1} in $CsCuCl_3$ (axial bond lengths 2.78 Å). Assuming an energy of ~150 000 cm^{-1} for the 4s orbital,[14] simple perturbation theory suggests a molecular orbital coefficient of ~0.2 for this orbital in the ground-state wave function of planar $CuCl_4^{2-}$. While this has not been confirmed directly for the copper(II) complex, EPR spectral measurements of the isotropic hyperfine constants of low-spin planar cobalt(II) complexes with $A_{1g}(d_{z^2})$ ground states suggest molecular orbital coefficients of 0.15–0.25 for the 4s orbital in these complexes also[15] and that the participation of this orbital in the ground state decreases on axial ligation.[15,16] It would, thus, seem that while the AOM is adequate to describe the bonding in metal complexes having significant ligand interactions along each of the cartesian molecular axes, in the case of planar compounds it is necessary to include the metal 4s orbital in the bonding scheme.

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Registry No. $[(EtNH_3)_2CuCl_4]$, 55940-27-7; $[(n\text{-}PrNH_3)_2CuCl_4]$, 55940-28-8.

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Synthesis, Properties, and X-Ray Structure of (Diethylenetriamine)copper(I) Carbonyl: a Highly Thermally Stable Copper(I) Amine Carbonyl

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Notwithstanding that copper(I) amine carbonyl chemistry is one of the oldest areas of carbonyl chemistry,[1,2] no thermally stable solution or solid-state copper(I)–amine carbonyl complexes have been isolated until recently.[3] The stabilization of the Cu–CO bond was variously ascribed to the electronic effect of the ancillary ligands around Cu(I) and/or to the

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