charge product for the reaction of $NiNTA^-$ with enH^+ still only produces a rate constant similar to that for the reaction with the neutral NH_3.

General Conclusions

We see in this and related work of a number of investigators some ways in which a proton attached to a ligand can affect the rate of metal complexing. If it is far removed from potential reaction sites, as in $TPTZH^+$, it has little effect. Often its role may be solely one of increasing the positive charge and decreasing the outer sphere association constant as in the reaction with Ni^{2+}. The proton may play a much more significant role by blocking the reaction site as in $bipyH^+$ and particularly $phenH^+$. Intramolecular hydrogen bonding may be more important in the latter because of the rigidity of phen, or there may be present an even more stable structure involving hydrogen bonding *via* a water molecule bridging the phenanthroline nitrogens.[33] The latter idea has not, however, been supported by recent work.[34] The lack of reactivity of these protonated forms, as well as of the zwitterions,[3] may reside in a reduced value for K_o and/or k_o in the Eigen mechanism.[16] One effect of protonation which apparently does not show up in our studies is the incidence of proton loss from a protonated intermediate being rate determining. This will rarely be the case with the slower reacting nickel (except perhaps in its reaction with the enol form of β-diketones[35]) but may be quite important in the reactions with very labile ions, such as Cu(II) ions.[19,36,37] Finally, protonation may lead to a radical structural change with the production of a unreactive tautomer, as in the hydroxy derivatives of pyridine and phenanthroline, typified by chelidamic acid and 4,7-dihydroxyphenanthroline.

Acknowledgment. We are grateful for a National Science Foundation Grant (GP 1963 and 5671) and a DuPont Teaching Fellowship (to J. C. C.) which supported this work.

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Cesium Tetrachlorocuprate. Structure, Crystal Forces, and Charge Distribution

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Abstract: The crystal and molecular parameters of cesium tetrachlorocuprate have been refined using an X-ray diffraction intensity data set. The crystal system is orthorhombic, space group *Pnam*, with four formula weights per unit cell; the unit cell parameters are $a = 9.7599\ (12)$, $b = 12.3967\ (12)$, and $c = 7.6091\ (9)$ Å. A total of 1786 independent reflections were used in least-squares refinement of the molecular parameters, leading to a final R factor (on F) of 5.5%. The anion has crystallographically imposed m symmetry and the three independent copper–chlorine bond lengths are 2.244 (4), 2.235 (4), and 2.220 (3) Å. The crystal forces acting upon the bonds within the anion were calculated, and after correction for their effects and for thermal motion the copper–chlorine bond length in an isolated anion is 2.283 Å. The charge distribution within the anion is estimated to be $[Cu^{0.60}(Cl^{-0.65})_4]^{2-}$ and this was compared with results obtained from semiempirical molecular orbital calculations. A normal coordinate analysis of the vibrational spectrum was performed, and there was good agreement between the force constant derived in this way and that derived from the structural results. Similar crystal force calculations were carried out using reported parameters for salts of the pentachlorocuprate anion, and it was concluded that there would be very little difference between the axial and equatorial copper–chlorine bond lengths in the absence of crystal forces.

The structure of cesium tetrachlorocuprate has been determined approximately using a limited X-ray diffraction data set[1] and the reported parameters have been refined by difference syntheses.[2] The anion has an unusual geometry in that coordination around the metal is intermediate between square planar and tetrahedral. The symmetry of the anion in the lattice closely approximates D_{2d}, and the extent of the flattening from T_d symmetry can be judged from the magnitude of the two angles greater than the tetrahedral angle. In cesium tetrachlorocuprate this angle (α) was reported to be about 124°, whereas in other salts of the anion[3] α is considerably larger (~130°); the possible significance of this difference is important, particularly as at least one empirical model for the bonding in this anion is expressed as a function of this angle.[4] To clarify this point, the structural parameters of cesium tetrachlorocuprate have been determined accurately using X-ray diffraction data collected using a four-circle diffractometer.

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Table I. Positional and Thermal Parameters[a] of Cs_2CuCl_4

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.23054 (16)	0.41806 (11)	0.25[b]	0.00637 (17)	0.00398 (11)	0.01209 (31)	−0.00060 (11)	0.0[b]	0.0[b]
Cs(1)	0.63399 (10)	0.39679 (7)	0.25[b]	0.00824 (11)	0.00540 (7)	0.02013 (23)	0.00020 (7)	0.0[b]	0.0[b]
Cs(2)	0.00556 (9)	0.67481 (7)	0.25[b]	0.00692 (10)	0.00432 (6)	0.01780 (20)	0.00022 (6)	0.0[b]	0.0[b]
Cl(1)	0.0054 (4)	0.3812 (3)	0.25[b]	0.0056 (3)	0.0060 (3)	0.0273 (10)	−0.0009 (3)	0.0[b]	0.0[b]
Cl(2)	0.3430 (4)	0.5751 (3)	0.25[b]	0.0077 (4)	0.0038 (2)	0.0285 (10)	−0.0012 (2)	0.0[b]	0.0[b]
Cl(3)	0.2937 (3)	0.3556 (2)	−0.0112 (3)	0.0108 (3)	0.0086 (2)	0.0125 (5)	0.0010 (2)	0.0007 (3)	−0.0025 (3)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Parameter fixed by symmetry.

Bonding in the tetrachlorocuprate anion has been investigated in some detail because the copper atom, here formally d^9, represents the relatively rare case of a "one-hole" system. The calculations have ranged from a simple, but exceedingly elegant explanation of the unusual geometry of the anion[5] to the more sophisticated semiempirical molecular orbital calculations.[6] One result of such calculations is an estimate of the charge distribution within the anion, but to date there has been no direct experimental determination of the charge distribution, and the validity of the calculations has usually been judged by agreement with spectroscopic results. Recently it has been shown that an estimate of the charge distribution within an anion can be made by analysis of accurate structural data by calculation of the crystal forces;[7] the refined parameters obtained for cesium tetrachlorocuprate were so treated and the results will be discussed in the light of the molecular orbital calculations.

The pentachlorocuprate anion has a trigonal-bipyramidal geometry in its hexaamminechromium(III) salt and the axial copper–chloride bonds are 0.095 Å shorter than the equatorial copper–chlorine bonds.[8] This would be regarded as a significant difference in bond lengths were it not that differences of up to 0.135 Å were observed in the zinc–chlorine bonds of the tetrachlorozincate anion in a hexaamminecobalt(III) salt.[9] The crystal forces acting upon the pentachlorocuprate salt to distort the copper–chlorine bond lengths were calculated to determine whether they are the cause of the differences between axial and equatorial bond lengths or whether this is a true feature of the anion.

Collection of X-Ray Diffraction Data

Crystal Data. Cesium tetrachlorocuprate, Cs_2CuCl_4, M = 471.15, is orthorhombic with a = 9.7599 (12), b = 12.3967 (12), and c = 7.6091 (9) Å;[10] U = 920.63 Å^3; Z = 4; the space group is *Pnam* (conditions for reflection are $h0l$, $h = 2n$; $0kl$, $k + l = 2n$). Crystals of the compound were prepared as described previously.[1] The cell constants were determined with Mo Kα radiation (λ 0.70930 Å) at a temperature of 18 (1)°, using the setting constants on a four-circle diffractometer of 12 high-angle reflections. Intensity data were collected using a crystal of dimensions 0.07 × 0.09 × 0.10 mm^3. Initially the crystal was aligned about the c axis of the cell, but to minimize double reflection the crystal was misset before data collection. The intensities were measured using a Picker four-circle diffractometer with crystal monochromated Mo Kα radiation, scanning in ω-2θ mode at a rate of 1°/min for a symmetric scan of 1.2° in 2θ with stationary-crystal, stationary-counter background counts for 10 sec measured at each end of the scan. Intensity data were collected for two octants (hkl and $h\bar{k}l$) of the orthorhombic crystal out to a Bragg angle of 40°. The intensities of three standard reflections were measured at intervals throughout data collection but, after an initial increase in intensity of about 7%, only minor variations were observed. The initial increase in intensity was assumed to be due to an increase in mosaicity of the crystal. The data were corrected for background and the changes in the standard reflections. The linear absorption coefficient is 108.5 cm^{-1} and an absorption correction was made. Because of the small crystal size, absorption was not a serious problem, the correction factors differing by less than 5%. The equivalent forms were averaged and the R factor of averaging ($R_{av} = 100[I_1 - I_2]/[I_1 + I_2]$, where I_1 and I_2 are the individual intensities) was 3.9% for those reflections with a positive net count and which were measured more than once. The independent reflections were corrected for Lorentz–polarization effects. Individual standard deviations, $\sigma(F^2)$, of the corrected intensities were calculated both from counting statistics and from the range of equivalent forms; the larger of these two estimates was used. A total of 5462 reflections were measured and processed. There were 1786 independent reflections with $F^2 > 0$ and, of these, 880 had $F^2 > \sigma(F^2)$.[11]

Refinement of the Structure

The reported values for the coordinates of all the atoms were used as input to least-squares refinement. The calculations were performed on an IBM 360/67 computer, and the programs used included modified versions of Zalkin's FORDAP and Busing, Martin, and Levy's ORFLS. The scattering factors for the neutral atoms were taken from the values of Cromer and Waber [12a] and the effects of anomalous dispersion were included in F_c using the values for f' and f'' given by Cromer.[12b] The function minimized in the refinement is $\Sigma w||F_o| - |F_c||^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, and initially only the 880 reflections with $F^2 > \sigma(F_o^2)$ were used. Refinement of the scale factor and positional and isotropic thermal parameters for all atoms led to an R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 10.9%. Following the method of Zachariasen,[12c] an extinction parameter was refined and anisotropic thermal parameters were refined for all atoms. The R factor converged to 3.1%, and, during the last cycle of refinement, no parameter changed by more than 5% of its standard deviation. Two further cycles of least-squares refinement were calculated using all 1786 reflections with $F^2 > 0$ and the final R factor was 5.5%. In the last two cycles, no parameter changed by more than 15% of its final standard deviation and the most significant result was a lowering of all estimated standard deviations by an average factor of 0.6. The best estimate of the extinction parameter was 1.72 (4) × 10^{-4}. A final difference Fourier synthesis revealed no peaks higher than 1.0 e/Å^3 and none of the maxima appeared to correspond with any chemically significant feature. Since scattering curves for neutral atoms were used to calculate the structure factors, it is perhaps not surprising that peaks up to 1.0 e/Å^3 were observed in the final difference Fourier. The final positional and thermal

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(11) Structure factors for cesium tetrachlorocuprate will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-8406. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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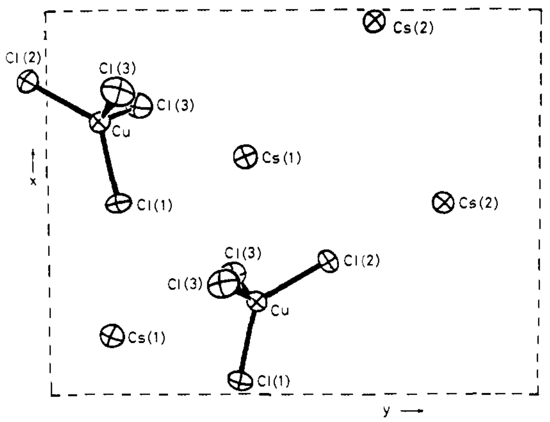

Figure 1. Cs_2CuCl_4: contents of the half of the unit cell at $Z = {}^1/_4$. Broken line shows the unit cell outline. The atoms are represented by 50% probability ellipsoids and were drawn using Johnson's ORTEP.

parameters and their standard deviations calculated from the inverse matrix are given in Table I. The root-mean-square thermal amplitudes of vibration are given in Table II.

Table II. Root-Mean-Square Amplitudes of Vibration (Å) along Principal Axes of Cs_2CuCl_4

Cu	0.165 (2)	0.186 (2)	0.188 (2)
Cs(1)	0.198 (1)	0.206 (1)	0.243 (1)
Cs(2)	0.179 (1)	0.187 (1)	0.228 (1)
Cl(1)	0.159 (5)	0.220 (5)	0.283 (5)
Cl(2)	0.159 (5)	0.205 (5)	0.289 (5)
Cl(3)	0.177 (4)	0.228 (4)	0.269 (4)

Description of the Structure

The crystal structure is built up by the packing of monomeric anions and cesium cations. There are two crystallographic mirror planes in the unit cell (at $z = {}^1/_4$ and $z = {}^3/_4$) and in these mirror planes lie all the atoms except the two Cl(3) atoms of each formula weight which lie approximately midway between the mirror planes. The anions have crystallographically imposed m symmetry. Table III lists all intra-anion distances and angles plus the inter-ion contacts less than or equal to 3.63 Å along with the appropriate angle; the esd's are calculated from the inverse matrix.

Table III. Selected Internuclear Distances (Å) and Angles (deg) in Cs_2CuCl_4

	(i) Within the Anion		
Cu-Cl(1)	2.244 (4)	Cl(1)-Cu-Cl(2)	131.2 (1)
Cu-Cl(2)	2.235 (4)	Cl(1)-Cu-Cl(3)	101.6 (1)
Cu-Cl(3)	2.220 (3)	Cl(2)-Cu-Cl(3)	99.7 (1)
Cl(1)-Cl(2)	4.078 (5)	Cl(3)-Cu-Cl(3)	127.1 (2)
Cl(1)-Cl(3)	3.459 (4)		
Cl(2)-Cl(3)	3.403 (4)		
Cl(3)-Cl(3)	3.975 (5)		
	(ii) Shortest Contacts between Ions		
Cl(1)-Cs(1)	3.630 (4)	Cu-Cl(1)-Cs(1)	165.3 (2)
Cl(2)-Cs(2)	3.483 (3)	Cu-Cl(2)-Cs(2)	177.7 (2)
Cl(2)-Cs(2)	3.518 (4)	Cu-Cl(2)-Cs(2)	81.2 (1)
Cl(2)-Cs(1)	3.599 (4)	Cu-Cl(2)-Cs(1)	81.5 (1)
Cl(3)-Cs(2)	3.460 (3)	Cu-Cl(3)-Cs(2)	105.9 (1)
Cl(3)-Cs(2)	3.488 (3)	Cu-Cl(3)-Cs(2)	147.8 (1)

Figure 1 shows the tetrachlorocuprate anions and cesium cations at $z = {}^1/_4$ (half the contents of the unit cell) projected onto the unit cell outline. None of the anisotropic atom vibrations are very eccentric, and each chlorine atom appears to be vibrating principally in a direction normal to the copper–chlorine bond axis. From an analysis of the vibrational spectrum (described later), a chlorine atom in a free tetrachlorocuprate anion should have a root-mean-square amplitude of vibration normal to the copper–chlorine bond greater by about 0.05 Å than that along the bond. Examination of Table II shows that this is about half of the effect calculated from the X-ray results, and presumably the other half is due to a libration of the whole anion within the crystal lattice.

The two large Cl–Cu–Cl angles within the anion in cesium tetrachlorocuprate average to 129.2° (the averaging is weighted with the other four angles to be consistent with D_{2d} symmetry and spherical geometry), and this is very close to the corresponding angles in other salts of this anion.[2,3] Thus it can be assumed that if this anion remains four-coordinate in the solid state, then there will be no large variation in this angle and other reasons must be sought for the observed changes in the d–d spectra.[4] In some tetrachlorocuprate salts, the anion has been described as square-planar,[13] but the copper atoms have a distorted six-coordinate geometry with four short and two long copper–chlorine internuclear distances; whether there are six covalent copper–chlorine bonds is open to discussion but there are at least strong electrostatic interactions and even these would destroy the "normal" geometry of the tetrachlorocuprate anion.

Effect of Crystal Forces upon the Anion Bond Lengths

In the crystal lattice of cesium tetrachlorocuprate the observed copper–chlorine bond lengths differ significantly, and the differences must be due to anisotropy of the applied crystal forces since it can be assumed that, in the absence of any forces external to the anion, the four bonds are equivalent. Calculation of the applied crystal forces and correction for their effects will yield the best estimate of the copper–chlorine bond length in the isolated anion. The electrostatic and short-range repulsive forces dominate the applied crystal forces and the calculation of these two forces will be discussed separately.

(i) The electrostatic forces which act to change the bond lengths within the anion were calculated as described previously[7] using a range of charges assumed for the chemical species in the crystal. Contributions up to a distance of 80 Å were included. Some of the results are shown in Table IV. As defined, a positive force acting upon a chlorine atom (relative to that acting upon copper) tends to compress that bond. The columns in Table IV headed Crystal force represent the sums of all contributions other than from the atoms within the anion under consideration. These are expressed as a function of the assumed charges and are always positive in this compound. The columns headed Internal force represent the sums of contributions from the atoms within the anion, and these are all negative.

(ii) The contribution of short-range repulsion to the potential energy of two particles, U_R, has been ex-

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Table IV. Electrostatic Forces[a] Applied to Tetrachlorocuprate Anion Bonds

Identifier	Charge on Cu	Charge on Cs	Charge on Cl	Force on Cl(1) Crystal	Force on Cl(1) Internal	Force on Cl(2) Crystal	Force on Cl(2) Internal	Force on Cl(3) Crystal	Force on Cl(3) Internal
1	1.20	1.0	−0.80	0.0411	−0.3052	0.0632	−0.2724	0.0753	−0.2602
2	0.80	1.0	−0.70	0.0494	−0.2278	0.0518	−0.2092	0.0610	−0.2021
3	0.68	1.0	−0.67	0.0508	−0.2067	0.0488	−0.1919	0.0570	−0.1861
4	0.60	1.0	−0.65	0.0515	−0.1933	0.0471	−0.1808	0.0544	−0.1758
5	0.52	1.0	−0.63	0.0519	−0.1802	0.0453	−0.1700	0.0519	0.1658
6	0.40	1.0	−0.60	0.0521	−0.1616	0.0429	−0.1544	0.0482	−0.1513
7	0.00	1.0	−0.50	0.0492	−0.1066	0.0366	−0.1078	0.0370	−0.1078

[a] All forces in millidynes.

pressed in two ways. One used by Lennard-Jones[14] makes the empirical assumption that U_R is inversely proportional to a high power of the separation of the two particles. The alternative expression was first proposed by Born and Mayer[15] on the basis of the form of the appropriate solution obtained from quantum mechanics, and it is this approach that will be used here. A convenient expression, first defined by Huggins,[16] is

$$U_R = bc \exp\{-a(r - r_1 - r_2)\}$$

where a and b are constants, c is a factor to allow for the effect of charge,[17] r is the internuclear separation of the two particles, and r_1 and r_2 are size parameters of the two particles. By assigning a value of 10^{-12} erg to b, a self-consistent set of values for r_1 and r_2 (the Huggins' radii) has been derived for the alkali metal cations and halide anions using compressibility data for alkali halide crystals;[16] some of the radii are shown in Table V as a function of the constant a. The accepted values of the corresponding ionic radii are also given in Table V, and it can be seen that they are larger than the Huggins' radii by a factor of 1.12 for the cations and 1.24 for the anions. Thus a reasonable estimate of the Huggins' radius can be made from the appropriate ionic radius. The force applied to change the bond lengths in the tetrachlorocuprate anion is equal to the gradient of the potential energy calculated in the bond directions. b was set equal to 10^{-12} erg; two values of a were used, 2.5 and 3.0; c was set equal to 1.0 and 0.75 for cesium-chlorine and chlorine-chlorine interactions, respectively; r is the appropriate internuclear separation in the crystal lattice; and values for the Huggins' radii for cesium and chlorine were chosen from the ranges 1.45–1.51 Å (see Table V) and 1.37–1.62 Å (derived from the shortest contacts in the crystal by multiplying the contact radius by 0.806), respectively. The only important contributions are from nearest neighbors, and thus the copper atom does not experience any applied force. Table VI lists some of the results, separated into the crystal effects (the sum of contributions from atoms outside the given anion) and internal effects (the sum of contributions from the chlorine atoms within the anion, the copper atom contribution not being included).

Table V. Size Parameters for Alkali Metal Cations and Halide Anions

Ion	Huggins' radius a = 2.9	Huggins' radius a = 3.0	Ionic radius Pauling	Ionic radius Goldschmidt
Li^+	0.475	0.570	0.68	0.60
Na^+	0.875	0.940	0.98	0.95
K^+	1.185	1.235	1.33	1.33
Rb^+	1.320	1.370	1.48	1.48
Cs^+	1.455	1.510	1.67	1.69
F^-	1.110	1.050	1.33	1.36
Cl^-	1.475	1.435	1.81	1.81
Br^-	1.600	1.560	1.96	1.95
I^-	1.785	1.750	2.19	2.16

With these results it is possible to compare the total force (crystal plus internal, electrostatic plus short-range repulsive) acting upon a bond with the observed bond lengths. A least-squares fit leads to values for k and d_0 in the equation

$$d = -kf + d_0$$

where d is the observed bond length, k is the reciprocal of the stretching force constant for the bond, f is the total applied force, and d_0 is the copper–chlorine bond length in the absence of any force. To recognize the assumptions of charges and Huggins' radii, the identifiers listed in Tables IV and VI are used. The final value of the function (S) minimized in the least-squares process is given for a few typical examples in Table VII, and it can be seen that this is a sensitive function of charge but does not vary greatly with the assumptions made in the calculation of the short-range repulsive forces. Charge set 4 clearly fits the data best and will be considered to be the experimentally derived charge distribution. The stretching force constants for the copper–chlorine bond ($= 1/k$) are also listed in Table VII, and the best estimate is 1.13 mdyn/Å. Calculation 4F is expressed graphically in Figure 2.

Since d_0 was calculated using the total force acting upon the bond, then it is equal to the copper–chlorine bond length in the hypothetical species $Cr–Cl^+$ in which the electron distribution within the bond is the same as in the tetrachlorocuprate anion. Of more interest is the bond length (d_1) in an isolated tetrachlorocuprate anion, and this is obtained in a manner analogous to that described elsewhere[7] but including the short-range repulsive forces. The isolated anion was assumed to have D_{2d} symmetry with two angles of 129.2° and four of 100.6°, and the derived values of the bond length are given in Table VII.

Vibrational Analysis of Cesium Tetrachlorocuprate

Definitive spectra of cesium tetrachlorocuprate have been reported,[18–21] and tentative assignments of the

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Table VI. Short-Range Repulsive Forces[a] Applied to Tetrachlorocuprate Anion Bonds

Identifier	Huggins' radius			Force on Cl(1)		Force on Cl(2)		Force on Cl(3)	
	Cs	Cl	a	Crystal	Internal	Crystal	Internal	Crystal	Internal
A	1.45	1.37	3.0	0.0027	−0.0049	0.0048	−0.0056	0.0071	−0.0054
B	1.45	1.49	3.0	0.0042	−0.0101	0.0075	−0.0116	0.0114	−0.0111
C	1.45	1.62	3.0	0.0071	−0.0220	0.0124	−0.0253	0.0198	−0.0241
D	1.48	1.37	2.5	0.0053	−0.0087	0.0092	−0.0097	0.0129	−0.0094
E	1.48	1.37	3.0	0.0029	−0.0049	0.0051	−0.0056	0.0076	−0.0054
F	1.48	1.49	2.5	0.0082	−0.0158	0.0135	−0.0177	0.0193	−0.0172
G	1.48	1.49	3.0	0.0045	−0.0101	0.0080	−0.0116	0.0212	−0.0111
H	1.48	1.62	2.5	0.0127	−0.0304	0.0209	−0.0339	0.0306	−0.0329
I	1.48	1.62	3.0	0.0075	−0.0220	0.0132	−0.0253	0.0208	−0.0241
J	1.51	1.37	3.0	0.0031	−0.0049	0.0055	−0.0056	0.0081	−0.0054
K	1.51	1.49	3.0	0.0048	−0.0101	0.0085	−0.0116	0.0129	−0.0111
L	1.51	1.62	2.0	0.0079	−0.0220	0.0140	−0.0253	0.0129	−0.0241

[a] All forces in millidynes.

Table VII. Analysis of Force Calculation Results for Cs_2CuCl_4

Identifiers		Stretching force constant for Cu–Cl bond, mdyn/Å	Bond length in isolated anion, Å	Sum of squares,[a] $S = \Sigma_i(d_i^{obsd} - d_i^{calcd})^2$
Electrostatic	Repulsive			
1	B	3.79	2.246	0.3083
1	F	3.81	2.246	0.3075
1	K	3.82	2.247	0.3065
2	B	1.82	2.258	0.0834
2	F	1.84	2.258	0.0840
2	K	1.86	2.258	0.0846
3	B	1.37	2.265	0.0167
3	F	1.39	2.264	0.0177
3	K	1.41	2.264	0.0185
4	B	1.11	2.270	0.0001
4	F	1.13	2.270	0.0000
4	K	1.15	2.270	0.0000
5	B	0.89	2.278	0.0426
5	F	0.91	2.278	0.0379
5	K	0.92	2.277	0.0337
6	B	0.66	2.290	0.4388
6	F	0.67	2.290	0.4036
6	K	0.68	2.290	0.3713

[a] This column has been multiplied by 10^4.

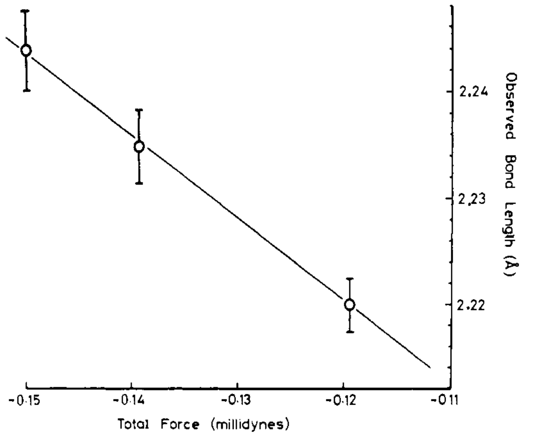

Figure 2. The variation of the copper–chlorine bond lengths in cesium tetrachlorocuprate with total force from calculation 4*F* (in Table VII). The vertical error bars represent 1 esd in the observed bond lengths.

bands have been made. However, in tetramethylammonium salts, the tetrachlorocuprate anion has a structure[22] very similar to that in the cesium salt, and yet a different set of assignments has been made.[23] Force constants have not been reported for the tetrachlorocuprate anion, and, in order to have a value to compare with that derived fom the structural results, a normal coordinate analysis has been performed. The solid-state spectra reported for cesium tetrachlorocuprate were used in the calculation because the structure of the anion is known in this compound. The gaseous anion approximation will be used even though maxima assigned to lattice vibrations were observed at 80 cm^{-1} and the anion modes are very little higher (in the region 100–300 cm^{-1}).

It is comparatively easy to classify the spectrum of cesium tetrachlorocuprate into the following four types of vibration: symmetric stretch, symmetric deformation, asymmetric stretch, and asymmetric deformation; these correspond to the ν_1, ν_2, ν_3, and ν_4 modes of pure tetrahedral symmetry. The nine normal modes of the anion under D_{2d} symmetry belong to the representations ($2A_1 + B_1 + 2B_2 + 2E$), all of which are Raman active and of which ($2B_2 + 2E$) are infrared active. The ν_2, ν_3, and ν_4 modes of tetrahedral symmetry all split under D_{2d} symmetry, ν_2 into ($A_1 + B_1$) and both ν_3 and ν_4 into ($B_2 + E$).

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(19) J. S. Avery, C. D. Burbridge, and D. M. L. Goodgame, *Spectrochim. Acta, Part A*, **24**, 1721 (1968).

(20) I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc. A*, 534 (1969).

(21) J. T. R. Dunsmuir and A. P. Lane, *ibid.*, 404 (1971).

(22) B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, **65**, 50 (1961).

(23) J. T. R. Dunsmuir and A. P. Lane, *J. Chem. Soc. A*, 2781 (1971).

Table VIII. Summary of Vibrational Spectra Reported for Cs_2CuCl_4 Frequencies in cm^{-1}

Method	Ref	$A_1(\nu)$	$A_1(\delta)$	$B_1(\delta)$	$B_2(\nu)$	$B_2(\nu)$	$E(\nu)$	$E(\delta)$
Powder ir	18a				288		256	
Powder ir	18b				292		257	
Powder Raman	19	295				116	250	134
Powder Raman	20	299	106			121	253	140
Single crystal Raman	20	297	103, 105	136	280	126, 120	256, 253, 251	149, 141
Powder ir	21				292	126	260	149
Single crystal ir	21				288	123	258	151

By assuming the Born–Oppenheimer approximation, the vibrational secular determinant can be written

$$|GF - \lambda E| = 0$$

G is the inverse kinetic energy matrix; F is the matrix describing potential energy and includes the force constants; λ is a matrix of elements $4\pi^2\nu_i^2$ where ν_i is an observed frequency; E is the identity matrix. The normal modes of vibration were defined in terms of a kinematically complete set of internal coordinates for the anion, and the redundancy was removed by application of symmetry arguments and group theory in the usual way. The vibrational secular determinant was solved using computer programs which are local modifications of those written by Schachtschneider.[24] Solution is obtained by two successive Jacobi diagonalizations, and then there is a least-squares fit of the defined force constants to the observed spectrum. A valence force field was used and, since there can be only seven observed frequencies, five force constants were defined: one stretching force constant, two bending force constants, and two constants for the interactions between stretching modes.

The frequency assignments used are those published with the Raman spectrum,[20] with the exception of the $B_1(\delta)$ mode as discussed below. Table VIII lists the reported vibrational spectra of cesium tetrachlorocuprate classified according to these frequency assignments. The frequency values used in the following calculations are the averages of the columns in Table VIII. The band at 280 cm^{-1} in the Raman spectrum was assigned to the $B_2(\nu)$ mode in agreement with the ir spectrum. Using frequency values for $A_1(\nu)$, $B_2(\nu)$, $B_2(\delta)$, $E(\nu)$, and $E(\delta)$, the five force constants were evaluated. From these force constants, the frequencies of $A_1(\delta)$ and $B_1(\delta)$ were calculated to be 101 and 135 cm^{-1}, respectively. The Raman spectrum does have maxima at 104 and 136 cm^{-1}, although the latter was assigned to one of the factor group split $E(\delta)$ modes; this was reassigned to $B_1(\delta)$, which does not seem to be inconsistent with the original data. A least-squares fit of the five force constants with the seven frequencies led to an average deviation between observed and calculated frequencies of 0.8 cm^{-1}, a satisfactory value. The final force constant values are 1.08 mdyn/Å, 0.37 mdyn Å/rad^2, 0.59 mdyn Å/rad^2, 0.43 mdyn/Å, and 0.17 mdyn/Å. The stretching force constant is in good agreement with that derived from the structural data. The larger of the two bending force constants applies to the smaller Cl–Cu–Cl angle, as is reasonable. The relatively large difference between the two interaction constants may be an artifact of the assumptions necessary to perform the calculation.

When the ν_3 (and ν_4) mode of tetrahedral symmetry splits into (B_2 + E) modes under D_{2d} symmetry, it is not obvious which of the two should be at the higher frequency. In the case of tetramethylammonium tetrachlorocuprate,[23] the assignments were made using the ordering opposite to that made for cesium tetrachlorocuprate, even though the anion has a closely similar structure. Using this alternative ordering and deriving the best set of force constants, the agreement between observed and calculated frequencies was much worse; the average deviation was 3.4 cm^{-1}, and some of the individual deviations were as high as 10 cm^{-1}. Thus the alternative ordering does seem less likely, even though this calculation employs many approximations.

Salts of the tetrachlorocuprate anion when dissolved in a noncoordinating solvent exhibit strong infrared absorption bands near 280 and 240 cm^{-1} with weaker absorptions near 119 and 84 cm^{-1}.[25] This is a strong indication that the anion symmetry in solution is still D_{2d}. It also provides some justification for the above calculation, because at least the two stronger bands of the solution spectrum are close to the $B_2(\nu)$ and $E(\nu)$ modes of the solid state spectrum, and thus the stretching force constant probably does not vary greatly.

By assuming a Boltzmann distribution of particles between the available vibrational states, the root-mean-square amplitudes of vibration at 18° were calculated with respect to the internal coordinates. They are 0.242 (Cu–Cl), 0.291 (large Cl–Cu–Cl angle), and 0.266 Å (small Cl–Cu–Cl angle).

Molecular Orbital Calculations for the $CuCl_4^{2-}$ and $CuCl_5^{3-}$ Anions

The earliest, and in many ways the most interesting, calculation performed upon the tetrachlorocuprate anion rationalized the observed geometry of the anion by the balance between ligand repulsions and the stabilization of the copper d orbitals.[5] The initial model invoked a central cupric ion surrounded by four chloride anions, and the total energy minimum was reached when the large Cl–Cu–Cl angle (α) was 119°. By including polarization of the chloride anions, the charge separation was effectively decreased and the energy minimum was reached with $\alpha = 123°$. Clearly if the charge distribution derived in the present paper were used, the optimum α would be larger (and therefore nearer the observed angle).

Semiempirical molecular orbital methods have been applied to the tetrachlorocuprate and pentachloro-

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(24) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules," VI, Technical Report No. 57-65, Shell Development Co., Emeryville, Calif.

(25) (a) D. Forster, *Chem. Commun.*, 113 (1967); (b) M. L. Good, C.-C. Chang, D. W. Wertz, and J. R. Durig, *Spectrochim. Acta, Part A*, **25**, 1303 (1969).

cuprate anions. These employ various approximations to solve the secular determinant

$$|H - GE| = 0$$

This discussion will be limited to the theoretically derived charge distributions because the other results of interest (such as predicted d–d and charge transfer spectra) are considered in detail in the original papers.[6,26] The reported charge distributions are listed in Table IX.

Table IX. Charge Distributions from Semiempirical Molecular Orbital Calculations

Ref	Charge upon Cu	Charge upon Cl
	(i) $CuCl_4^{2-}$ Anion	
6a	0.82	−0.70
6b	0.25	−0.56
6c (tetrahedral)	0.92	−0.73
6c (square planar)	0.80	−0.70
a	1.08	−0.77
	(ii) $CuCl_5^{3-}$ Anion	
26	0.23	−0.65
a	1.05	−0.79 (axial) −0.82 (equatorial)

[a] Results obtained by this author.

For direct comparison it would be of interest to have results for the two anions obtained using identical approximations. To this end, extended Hückel calculations were performed on the two anions. The Hamiltonian matrix was set up initially by assuming the diagonal elements, H_{ii}, are equal to the negative of the valence orbital ionization potential (VOIP). The Wolfsberg–Helmholtz approximation was used to set up the offdiagonal elements, H_{ij} (using an arithmetic mean). The calculations were repeated to a self-consistent charge and configuration by assuming the values of H_{ii} varied linearly with charge. While the variation of VOIP with charge is best described by a quadratic equation,[27] it is linear to a good approximation for this charge range. The charges were calculated using a Mulliken population analysis, and the final values are shown in Table IX.

For the tetrachlorocuprate anion, the calculation of Lohr and Lipscomb[6a] approaches the experimentally derived results well. This vindicates the conclusions drawn by Cotton in his critical discussion[6d] of the various approximations used in semiempirical molecular orbital calculations. The results reported in this present paper yield a value for the charge separation which is too high, a feature commonly observed in extended Hückel calculations. However, the comparison with the pentachlorocuprate anion is interesting. Since the average charge upon chlorine must be more negative in the pentachlorocuprate anion, the charge calculated upon copper is rather less positive. Furthermore, the charge upon an equatorial chlorine is more negative than upon an axial chlorine; the equatorial bond order is calculated to be higher than the axial bond order, even though the bond lengths were set equal in the calculation (with D_{3h} symmetry for the anion).

Discussion of the Results for Cesium Tetrachlorocuprate

The most satisfying aspect of this paper is its self-consistency. The force constant and charge distribution derived from the structural results agree well with those derived by other means. The two force constants are only equivalent when the simple harmonic oscillator is a good model for the extension and compression of a bond. The crystal only exerts a compressive force, and, if large distortions were observed, then the "static" force constant would be larger than the "dynamic" force constant. The distortion of the anion in the crystal will result in destabilization; this should be included in calculations of lattice energy and is 0.8 kcal/mol. The lattice energy of cesium tetrachlorocuprate has been calculated as a function of charge without this small correction.[28] At the charge distribution indicated by the structural results, the lattice energy is 336.0 kcal/mol after including this correction and the experimental value is 333 (2), which is in excellent agreement. This is further confirmation of the derived charge distribution and shows that the assumption of a +1.0 charge upon cesium is valid. The goodness of fit (as indicated by S in Table VII) is the same when all three charges are multiplied by a common factor. The choice for cesium was made from chemical sense and is vindicated by the agreement in force constants and lattice energy.

One clear result is the bond length in an isolated tetrachlorocuprate anion. As Table VII shows, the calculated value does not vary greatly with the assumption made, and the indicated value is 2.270 Å. No thermal motion correction has been made. The thermal motion correction calculated using the riding model is similar for the three independent bonds in the compound and the average is 0.013 Å, making the best estimate of the bond length to be 2.283 Å. This is significantly longer than the mean of the observed bond lengths corrected for thermal motion. The estimated standard deviation quoted in most crystallographic papers is a parameter of definite significance but which actually applies to a parameter not necessarily of interest. As this paper shows, correction for crystal force effects can be at least as important as thermal motion corrections. When bonds chemically equivalent in solution are found to differ in the solid state by more than the esd, it has been fashionable to suspect the esd is too low; in fact, when diffraction data are correctly measured and processed, the esd is correct and it is the parameter which is not what we expect. Figure 2 expresses this clearly, because the line of best fit passes within 1 esd of each observed parameter, but the observed parameters differ from each other by several esd's.

Calculations upon the Pentachlorocuprate Anion

While potentially most interesting, the calculations for the pentachlorocuprate anion are necessarily less definitive because of the lack of information.

(i) **Vibrational Analysis.** Even the most recent report[29] of the infrared and Raman spectra of salts of this anion is not sufficiently complete for a normal coordinate analysis. From the position of the $A_1(\nu)$

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(26) W. E. Hatfield, H. D. Bedon, and S. M. Horner, *Inorg. Chem.*, 4, 1181 (1965).

(27) H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, 3, 458 (1965).

(28) A. B. Blake and F. A. Cotton, *Inorg. Chem.*, 2, 906 (1963).

(29) T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernal, *ibid.*, 9, 459 (1970).

band of the anion (260 cm^{-1}), the stretching force constant for the copper–chlorine bond is 0.91 mdyn/Å. As expected, this is lower than that in the tetrachlorocuprate anion. In principle there should be two stretching force constants for the pentachlorocuprate anion, but they would not be very greatly different and from the present information no more precise estimate is possible.

(ii) Electrostatic Forces Acting within the Anion. One important factor affecting the relative lengths of axial and equatorial bonds in a trigonal-bipyramidal array is the interplay of electrostatic forces within the anion. If we consider an idealized array of symmetry D_{3h} with all bonds of length equal to 2.4 Å, then for a species of charge distribution $[M^{0.6}(X^{-0.72})_5]^{3-}$ there will be a force applied to the axial ligands (in the metal–ligand bond direction) more negative by 0.0054 mdyn than that applied to the equatorial ligands. For a stretching force constant of 0.9 mdyn/Å, this would lead to a lengthening of an axial bond of 0.006 Å relative to an equatorial bond. However, this simple model may not be applicable to the pentachlorocuprate anion because semiempirical molecular orbital calculations indicate that there may be a more negative charge upon the equatorial chlorine atoms than upon the axial chlorine atoms. For the same geometrical array but of charge distribution $[M^{0.6}(X_{eq}^{-0.732})_3(X_{ax}^{-0.702})_2]^{3-}$, the situation is qualitatively reversed; it is the equatorial bond which should be the longer by 0.002 Å, relative to the axial bond (purely from electrostatic considerations). Since the actual charge distribution in the pentachlorocuprate anion is not known, it is uncertain whether the axial or the equatorial bond should be the longer from electrostatic considerations alone, but in any case the effect is small.

(iii) Observed Structure and the Calculation of Crystal Forces. The structures of the hexaamminechromium(III)[8] and hexaamminecobalt(III)[30] salts of the pentachlorocuprate anion have been determined accurately. The two salts are very closely isostructural and the observed copper–chlorine bond lengths are 2.296 (axial) and 2.392 Å (equatorial). The anion has crystallographically imposed D_{3h} symmetry in the crystal lattice, and there is only one independent estimate of each bond length. Consequently there is no way to derive force constants or to judge charge distributions from the anion distortions. The range of charges assumed for copper and chlorine was chosen by consideration of the values derived for the tetrachlorocuprate anion and using the molecular orbital calculation results. The charge distribution within the two cations is likely to be similar (this is indicated by semiempirical molecular orbital calculations)[31] and Table X shows the results of an electrostatic force calculation using the values 1.02 (Cr), 0.30 (N), and 0.01 (H).[32] These values are close to those estimated from X-ray scattering curves.[8] Other cation charge distributions have been used and similar results obtained. The short-range repulsive effects were also calculated, but these are not significantly different for the two types of bond.

Table X. Electrostatic Forces[a] Applied to Anion in $[Cr(NH_3)_6][CuCl_5]$

Charges			Force on Cl(eq)		Force on Cl(ax)	
Cu	Cl(eq)	Cl(ax)	Crystal	Internal	Crystal	Internal
0.75	−0.75	−0.75	0.035	−0.301	0.177	−0.307
0.50	−0.70	−0.70	0.035	−0.263	0.154	−0.267
0.65	−0.75	−0.70	0.037	−0.290	0.156	−0.283
0.40	−0.70	−0.65	0.035	−0.252	0.106	−0.245
0.60	−0.70	−0.75	0.033	−0.273	0.176	−0.291

[a] All forces in millidynes.

(iv) Discussion of the Results. Examination of Table X reveals that the crystal force has a much greater compressive effect upon the axial bond than upon the equatorial bond. The charge upon copper is likely to be about 0.6 and thus the force difference is about 0.09 mdyn. Using a force constant of 0.9 mdyn/Å, this means that the axial bond should be about 0.1 Å shorter than the equatorial bond purely from crystal force effects. In conclusion, some doubt must be placed upon the use of these structural results to deduce that the axial bond is significantly shorter than the equatorial bond because, when corrected for electrostatic crystal force effects calculated as above, both bond lengths are approximately 2.42 Å. The molecular orbital calculations indicate that the equatorial copper–chlorine bond order is slightly less than the axial bond order, but this apparently does not have a major effect upon the bond lengths.

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(30) I. Bernal, N. Elliot, R. A. Lalancette, and T. Brennan, *Progr. Coord. Chem.*, 518 (1968).

(31) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 3, 1004 (1964).

(32) These values were indicated as the best fit from a crystal force calculation performed using the known structural parameters of $[Co(NH_3)_6][ZnCl_4][Cl]$. The large distortions within the tetrachlorozincate anion were accounted for: J. A. McGinnety, to be submitted for publication.