

of 38.1^{17} and 48.1^{18} which constrain the Fe atom into the trigonal bipyramid coordination. In the ferretane ring the internal Fe ring angle is $68.9(2)^{\circ}$ which allows the Fe to assume an octahedral coordination.

The packing of the molecules in a unit cell is illustrated in Figure 5. All the stereo illustrations were drawn by a computer using program ORTEP by Johnson.¹⁸ The molecules are held together solely by van der Waals forces. There are no intermolecular contacts less than van der Waals radii. The closest intermolecular approach is O(22) ··· O(24) at 3.20 Å. The closest C-O approach is C(21) ··· O(24) at

(18) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

3.33 Å, the closest C-C approach is C(13) ··· C(13) at 3.54 Å, and the closest intermolecular approach to the Fe atom is Fe ··· O(24) at 4.21 Å.

Registry No. Dibenzosimibullvaleneiron tetracarbonyl, 50790-65-3.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1054.

Contribution from the Sterling Chemistry Laboratory,
Yale University, New Haven, Connecticut 06520

Crystal Structure, Crystal Forces, and Charge Distribution in Salts of the Tetrachlorozincate Anion

JOHN A. MCGINNETY

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The crystal and molecular parameters of cesium tetrachlorozincate, Cs_2ZnCl_4 , have been determined 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 $a = 9.7577(15)$, $b = 12.9704(16)$, and $c = 7.4004(10)$ Å. A total of 2119 independent reflections was used in least-squares refinement of the molecular parameters, the R factor (on F) converging to 5.7%. The anion has crystallographically imposed m symmetry and the three independent zinc-chlorine bond lengths are 2.249(3), 2.259(3), and 2.252(2) Å. Analysis of the relationship between crystal force field and the observed anion bond lengths was not successful, presumably because the differences between the lengths of these bonds are so small. After correction for thermal motion, the zinc-chlorine bond length in an isolated anion was estimated to be in the range 2.28–2.31 Å. The structural parameters of hexaamminecobalt tetrachlorozincate chloride, $[\text{Co}(\text{NH}_3)_6][\text{ZnCl}_4][\text{Cl}]$, have been reported (D. W. Meek and J. A. Ibers, *Inorg. Chem.*, 9, 465 (1970)) and the tetrachlorozincate anion is significantly distorted in the crystal lattice. The major cause of the bond length distortions is anisotropy in the applied electrostatic crystal forces and the analysis indicated that the charge distribution within the anion is $[\text{Zn}^{1.04}(\text{Cl}^{-0.76})_4]^{2-}$, with a bond length in an isolated anion of 2.30 Å (after correction for thermal motion) and a stretching force constant for the zinc-chlorine bond in the anion of 1.31 mdyn/Å. This value for the stretching force constant is 14% larger than that derived by normal-coordinate analysis of the vibrational spectrum, due to a breakdown of the assumption of a linear variation of bond length with applied force. Charge distributions within complex chloro anions can also be obtained from nuclear quadrupole resonance spectra and molecular orbital calculations; comparisons among the results obtained by the three methods, where applicable, for the tetrachlorozincate, tetrachlorocuprate, pentachlorozincate, and pentachlorocuprate anions show an overall agreement in the trends, if not in the absolute magnitudes.

Introduction

The crystal and molecular structure of hexaamminecobalt tetrachlorozincate chloride, $[\text{Co}(\text{NH}_3)_6][\text{ZnCl}_4][\text{Cl}]$, has been reported¹ and the tetrachlorozincate anion is markedly distorted from its free equilibrium geometry, which is ideally tetrahedral. It has been shown that distortions of bond lengths within complex anions observed in the solid state can be rationalized in terms of applied crystal forces^{2,3} and this approach was applied to the above-mentioned distortions, which are the largest known in any structure determined to a high degree of precision.

Cesium tetrachlorozincate has been shown to be isostructural with $\beta\text{-K}_2\text{SO}_4$,⁴ but the atomic parameters have not been reported. The structural parameters were determined using X-ray diffraction data collected using a

four-circle diffractometer. It was hoped that the complex anion in this salt would be less distorted and that the crystal force analyses in the two ZnCl_4^{2-} salts could be usefully compared; unfortunately the bond lengths in the complex anion in Cs_2ZnCl_4 were so close in magnitude to each other that the crystal force analysis was not successful. However the length of the Zn-Cl bond expected in the absence of crystal forces was similar in the two compounds, providing some support for the validity of the method of crystal force analysis.

The charge distribution within the ZnCl_4^{2-} anion can be derived from the crystal force analysis and also from nuclear quadrupole resonance spectra and molecular orbital calculations. Charge distributions obtained in these ways are compared for this and other complex chloro anions.

Collection and Reduction of X-Ray Diffraction Data for Cs_2ZnCl_4

Crystal Data. Cesium tetrachlorozincate, Cs_2ZnCl_4 , mol wt 473.0, is orthorhombic with $a = 9.7577(15)$, $b = 12.9704(16)$,

(1) D. W. Meek and J. A. Ibers, *Inorg. Chem.*, 9, 465 (1970).

(2) J. A. McGinnety, *Acta Crystallogr., Sect. B*, 28, 2845 (1972).

(3) J. A. McGinnety, *J. Amer. Chem. Soc.*, 94, 8406 (1972).

(4) B. Brehler, *Z. Kristallogr., Kristallogeometrie, Kristalphys., Kristallchem.*, 109, 68 (1957).

$c = 7.4004$ (10) Å (the numbers in parentheses here and elsewhere in this paper are estimated standard deviations in units of the last digit); $U = 936.6$ Å⁻³; $Z = 4$; the conditions for reflection are $h0l$, $h = 2n$; $0kl$, $k + l = 2n$, which are consistent with space groups $Pna2_1$ and $Pnam$, the latter being adopted in agreement with earlier work⁴ (confirmatory evidence for this space group was obtained from the successful refinement of the structure). Crystals of the compound were prepared as described previously.⁴ The cell constants were determined with Mo $K\alpha_1$ radiation (λ 0.70930 Å) at a temperature of 20 (1)°, using the setting constants on a four-circle diffractometer of 12 reflections. The crystal chosen for data collection was split to length and was bounded by the forms $\{100\}$, $\{010\}$, and $\{001\}$ with distances between these pairs of faces of 0.12, 0.05, and 0.24 mm, respectively. Initially the crystal was aligned about the c axis of the cell but was misset before data collection. The intensities were measured using a Picker four-circle diffractometer with crystal-monochromated Mo $K\alpha$ 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 $\bar{h}\bar{k}l$) of the orthorhombic crystal out to a Bragg angle of 40°. Three standard reflections (230, 033, 403) were selected to represent a range of intensities and Bragg angles and different regions of reciprocal space; their intensities were measured at intervals and increased to a moderate extent (~15%) during data collection. Since the room temperature remained constant ($\pm 1^\circ$) throughout the experiment, the changes must be within the crystal and an increase in crystal mosaicity may well be a major factor. The integrated intensities of the standard reflections were in the range 10–20% of the integrated intensity of the strongest reflection and they all increased to about the same extent (within experimental error). The data were corrected for background and the changes in the standard reflections. The linear absorption coefficient is 104.3 cm⁻¹ and the data were corrected for absorption, the transmission coefficients ranging from 0.30 to 0.60.⁵ The equivalent forms, which had been collected at widely differing times, 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 6.2% for the 656 reflections classified as observed and measured more than once; this value is reasonable and lends support to the corrections made on the basis of the changing intensities of the standard reflections. 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 assigned to the reflection. A total of 5930 reflections were measured and processed. There were 3068 independent reflections and 679 of these could be classified observed using the criterion that at least one form have a net count greater than 3 times the estimated standard deviation (calculated from counting statistics) of the total background counts. In order to check the efficacy of the absorption correction program, the uncorrected data were also reduced.

Refinement of the Structure of Cs₂ZnCl₄

This compound is isostructural with Cs₂CuCl₄ and initial values for the coordinates of all the atoms were taken from that known structure.³ The scattering factors were calculated using analytical approximations for neutral atoms⁶ and the effects of anomalous dispersion⁷ were included in F_o . The function minimized in refinement was $\sum w||F_o| - |F_c||^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Refinement of the scale factor, an extinction parameter, and positional and anisotropic thermal parameters for all atoms resulted in a convergence of the R factor to 8.5% for the 679 observed reflections when the data were not corrected for absorption. Using the absorption-corrected data, three further cycles of refinement resulted in an R factor of 3.4% for the 679 observed reflections; this confirmed the value of the absorption correction. The weighted R factor, $R_w = \sum w(F_o - F_c)^2/\sum wF_o^2$, was 3.8%. Since there is no valid reason to exclude any data from the least-squares refinement (apart, possibly, from the computing time needed), two

further cycles of refinement were performed using the 2119 measured reflections with $F^2 > 0$, corrected for absorption. The final values of the R factor and weighted R factor were 5.7 and 4.1%, respectively, and the error in an observation of unit weight was 0.63. In these two final cycles, the parameters changed by up to 90% of their final estimated standard deviations; the most interesting change is that the final estimated standard deviations were about 60% of the values obtained using only the observed reflections. Thus the precision of the experiment was improved by avoiding the arbitrary exclusion of part of the data set; whether the accuracy of the experiment was similarly improved is not clear, but there is no reason to assume the contrary. The most correct procedure for a least-squares refinement, in a statistical sense, is to use all reflections (even those with negative values for F^2) in a refinement on F^2 ; model calculations⁸ emphasize this point. However, in a refinement on F , one can reject those reflections with negative F^2 (because F is imaginary) and zero F^2 (because the weight would also be zero).

The final values of the positional and thermal parameters and their standard deviations calculated from the inverse matrix are given in Table I. The root-mean-square amplitudes of vibration are given in Table II. The observed and final calculated structure factors are available.⁹

Description of the Structure for Cs₂ZnCl₄

Cesium tetrachlorozincate is isostructural with cesium tetrachlorocuprate and β -potassium sulfate, for which descriptions of the crystal structure have been published.^{2,3} Table III lists all intraanion distances and angles plus the interion contacts less than 3.60 Å along with the appropriate angle; the estimated standard deviations are calculated from the inverse matrix by a standard error propagation method.⁵ Figure 1 shows the tetrachlorozincate anions and cesium cations centered at $z = 1/4$ (half the contents of the unit cell) projected on to 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 zinc-chlorine bond axis. Thermal motion corrections for the Zn-Cl bond lengths were calculated using the riding model and the corrections (in order) were 0.013, 0.014, and 0.018 Å.

Comparisons can be made between the distortions of the complex anion observed in this crystal structure and those of the anions in the isostructural crystals β -K₂SO₄, K₂CrO₄,² and K₂MnO₄.¹⁰ Table IV lists the distortions from the ideal tetrahedral angle of the independent bond angles within the complex anions in these compounds; also listed are the symmetry bending force constants obtained by analysis of vibrational spectra¹¹ (the symmetry constants can be used in this context, rather than the internal coordinate constants, because it is simply the gross effect that is being examined and no quantitative analysis is being attempted). At least for the most distorted angles, the magnitude of the distortions within a given anion is very approximately inversely proportional to the bending force constant for that anion, showing that the distortions may well be due to a systematic crystal effect. Another noteworthy point is that the Zn-Cl(1) and Zn-Cl(2) internuclear distances are respectively the shortest and longest within the anion of Cs₂ZnCl₄; this situation is paralleled in β -K₂SO₄, K₂CrO₄, and K₂MnO₄. While Cs₂CuCl₄ is also isostructural with Cs₂ZnCl₄, comparisons of the above type cannot be made because there are electronic reasons why CuCl₄²⁻ should not be tetrahedral.

(5) Calculations were performed on an IBM 370/155 computer and the programs used included modified versions of Zalkin's FORADP, Busing, Martin, and Levy's ORFLS and ORFFE, Johnson's ORTEP, Coppens and Hamilton's DATAP, Hoffmann's ICON, and those of Schachtschneider for vibrational analysis.

(6) D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, Sect. A, **24**, 321 (1968).

(7) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(8) F. L. Hirschfeld and D. Rabinovich, *Acta Crystallogr.*, Sect. A, **29**, 510 (1973).

(9) See paragraph at end of paper regarding supplementary material.

(10) G. J. Palenik, *Inorg. Chem.*, **6**, 507 (1967).

(11) B. Krebs, A. Muller, and A. Fadini, *J. Mol. Spectrosc.*, **24**, 198 (1967).

Table I. Positional and Thermal Parameters^a of Cs₂ZnCl₄

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.23516 (7)	0.42142 (6)	0.25 ^b	0.00566 (7)	0.00332 (5)	0.01045 (15)	-0.00004 (5)	0.0 ^b	0.0 ^b
Cs(1)	0.64076 (5)	0.39875 (5)	0.25 ^b	0.00786 (5)	0.00863 (5)	0.01602 (12)	-0.00107 (4)	0.0 ^b	0.0 ^b
Cs(2)	-0.02191 (4)	0.67595 (3)	0.25 ^b	0.00635 (4)	0.00372 (3)	0.01504 (10)	0.00010 (3)	0.0 ^b	0.0 ^b
Cl(1)	0.0059 (2)	0.4030 (2)	0.25 ^b	0.0058 (2)	0.0060 (1)	0.0238 (5)	-0.0009 (1)	0.0 ^b	0.0 ^b
Cl(2)	0.3115 (2)	0.5858 (2)	0.25 ^b	0.0091 (2)	0.0038 (1)	0.0251 (5)	-0.0016 (1)	0.0 ^b	0.0 ^b
Cl(3)	0.3238 (1)	0.3459 (1)	0.0022 (2)	0.0099 (1)	0.0091 (1)	0.0138 (3)	0.0024 (1)	-0.0007 (2)	-0.0053 (2)

^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.

Table II. Root-Mean-Square Amplitudes of Vibration (Å) along Principal Axes of Cs₂ZnCl₄

Zn	0.165 (1)	0.169 (1)	0.170 (1)
Cs(1)	0.191 (1)	0.211 (1)	0.274 (1)
Cs(2)	0.174 (1)	0.179 (1)	0.204 (1)
Cl(1)	0.164 (2)	0.229 (3)	0.257 (3)
Cl(2)	0.163 (3)	0.223 (3)	0.264 (3)
Cl(3)	0.156 (2)	0.210 (2)	0.308 (2)

Table III. Selected Internuclear Distances (Å) and Angles (deg) in Cs₂ZnCl₄

(i) Within the Anion			
Zn-Cl(1)	2.249 (3)	Cl(1)-Zn-Cl(2)	115.34 (8)
Zn-Cl(2)	2.259 (3)	Cl(1)-Zn-Cl(3)	109.62 (5)
Zn-Cl(3)	2.252 (2)	Cl(2)-Zn-Cl(3)	106.52 (5)
Cl(1)-Cl(2)	3.809 (3)	Cl(3)-Zn-Cl(3)	109.03 (8)
Cl(1)-Cl(3)	3.679 (2)		
Cl(2)-Cl(3)	3.615 (3)		
Cl(3)-Cl(3)	3.667 (3)		
(ii) Shortest Contacts between Ions			
Cl(1)-Cs(2)	3.550 (2)	Zn-Cl(1)-Cs(2)	88.30 (6)
Cl(1)-Cs(1)	3.563 (2)	Zn-Cl(1)-Cs(1)	174.81 (9)
Cl(2)-Cs(2)	3.456 (2)	Zn-Cl(2)-Cs(2)	90.51 (6)
Cl(2)-Cs(1)	3.491 (2)	Zn-Cl(2)-Cs(1)	171.58 (8)
Cl(3)-Cs(2)	3.475 (2)	Zn-Cl(3)-Cs(2)	157.97 (6)
Cl(3)-Cs(1)	3.498 (2)	Zn-Cl(3)-Cs(1)	98.41 (5)

Table IV. Angular Distortions^a (deg) Observed within the Complex Anions in Isostructural Compounds of General Formula A₂BX₄^b

	K ₂ SO ₄	K ₂ CrO ₄	K ₂ MnO ₄	Cs ₂ ZnCl ₄
δ [X(1)-B-X(2)]	0.5	0.7	1.3	5.9
δ [X(1)-B-X(3)]	0.1	0.4	0.6	0.2
δ [X(2)-B-X(3)]	-0.4	-0.8	-1.2	-3.0
δ [X(3)-B-X(3)]	0.1	0.1	-0.4	-0.4
X-B-X symmetry bending force const, mdyn/Å	0.64	0.41	0.34	0.16

^a The angular distortion, δ [X-B-X], is defined as the observed angle minus the ideal tetrahedral angle, 109.5°. ^b Atom nomenclature is consistent with that in the present paper.

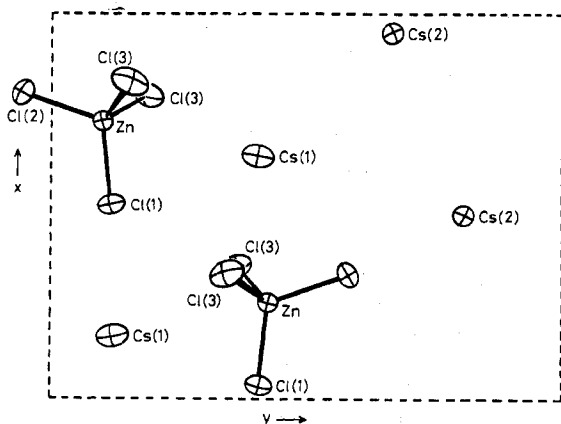


Figure 1. Cs₂ZnCl₄: contents of the half of the unit cell centered at $Z = 1/4$. Broken line shows the unit cell outline. The atoms are represented by 50% probability ellipsoids.⁵

The maximum difference between the observed bond lengths is only 0.011 (5) Å, which is too small and is of insufficient statistical significance for the results of a crystal force analysis to be quantitatively meaningful. Qualitatively, the situation seems normal: the anion appears to suffer a slight compression in the crystal lattice and the major anisotropy in the applied crystal field is due to the sum of the electrostatic contributions (these two observations hold true over a wide range of the parameters assumed in the calculation). A rough estimate of the Zn-Cl bond length expected in the absence of crystal forces can be made. The mean of the observed Zn-Cl bond lengths is 2.269 Å (after correction for thermal motion) and the crystal force field typically results in an average shortening of the observed bond lengths in a complex anion of between 0.01 and 0.04 Å;¹² thus the free anion bond length should be in the range 2.28-2.31 Å.

Analysis of the Vibrational Spectra of Salts of the ZnCl₄²⁻ Anion

The vibrational spectra of several salts of the tetrachlorozincate anion have been reported.¹³ Average values for the four frequencies expected for a tetrahedral species are 285 (ν_1), 114 (ν_2), 295 (ν_3), and 135 (ν_4) cm⁻¹. A normal-coordinate analysis was performed using three valence force constants, one stretching, one bending, and one stretch-stretch interaction constant. A least-squares fit led to final values for the force constants of 1.15, 0.53, and 0.18 mdyn/Å with an average deviation of 3.5 cm⁻¹ between observed and calculated frequencies. Another normal-coordinate analysis has been reported, using somewhat imprecise frequencies;¹⁴ the derived value for the stretching force constant was identical.

Tentative correlations have been made between the static distortion of anions such as ZnCl₄²⁻ and CuCl₄²⁻ in a crystal lattice and the magnitude of the splitting observed for the ν_3 mode.^{13h} This correlation was based in part upon an inaccurate value for the static distortion in Cs₂CuCl₄. It seems likely that the splittings are in fact due to a more complete breakdown of the isolated anion approximation.

Calculations upon Hexaamminecobalt(III) Tetrachlorozincate(II) Chloride

This compound provides an excellent test of the validity of the crystal force calculation because the structure has been determined very precisely¹ and the tetrachlorozincate anion is grossly distorted from the ideal tetrahedral geometry.

- (12) J. A. McGinety, *Acta Crystallogr., Sect. A*, **28**, S53 (1972).
 (13) (a) R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1198 (1963); (b) A. Sabatini and L. Sacconi, *J. Amer. Chem. Soc.*, **86**, 17 (1964); (c) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **5**, 2232 (1965); (d) J. S. Avery, C. D. Burbridge, and D. M. L. Goodgame, *Spectrochim. Acta, Part A*, **24**, 1721 (1968); (e) M. L. Good, C.-C. Chang, D. W. Wertz, and J. R. Durig, *ibid.*, 1303 (1969); (f) I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc. A*, 534 (1969); (g) T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernal, *Inorg. Chem.*, **9**, 459 (1970); (h) J. T. R. Dunsmuir and A. P. Lane, *J. Chem. Soc. A*, 404, 2781 (1971).
 (14) A. Muller and B. Krebs, *J. Mol. Spectrosc.*, **24**, 180 (1967).

Table V. Analysis of the Electrostatic Crystal Forces Applied to the Tetrachlorozincate Anion in $[\text{Co}(\text{NH}_3)_6][\text{ZnCl}_4][\text{Cl}]$

Charge ^a upon Cl ligand in $[\text{ZnCl}_4]^{2-}$	Charge ^a upon N in $[\text{Co}(\text{NH}_3)_6]^{3+}$	Charge ^a upon H in $[\text{Co}(\text{NH}_3)_6]^{3+}$	Electrostatic crystal forces ^b applied to anion bonds, mdyN			Sum of squares ^{c,d}	Str force const for Zn-Cl bond, mdyN/Å	Bond length in isolated ZnCl_4^{2-} anion, ^d Å
			Zn-Cl(1)	Zn-Cl(2)	Zn-Cl(3)			
0.85-	0.30+	0.00	-0.180	0.174	0.051	0.1376	1.58	2.294
0.80-	0.30+	0.00	-0.152	0.158	0.042	0.0247	1.43	2.296
0.75-	0.30+	0.00	-0.126	0.142	0.036	0.0005	1.31	2.296
0.70-	0.30+	0.00	-0.100	0.125	0.029	0.0359	1.15	2.299
0.65-	0.30+	0.00	-0.074	0.108	0.025	0.1171	1.00	2.301
0.75-	0.30+	0.02+	-0.123	0.139	0.038	0.0037	1.27	2.297
0.75-	0.30+	0.04+	-0.120	0.137	0.039	0.0108	1.23	2.298
0.75-	0.20+	0.00	-0.131	0.147	0.037	0.0087	1.38	2.297
0.75-	0.40+	0.00	-0.122	0.138	0.036	0.0352	1.24	2.299

^a The total charges associated with the cation, chloride, and tetrachlorozincate anions are always assumed to be 3+, 1-, and 2-, respectively. ^b As defined,² a positive force is bond compressive and a negative force is bond extensive. ^c Defined previously.³ A minimum indicates that the choice of charge parameters may be reasonable. The numbers in this column have been multiplied by 10^4 . ^d Calculated using the total applied force, *i.e.*, crystal (given in this table) plus internal (*i.e.*, intraanion electrostatic forces, which are easily calculable).

The three independent zinc-chlorine bond lengths within the anion are 2.358 (2), 2.269 (1), and 2.223 (2) Å; the differences between these bond lengths are highly significant and no satisfactory explanation of these differences was made in the original structure report. The four potentially most important types of crystal force in this compound are electrostatic, polarization, short-range repulsive, and hydrogen bonding.

The electrostatic crystal forces were calculated as described before by assuming various charges for the chemical species in the lattice. The cation, chloride, and tetrachlorozincate anions were assumed to have total charges of 3+, 1-, and 2-, respectively. The charge ranges used for hydrogen, nitrogen, and the chlorine atoms of the tetrachlorozincate anion were 0.00-0.04+, 0.20-0.40+, and 0.50-1.00-, respectively. Table V shows the results of some of these calculations (the terms used as column headings are as defined before³). One obvious feature of these results is that there is a large negative crystal force acting upon Cl(1) and a large positive force acting upon Cl(3) for all of these values of the assumed charges. Since the longest zinc-chlorine bond has a bond-extensive force acting upon it and the shortest zinc-chlorine bond has a bond-compressive force acting upon it, then it is clear that the electrostatic crystal forces do indeed make a major contribution toward the observed anion distortion.

The polarization¹⁵ and short-range repulsion³ forces were calculated using a reasonable range of the necessary parameters (including only nearest neighbours), and their net contribution to the total crystal field applied to any one chlorine ligand was small; furthermore they affected each of the chlorine ligands to about the same extent (within 0.005 mdyN). The possibility that hydrogen bonding is a major cause of the anion distortions was discussed fully in the original structure report and it was concluded that the differences in bond lengths within the tetrachlorozincate anion were not due to hydrogen bonding. The above-mentioned polarization force calculation may possibly be an order-of-magnitude parameterization of the effect of hydrogen bonding when the interactions between the hydrogen atoms of the cation and the chlorine ligands of the anion are considered; examination of these terms provides some support for the conclusion that hydrogen bonding does not distort the anion bond lengths significantly. Thus it seems that the observed anion distortion is almost completely due to anisotropy of the applied electrostatic

crystal force field and the other types of forces will not be discussed further.

The goodness of fit between observed bond lengths and total electrostatic force was used as the criterion to determine a realistic charge distribution. The goodness of fit varies greatly with the charge distribution within the tetrachlorozincate anion and is best with the distribution $[\text{Zn}^{1.0+}\text{Cl}_4^{0.75-}]^{2-}$; when the charge upon chlorine is changed by $0.05\pm$, the fit is significantly worse. The goodness of fit is less sensitive toward the charge distribution within the anion and the indicated distribution is $[\text{Co}^{1.2+}(\text{N}^{0.3+}\text{H}_3^{0.0})_6]^{3+}$. The results obtained using this charge distribution are expressed graphically in Figure 2; the stretching force constant for the Zn-Cl bond is 1.31 mdyN/Å and the bond length in the absence of crystal forces is 2.296 Å (indicated by the horizontal arrow in Figure 2). This bond length can be corrected for thermal motion using the riding model and the best estimate of the Zn-Cl bond length is 2.30 Å using the structural data from this crystal. This falls in the range estimated from the structural parameters of Cs_2ZnCl_4 , which might seem trivial, except for the fact that none of the bond lengths observed in this compound fall in this range.

The tetrachlorozincate anion is so distorted in the crystal lattice of $[\text{Co}(\text{NH}_3)_6][\text{ZnCl}_4][\text{Cl}]$ that it is pertinent to question whether the assumption of a linear variation of bond length with applied force is appropriate. The Morse equation can be set in a convenient form by expansion of the exponential terms giving

$$f = -k(d - d_1) + k'(d - d_1)^2 - \dots \quad (1)$$

where f is applied force, d is the observed bond length, d_1 is the bond length in the absence of applied force, and k and k' are constants (k' being equal to k multiplied by a factor of between 0.5 and 5.5 \AA^{-1}). The assumption of a linear variation of bond length with applied force is equivalent to including only the first term on the right-hand side of this equation; this assumption is widely used in the analysis of vibrational spectra and k is the stretching force constant for the bond. For distortions of 0.02 Å, the magnitude of the second term is only about 3% of that of the first (higher terms are even smaller) and therefore the second and higher terms can be omitted without serious error. However, for distortions of 0.1 Å, the second term is about 15% of the first and thus the errors could be appreciable if the second term is omitted. The value derived above from the structural data for the stretching force constant of the bond is 1.31 mdyN/Å, considerably larger than the value of 1.15 mdyN/Å, obtained by analysis of

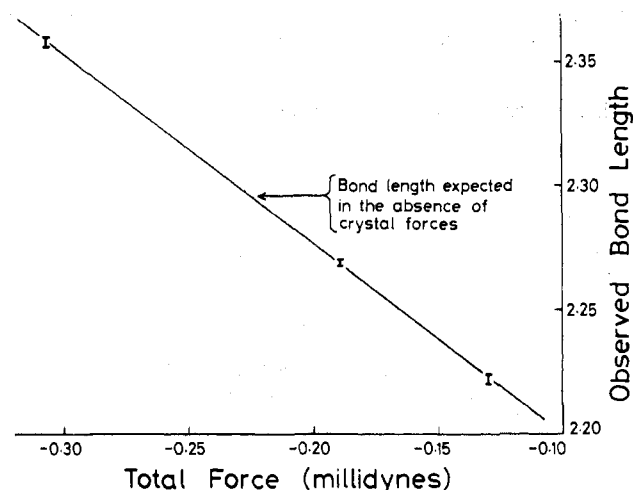


Figure 2. $[\text{Co}(\text{NH}_3)_6][\text{ZnCl}_4][\text{Cl}]$: the variation (assumed linear) of the observed zinc-chlorine bond lengths with total electrostatic crystal force, *i.e.*, the sum of the crystal force given in Table V and internal force. The point charges used to calculate the electrostatic forces are 1.2+ (Co), 0.3+ (N), 0.0 (H), 1.0+ (Zn), 0.75- (Cl ligand in ZnCl_4^{2-}), and 1.0- (Cl^- anion). The vertical error bars represent 1 esd in the observed bond lengths.

the vibrational spectrum. Unfortunately eq 1 cannot be used to relate the observed bond lengths and the calculated applied forces unless the value of k is taken from the vibrational analysis; by setting $k = 1.15 \text{ m dyn}/\text{\AA}$, the derived values for d_1 and k' are 2.294 Å and 1.43 $\text{m dyn}/\text{\AA}^2$. The value derived for the stretching force constant from structural data should be regarded as an upper limit if a linear variation of bond length with applied force is assumed and it will only be a reasonable approximation if the bond length distortions are small.

A further calculation was performed with artificial coordinates for Cl(1), all other coordinates being correct. The changes were such that the Zn-Cl(1) bond direction was maintained but the bond length was reduced to 2.296 Å. The calculated electrostatic crystal force applied to Cl(1) was somewhat more bond extensive than that calculated using correct coordinates. In the formation of a crystal, there has to be some means to relax the local potential energy gradients and bond extension or contraction is one way to do this; such changes require energy, resulting in a decrease in the stability of the crystal (about 2 kcal/mol in this case).

There are also statistically significant differences between the Co-N bond lengths observed in the cation. The interplay of forces within the cation is more complicated than within the anion due to the presence of hydrogen atoms, the positions of which are not known accurately. A successful analysis of the relationship between the observed structure of the cation and the crystal forces was not possible.

Charge Distribution within the Anions MCl_4^{2-} and MCl_5^{3-} ($\text{M} = \text{Zn, Cu}$)

Three methods of obtaining a value for the charge distribution will be discussed: nuclear quadrupole resonance spectra, semiempirical molecular orbital calculations, and the structural analysis method applied in the previous section of this paper. The results of the three methods are shown in Table VI and each gives different magnitudes for the charges; this is not surprising in view of the different approximations in each method. However there is agreement in the relative ordering of the charge distributions for the zinc and copper anions and in the conclusion that

Table VI. Estimates of the Charge Distribution in Complex Chloroanions

Anion	Charge upon chlorine ligand		
	Structural analysis	Molecular orbital calcn	Analysis of nqr spectrum
ZnCl_4^{2-}	0.75 ^{-a}	0.81-	0.78-
CuCl_4^{2-}	0.65 ^{-b}	0.77-	0.74-
ZnCl_5^{3-}		0.82-, ^c 0.80 ^{-d}	
CuCl_5^{3-}		0.79-, ^c 0.81 ^{-d}	0.75-, ^c 0.77 ^{-d}

^a Using the structural parameters of $[\text{Co}(\text{NH}_3)_6][\text{ZnCl}_4][\text{Cl}]$.
^b Using the structural parameters of Cs_2ZnCl_4 .
^c Axial chlorine ligand (of a trigonal-bipyramidal array).
^d Equatorial chlorine ligand (of a trigonal-bipyramidal array).

there is a moderate positive charge upon the central metal.

The ^{35}Cl nqr spectra of salts of the anions ZnCl_4^{2-} , CuCl_4^{2-} , and CuCl_5^{3-} have been measured.¹⁶ The reported frequencies for ZnCl_4^{2-} , CuCl_4^{2-} , and CuCl_5^{3-} are 8.9 (mean of three peaks in Cs_2ZnCl_4), 10.6 (mean of three peaks in Cs_2CuCl_4), and 9.6 and 10.4 (equatorial and axial peaks, respectively, in $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$) MHz. The simplest treatment¹⁷ ignores the crystal field gradient (among other approximations) and the derived charges are shown in Table VI. The crystal field gradients have been calculated; there was not a linear correlation between the structure of the spectra and the field gradient for the crystallographically independent ligands. Comparisons between the average frequencies are probably qualitatively correct because the crystal field gradients were of the same sign and order of magnitude.

The semiempirical molecular orbital calculations (of the extended Huckel type) were all made using similar approximations. The initial values for H_{ii} were set equal to the negative of the ionization potential for that orbital and $\partial H_{ii}/\partial q$ was taken as a 2 eV/ electron charge unit.¹⁸ The charges, q , were calculated using a Mulliken population analysis. The result of a calculation upon ZnCl_5^{3-} is included in Table VI for comparison; a trigonal-bipyramidal structure was assumed for this anion.

The overall tendencies shown in Table VI are consistent. The magnitude of the charge upon the chlorine ligand in ZnCl_4^{2-} is greater than that in CuCl_4^{2-} (which is to be expected on the basis of the greater electronegativity of copper, relative to zinc). Also the magnitude of the charge upon an equatorial chlorine ligand in CuCl_5^{3-} is greater than that upon the axial ligands. Interestingly the molecular orbital calculations indicate the converse may be true for ZnCl_5^{3-} , an anion which has not been isolated.

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Registry No. Cs_2ZnCl_4 , 13820-35-4; $[\text{Co}(\text{NH}_3)_6][\text{ZnCl}_4][\text{Cl}]$, 25969-32-8; ZnCl_4^{2-} , 15201-05-5; CuCl_4^{2-} , 15489-36-8; ZnCl_5^{3-} , 51018-44-1; CuCl_5^{3-} , 44237-10-7.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1057.

(16) (a) D. E. Scaife, *Aust. J. Chem.*, **24**, 1315 (1971); (b) *ibid.*, **24**, 1993 (1971).

(17) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

(18) F. A. Cotton, *Rev. Pure Appl. Chem.*, **16**, 175 (1966).