Discussion

As can be seen in Figure 1, the structure consists of layers of $Sb_2F_7^-$ dimers separated by layers of Cs^+ ions. Also shown is the structure as proposed by Byström and Wilhelmi. Comparison of the two structures shows the metric relationships between the heavy atoms to be approximately the same, but the fluorine positions are grossly different. Table II shows the distances for cesium coordination.

TABLE II

DISTANCES FOR THE CESIUM COORDINATION (Å)[a]

Cs–F(2)	3.153	Cs–F′(4)	3.208
Cs–F′(2)	3.247	Cs–F″(4)	3.161
Cs–F(4)	3.195		

[a] Least-squares errors are 0.002 Å.

Figure 2 shows the distances and angles in the $Sb_2F_7^-$ ion. The idealized geometry of the ion can be described as two trigonal bipyramids joined by an axial corner. The lone pairs of electrons are apparently contained in the equatorial plane. The closest nonbonded Sb–F distance is 2.77 Å.

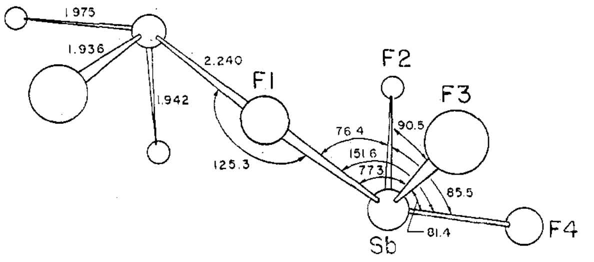

Figure 2.—Distances and angles in the $Sb_2F_7^-$ ion.

The F_{ax}–Sb–F_{ax} angle of 151.6° and the F_{eq}–Sb–F_{eq} angle of 90.5° are both drastically distorted from the values for an ideal trigonal bipyramid in such a way as to minimize lone-pair–bond repulsions, Sb–F_{ax} is significantly longer than the average Sb–F_{eq} distance, and the overall conformation of the ion minimizes lone-pair–lone-pair repulsions. All of these observations are in accord with the electron-pair repulsion theory of Gillespie and Nyholm,[18,19] and indeed these features of the geometry have been predicted by others in various attempts to reinterpret the results by Byström and Wilhelmi. The bridging fluorine on the crystallographic twofold axis has an included angle of 125.3° between the antimony atoms at 2.240 Å. The lack of an obvious stereochemical reason for the bent fluorine bridge supports the thesis that these bridges tend to be bent in the absence of π bonding.[20] The nonlinear angle about the fluorine can be rationalized either in the MO scheme in terms of a three-center two-electron bond in which the fluorine orbitals involved are primarily p orbitals or in the valence-bond scheme in terms of the resonance structures $[F_3Sb{:}F]^-SbF_3 \rightleftarrows F_3Sb[F{:}SbF_3]^-$ again in which p orbitals on the fluorines are the chief participants.

Acknowledgments.—Acknowledgment is due Dr. D. T. Cromer for his assistance with the data collection process.

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CONTRIBUTION FROM THE ANORGANISCH-CHEMISCHES INSTITUT
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The Crystal Structure of Tellurium Tetrachloride

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The crystal structure of tellurium tetrachloride has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group $C2/c$ of the monoclinic system with a = 17.076, b = 10.404, c = 15.252 Å, β = 116.82°. The unit cell contains 16 formula units of $TeCl_4$. Calculated and observed densities are 2.959 and 2.96 g/cm^3, respectively. The data have been collected for a twinned crystal and have been reduced according to the kind of twinning. The structure has been refined by least-squares methods to a final R factor of 0.061 for 2948 nonequivalent reflections. The structure consists of isolated tetramers, Te_4Cl_{16}, which have a cubane-like structure with approximate T_d symmetry and with Te and Cl atoms occupying alternating corners of the cubane skeleton. Every Te atom has three neighboring terminal Cl atoms with an average distance of 2.311 Å. With these it is forming an equilateral trigonal pyramid. The coordination of the Te is completed to a distorted octahedron by three bridging chlorine atoms with much longer Te–Cl bond lengths (average 2.929 Å). In the polar limiting case the structure may be described, in a rough approximation, as an arrangement of $TeCl_3^+$ ions with nearly C_{3v} symmetry and of Cl^- ions. The structure data suggest possible concentration of the nonbonding Te electrons toward the center of the cubane skeleton. From the unexpected crystal structure some unexplained properties of solid tellurium(IV) chloride (correctly formulated tetra-μ_3-chloro-tetrakis[trichlorotellurium(IV)]) can be understood.

Introduction

In the last few years a large number of papers on possible structures of the solid selenium and tellurium tetrachlorides and -bromides have been published, but in the absence of direct X-ray structure determinations it was impossible to give an unequivocal interpretation of the partly controversial results.

According to an early electron diffraction investigation[1] tellurium tetrachloride is monomeric in the vapor

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(1) D. P. Stevenson and V. Schomaker, *J. Amer. Chem. Soc.*, **62**, 1267 (1940).

state with C_{2v} symmetry of the molecule. The molecule can be described as a trigonal bipyramid with the lone pair located at one of the equatorial positions.

This structure which is also known to be present in gaseous SF_4 and SeF_4 agrees with predictions based on valence-shell electron pair repulsion considerations.[2] All available results show that in solid $TeCl_4$ the stereochemical influence of the inert electron pair is evidently more complex.

The dipole moment of the tetrachloride in benzene solution,[3] its solubility in nonpolar solvents,[4] the nuclear quadrupole resonance spectrum,[5] and Raman together with infrared spectra[6,7] have been put forward as proof in favor of an essentially C_{2v} molecular structure in the solid state.

On the other hand molten tellurium tetrachloride conducts electricity.[8] Most of the authors[9-14] reporting Raman and far-infrared spectra interpret their results on molten, solid, and dissolved $TeCl_4$ as being consistent with an ionic formulation $TeCl_3^+Cl^-$, where the cation has a pyramidal (C_{3v}) structure. A strong argument in support of this was the remarkable similarity of the vibrational frequencies for the $TeCl_3$ ion with those for the isoelectronic antimony trichloride, which has been shown[15] by structural analysis to form a trigonal pyramid with C_{3v} symmetry. Additional evidence for different structure models has been derived from studies of $TeCl_4$ solutions in polar and nonpolar solvents[16-20] or from bonding considerations on the methyltellurium chlorides.[21]

Attempts have already been made to determine the crystal structures of the tetrachloride and the tetrabromide[22-24] as well as that of the tetraiodide[25] by single-crystal X-ray methods. The lattice parameters and space groups have been reported, but because of crystal twinning and problems of strong pseudosymmetry it was impossible to solve the complete structures and to distinguish between the proposed more ionic (C_{3v}) and more covalent (C_{2v}) structural models.

The structure of tellurium tetrafluoride has been reported recently.[26] In it each tellurium atom is surrounded by three terminal and two bridging fluorine atoms arranged at the apices of a distorted square pyramid. The cis-bridging fluorine atoms link these units into endless chains.

In order to get a quantitative structural basis for the discussion of the previous conflicting results on $TeCl_4$ (and also on $SeCl_4$ and $TeBr_4$) we started an X-ray structure analysis on tellurium tetrachloride. As part of our structural investigations on the stereochemical influence of the nonbonding electron pairs in S(IV), Se(IV), and Te(IV) compounds, the results are reported here.[27]

Measurement and Reduction of the X-Ray Data

$TeCl_4$ was prepared by direct reaction of the elements.[28] It was purified by vacuum sublimation and was recrystallized from benzene. The composition was checked by chemical analysis. Because $TeCl_4$ is very sensitive to hydrolysis, all operations had to be done with careful exclusion of moisture The needle-shaped (elongated along c) colorless, transparent crystals were sealed in Lindemann capillaries to prevent hydrolysis.

Despite a long search it was impossible to find any suitable single crystals. The crystals are invariably twinned on (100) (see below). This is in accordance with the results reported by previous authors.[22-24] After a preliminary survey had shown that the intensities could be evaluated quantitatively in spite of the twinning, it was decided to use a twinned crystal for data collection.

Weissenberg and precession photographs indicated Laue symmetry $2/m$. Taking into account the principle of twinning the systematic absences were found to be hkl with $h + k = 2n + 1$ and $h0l$ with $l = 2n + 1$. This is consistent with the centrosymmetric space group $C2/c$-C_{2h}^6 (no. 15) and the corresponding noncentrosymmetric one Cc-C_s^4 (no. 9). $C2/c$ being the correct choice was initially suggested by intensity statistics and confirmed later in the course of the structure determination. The monoclinic unit cell has the following parameters (at 20°, obtained by least-squares refinement of diffractometer settings for 20 reflections; errors given are 3σ): $a = 17.076$ (8), $b = 10.404$ (5), $c = 15.252$ (8) Å, $\beta = 116.82$ (5)°. Space group and cell dimensions are in good accord with those reported earlier.[22-24]

The density was determined pycnometrically (cyclohexane) to be $d_m = 2.96 \pm 0.02$ g/cm³. Previous literature values are around 3.01 g/cm³.[23,29] With 16 $TeCl_4$ formula units in the cell the calculated density is $d_x = 2.959$ g/cm³. The twinned crystal used for the quantitative measurements had the dimensions 0.14 × 0.20 × 0.36 mm. Intensity data were collected on a computer-controlled Hilger-Watts four-circle diffractometer (Mo K radiation, $\lambda(K\alpha_1)$ 0.70926 Å, Zr filter, ω–2θ scan method, scintillation counter, pulse height discrimination). The receiving aperture was 3.5 mm in diameter. The ω and 2θ circles were scanned for 240 sec in steps of 0.02° over 0.96° in θ, with a take-off angle of 3.5°. Individual background counts (24 sec each) were taken at each end of the scan. A standard reflection was measured every 30 reflections to ensure stability of operation. The source to crystal and crystal to counter distances were 21 cm and 30 cm, respectively. The mosaic spread of the peaks was within normal limits, as indicated by a narrow-source, open-counter peak width of $\theta = 0.07$–$0.09°$ for an average reflection.

A complete set of unique data within the sphere $(\sin\theta)/\lambda < 0.66$ Å^{-1} was recorded for both parts of the twin, yielding a total of 2948 nonequivalent reflection intensities reduced to one individuum. The linear absorption coefficient for Mo $K\alpha$ radiation

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TABLE I

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS ($\times 10^5$ EXCEPT B) FOR Te_4Cl_{16} WITH ESTIMATED STANDARD DEVIATIONS[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B, Å^2
Te(1)	35,786 (3)	52,737 (5)	18,100 (4)	258 (2)	744 (5)	406 (3)	54 (2)	131 (2)	35 (3)	2.92 (2)
Te(2)	49,736 (3)	23,303 (5)	10,886 (4)	269 (2)	675 (5)	359 (3)	6 (2)	131 (2)	−22 (3)	2.73 (2)
Cl(1)	25,487 (17)	52,549 (30)	1,738 (20)	371 (11)	1477 (34)	517 (14)	58 (14)	97 (10)	81 (17)	4.79 (8)
Cl(2)	25,735 (17)	51,449 (28)	24,339 (22)	376 (10)	1428 (32)	689 (17)	116 (15)	279 (11)	76 (19)	4.67 (7)
Cl(3)	36,607 (21)	74,968 (26)	18,933 (24)	646 (16)	905 (25)	753 (18)	67 (15)	309 (14)	65 (17)	5.18 (8)
Cl(4)	36,655 (14)	24,820 (23)	18,444 (17)	306 (9)	947 (22)	463 (12)	−68 (10)	155 (9)	−30 (12)	3.48 (5)
Cl(5)	49,963 (15)	51,275 (22)	12,160 (17)	369 (9)	843 (20)	475 (12)	−1 (11)	187 (9)	71 (12)	3.54 (5)
Cl(6)	49,911 (20)	1,150 (24)	12,263 (21)	635 (14)	800 (21)	604 (15)	1 (14)	285 (12)	−5 (14)	4.44 (7)
Cl(7)	60,643 (17)	24,076 (25)	5,850 (20)	373 (10)	1146 (26)	619 (15)	87 (13)	266 (10)	81 (16)	4.10 (6)
Cl(8)	38,345 (16)	23,841 (26)	95,284 (18)	379 (10)	1207 (27)	407 (12)	−38 (13)	84 (9)	33 (14)	4.09 (6)

[a] Esd's here and in succeeding tables are given in parentheses in units of the least significant digits. B values are taken from the last refinement cycle before the anisotropic temperature factors were introduced in the analytical form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

is $\mu = 66.9$ cm^{-1}; the minimum and maximum absorptions for the crystal used are $\mu R = 0.47$ and $\mu R = 1.46$. An absorption correction was applied, the crystal faces in the elongated prism being (100), (010), and, as an approximation to the plane produced by the combination of the (001) faces of the (polysynthetic) twins, $(10\bar{2})$. No correction was applied for extinction. The data were reduced by Lorentz and polarization corrections to relative F_o values in the usual way and brought to an approximate absolute scale according to the Wilson method.

Twinning.—The $TeCl_4$ crystals are twinned on (100) (*cf.* ref 22); *i.e.*, crystal A and crystal B[30] have the crystallographic bc plane as their common mirror plane. The fit of the two mirrored lattices is close to ideal. The short diagonal of the ac plane (17.005 Å) corresponds closely to the length of cell edge a, the angle between this diagonal and c (63.66°) is close to 180-β, and the direction [102] forms an angle of 89.70° with the c axis. Figure 1 shows a general reciprocal lattice plane ($k = 2n$) of a twinned crystal. Three types of reflections are present: (I) with $l = 2n + 1$ for crystal A, (II) with $l = 2n + 1$ for crystal B, (III) with $l = 2n$ for crystal A, almost ideally coinciding with B reflections of the same type. The indices of the overlapping A and B reflections of type III are related to each other by the transformation matrix

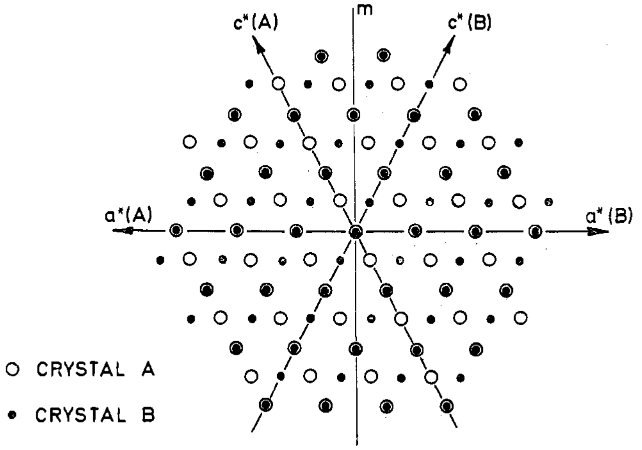

Figure 1.—Solid $TeCl_4$: superposition of two reciprocal lattice levels ($k = 2n$) produced by twinning on (100).

$$\begin{pmatrix} -1 & 0 & -1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

To obtain precise intensity data, slightly different orientation matrices were used for data sets I and II; the mean value of the two matrices was used to collect set III.

Detailed analyses of the peak profiles of some high-angle reflections showed that, under the measuring conditions used, the fully integrated intensities of both overlapping reflections in data set III were recorded without loss of precision. Data sets I and II were used to calculate the scale factor (A:B = 3.79) for the intensity reduction of set III to one individuum.

Determination and Refinement of the Structure

The interpretation of the three-dimensional Patterson synthesis was ambiguous because the structure has marked pseudosymmetries, but with the knowledge of the kind of twinning it could be assumed that Te and Cl atoms would be concentrated especially on the mirror planes. Under the assumption of centrosymmetry it was possible to find the positions of the two tellurium atoms. After some refinement of their parameters, subsequent difference Fourier maps yielded eventually the x and z parameters of all Cl atoms. The y parameters could not be fixed unambiguously from the Patterson function. Several possibilities have been calculated from which all y parameters finally resulted.

The subsequent three-dimensional least-squares refinement of all atoms was carried out with isotropic thermal parameters. Later the anisotropic vibration was taken into account. The atomic scattering factors of Te and Cl were used as given by Ibers in ref 31. Anomalous dispersion corrections were applied for Te, using the $\Delta f'$ and $\Delta f''$ values calculated by Cromer.[32,33] The expression minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was based on the standard deviations σ of the reduced counting rates with an additional term, being proportional to the net intensity: $w = 4F_o^2/[\sigma(F_o^2)]^2$ with $\sigma(F_o^3) = ([\sigma(I)]^2 + (0.03I)^2)^{1/2}(1/Lp)$. An analysis of the residuals showed this scheme to be adequate. Only reflections with $I < 2\sigma(I)$ were treated as unobserved (225 reflections) and given zero weight.

With isotropic temperature factors the least-squares refinement converged to the following R values (including zero reflections): $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.089$, $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2} = 0.087$. Taking the anisotropic thermal vibration into account the final R values resulted: $R_1 = 0.066$, $R_2 = 0.061$.

Application of Hamilton's statistical test[34] on R_2 indicates that this improvement highly justifies the significance of the anisotropic vibration data. There was no significant difference in the R factors for the directly measured data sets I and II, in comparison with those of set III which were obtained by difference. A final three-dimensional difference Fourier synthesis did not show any significant peaks higher than 3 e$^-$ Å^{-3} (about 10% of Cl peak height). The standard error of an observation of unit weight is 3.2 e$^-$.

The final positional and thermal parameters after the refinement, including the standard deviations obtained from the inverse matrix, are summarized in Table I. Table II gives the

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(30) The notations "crystal A" and "crystal B" are supposed to symbolize the two different orientations within the twin and do not mean that there are actually only two individua present. The experimental evidence suggests that in the actual crystals we have polysynthetic microtwinning, but in the present considerations this does not make any difference.

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(34) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

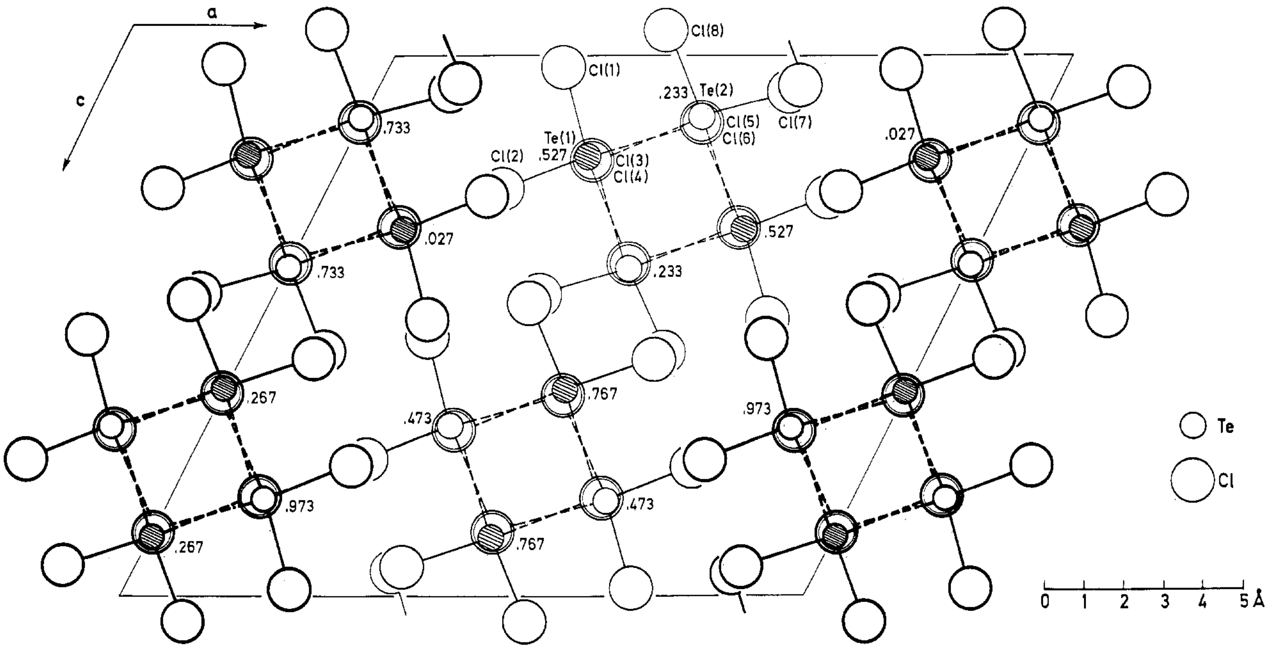

Figure 2.—Projection of the structure down the *y* axis. The numbers given are the *y* parameters of the Te atoms in fractions of *b*.

TABLE II

RMS COMPONENTS OF THERMAL DISPLACEMENT ALONG PRINCIPAL AXES AND DIRECTIONS OF AXES[a]

	Axis	Rms amplitude, Å	Direction cosines		
Te(1)	1	0.206	−0.200	−0.918	−0.342
	2	0.200	−0.514	−0.199	0.834
	3	0.170	−0.834	0.343	−0.432
Te(2)	1	0.196	−0.335	−0.848	0.412
	2	0.184	−0.508	0.531	0.679
	3	0.178	−0.794	0.018	−0.608
Cl(1)	1	0.286	0.002	−0.985	−0.173
	2	0.256	0.805	0.104	−0.584
	3	0.194	0.593	−0.137	0.793
Cl(2)	1	0.285	−0.169	−0.936	−0.307
	2	0.251	−0.086	−0.296	0.951
	3	0.193	−0.982	0.187	−0.030
Cl(3)	1	0.278	−0.965	−0.162	−0.204
	2	0.267	−0.230	0.170	0.958
	3	0.220	−0.121	0.972	−0.199
Cl(4)	1	0.231	0.278	−0.955	0.101
	2	0.213	0.427	0.029	−0.903
	3	0.185	0.860	0.295	0.416
Cl(5)	1	0.226	−0.299	0.749	0.591
	2	0.208	−0.882	0.019	−0.471
	3	0.200	−0.364	−0.662	0.655
Cl(6)	1	0.275	−0.968	−0.005	−0.251
	2	0.235	−0.251	−0.035	0.967
	3	0.209	−0.014	0.999	0.033
Cl(7)	1	0.260	−0.173	−0.826	−0.537
	2	0.233	−0.062	−0.535	0.843
	3	0.193	−0.983	0.179	0.041
Cl(8)	1	0.263	0.443	−0.874	−0.201
	2	0.238	0.804	0.487	−0.341
	3	0.185	0.396	−0.011	0.918

[a] Direction cosines refer to an orthogonal coordinate system with axes parallel to *a*, *b*, and c^*.

dimensions and orientations of the vibration ellipsoids for all atoms. Observed and calculated structure factor amplitudes are given elsewhere.[35]

Description of the Structure and Discussion

The crystal structure of tellurium tetrachloride consists of isolated tetramers Te_4Cl_{16}, which have only Cl···Cl van der Waals contacts to neighboring Te_4Cl_{16} molecular units. These tetramers have a cubane-like structure with Te and Cl atoms occupying alternatively the corners of the Te_4Cl_4 cubane skeleton.

In Table III bond lengths, bond angles, and nonbonded distances within the Te_4Cl_{16} units are listed together with their estimated standard deviations. In Figure 2 the projection of the unit cell along *b* is shown; Figure 3 gives the configuration and the atomic designations of one Te_4Cl_{16} molecule.

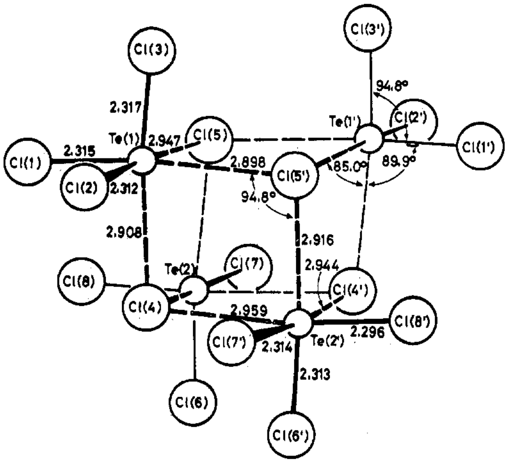

Figure 3.—Te_4Cl_{16} molecular unit (twofold crystallographic axis vertical) with individual bond distances and mean values of chemically equivalent bond angles.

Every Te atom has three neighboring terminal Cl atoms at an average bond length of 2.311 Å. Together with these it forms an equilateral trigonal pyramid with mean bond angles Cl(t)–Te–Cl(t) of 94.8° (t = terminal). The coordination of tellurium is completed to a strongly distorted octahedron by three bridging Cl

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[35] A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG) IN THE Te_4Cl_{16} MOLECULES OF SOLID TELLURIUM TETRACHLORIDE (WITH STANDARD DEVIATIONS)[a]

	Bonded Distances		
Te(1)–Cl(1)	2.315 (3)	Te(1)–Cl(4)	2.908 (3)
Te(1)–Cl(2)	2.312	Te(1)–Cl(5)	2.947
Te(1)–Cl(3)	2.317	Te(1)–Cl(5′)	2.898
Te(2)–Cl(6)	2.313	Te(2)–Cl(4)	2.944
Te(2)–Cl(7)	2.314	Te(2)–Cl(4′)	2.959
Te(2)–Cl(8)	2.296	Te(2)–Cl(5)	2.916
Av Te–Cl(t)	2.311	Av Te–Cl (b)	2.929
	Nonbonded Distances		
Te(1)···Te(1′)	4.333 (1)	Te(1′)···Te(2)	4.314 (1)
Te(1)···Te(2)	4.316	Te(1′)···Te(2′)	4.316
Te(1)···Te(2′)	4.314	Te(2)···Te(2′)	4.265
		Av	4.309
Cl(1)···Cl(2)	3.430 (4)	Cl(4)···Cl(4′)	4.068 (6)
Cl(1)···Cl(3)	3.381	Cl(4)···Cl(5)	3.953 (4)
Cl(2)···Cl(3)	3.391	Cl(4)···Cl(5′)	3.930 (4)
Cl(6)···Cl(7)	3.409	Cl(4′)···Cl(5)	3.930 (4)
Cl(6)···Cl(8)	3.401	Cl(4′)···Cl(5′)	3.953 (4)
Cl(7)···Cl(8)	3.400	Cl(5)···Cl(5′)	3.911 (6)
Av Cl(t)···Cl(t)	3.402	Av Cl(b)···Cl(b)	3.958
Cl(1)···Cl(4)	3.751 (4)	Cl(6)···Cl(4)	3.742 (4)
Cl(1)···Cl(5)	3.744	Cl(6)···Cl(4′)	3.727
Cl(2)···Cl(4)	3.671	Cl(7)···Cl(4′)	3.736
Cl(2)···Cl(5′)	3.708	Cl(7)···Cl(5)	3.721
Cl(3)···Cl(5)	3.804	Cl(8)···Cl(4)	3.673
Cl(3)···Cl(5′)	3.699	Cl(8)···Cl(5)	3.755
		Av Cl(t)···Cl(b)	3.729
	Bond Angles		
Cl(1)–Te(1)–Cl(2)	95.7 (2)	Cl(4)–Te(1)–Cl(5)	84.9 (2)
Cl(1)–Te(1)–Cl(3)	93.7 (2)	Cl(4)–Te(1)–Cl(5′)	85.2 (2)
Cl(2)–Te(1)–Cl(3)	94.2 (2)	Cl(5)–Te(1)–Cl(5′)	84.0 (3)
Cl(6)–Te(2)–Cl(7)	94.9 (2)	Cl(4)–Te(2)–Cl(4′)	87.1 (3)
Cl(6)–Te(2)–Cl(8)	95.1 (2)	Cl(4)–Te(2)–Cl(5)	84.8 (2)
Cl(7)–Te(2)–Cl(8)	95.0 (2)	Cl(4′)–Te(2)–Cl(5)	84.0 (2)
Av Cl(t)–Te–Cl(t)	94.8	Av Cl(b)–Te–Cl(b)	85.0
Te(1)–Cl(4)–Te(2)	95.1 (2)	Te(1)–Cl(5)–Te(1′)	95.7 (3)
Te(1)–Cl(4)–Te(2′)	94.7 (2)	Te(1)–Cl(5)–Te(2)	94.8 (2)
Te(2)–Cl(4)–Te(2′)	92.6 (3)	Te(1′)–Cl(5)–Te(2)	95.8 (2)
		Av	94.8

[a] The coordinates of the atoms with primed indices are related to the data of Table I by the transformation $\bar{x}$, y, $1/2 - z$. Cl(t) = terminal chlorine; Cl(b) = bridge chlorine.

atoms of the Te_4Cl_4 cube with much larger bond distances (average 2.929 Å) and mean bond angles Cl(b)–Te–Cl(b) of 85.0° (b = bridge). In effect the Te is displaced from the center of the coordination octahedron parallel to a C_3 axis.

The exact symmetry of the Te_4Cl_{16} unit is C_2 (twofold axis along *b*); deviations from the idealized T_d symmetry are only very small, however significant within the limits of accuracy (see Table III).

If the cubane-like Te_4Cl_4 skeleton is formally regarded as two interpenetrating tetrahedra, the radial distortion of the cube is such that the Te_4 tetrahedron (mean Te···Te 4.309 Å) is significantly larger than the one with 4 Cl at its corners (mean Cl···Cl 3.958 Å).

The Te–Cl(t) bond distances are only slightly shorter than the corrected sum of the single covalent bond radii of 2.34 Å,[36] showing that approximately (predominantly covalent) single bonds are present (see below). The same value within experimental error (2.33 ± 0.02 Å) has been found for monomeric $TeCl_4$ (C_{2v}) in the vapor state.[1] Interestingly, a bond length of 2.31 Å had been estimated by Gerding and Houtgraaf[9] from spectroscopic data for assumed $TeCl_3^+$ ions in solid $TeCl_4$.

In a recent crystal structure analysis of $TeCl_3^+AlCl_4^-$[37] we found Te–Cl bond lengths of 2.276 Å (av) in the pyramidal $TeCl_3^+$ ions with three more Cl (from $AlCl_4^-$) at a distance of 3.062 Å (av) completing an octahedral coordination around Te. The $TeCl_6^{2-}$ ion for which recent X-ray studies have again confirmed the surprising regular octahedral coordination of Te(IV) by Cl atoms has Te–Cl bond lengths of 2.54 Å.[38]

$TeCl_3^+$ (in $TeCl_3^+AlCl_4^-$) and $TeCl_6^{2-}$ may be regarded as the limiting cases in describing the bonding of octahedrally coordinated Te–Cl compounds (parallel to decreasing stereochemical activity of the "inert" pairs of tellurium): three strong covalent and three much longer ionic bonds around Te in $TeCl_3^+AlCl_4^-$ (difference between short and long bonds 0.8 Å, mean bond length in the octahedron 2.67 Å); six equivalent covalent bonds (2.54 Å) in $TeCl_6^{2-}$. Coordination and bonding in solid $TeCl_4$ is intermediate between these extremes. The difference between short and long Te–Cl bonds is 0.6 Å; the mean bond length in the distorted octahedra is 2.62 Å. It is to be assumed that there is only partial transfer of charge from the bridging chlorines to Te, leaving some polar character in the long bridge bonds. There is, however, no doubt that the description as Te_4Cl_{16} molecular units is a better approximation to the true nature of the compound than, in the polar limiting case, as an arrangement of $TeCl_3^+$ and Cl^- ions.

The only other known Te(IV)–Cl bond lengths in similar compounds are 2.480 and 2.541 Å in $(CH_3)_2TeCl_2$,[39] 2.536 and 2.520 Å in *trans*-$TeCl_4(SC(N(CH_3)_2)_2)_2$,[40] and 2.386 and 2.717 Å (mean 2.55 Å) in $(ClC_2H_4)TeCl_3$.[41] They agree qualitatively with the average values for $TeCl_4$, but in the absence of knowledge about the electronic structure of Te(IV) compounds and of more data it is difficult to draw quantitative conclusions, *e.g.*, about possible π-bond contributions.

It is interesting to note that only few of the previous papers on solid $TeCl_4$[11] had taken an oligomeric or polymeric structure explicitly into account but that qualitative predictions given by Wynne and Pearson[21] on the coordination number of Te in $TeCl_4$ were fully confirmed. Postulating a strong trans effect of the alkyl groups within the series R_nTeCl_{4-n} effective coordination numbers for Te in the solid were expected to be 6 for $n = 0$ and 5 for $n = 1$. Besides $n = 0$ ($TeCl_4$) the case $n = 1$ was confirmed recently by the structure determination of $(ClC_2H_4)TeCl_3$.[41]

The mean bond angles within the terminal $TeCl_3$ groups (C_{3v}) of $TeCl_4$ (94.8°) are remarkably similar to those in the $TeCl_3^+$ ions of $TeCl_3^+AlCl_4^-$ (95.0°)[37] and in the isoelectronic $SbCl_3$ molecule in the solid (95.2°),[15] suggesting very similar bonding within these groups.

It is difficult to decide on the stereochemical activity of the tellurium nonbonding electron pairs. They may be concentrated in the triangular faces defined by the bridging Cl atoms of the Te_4Cl_{16} cube. This would be supported by the relatively large Te···Te separations within the cube, and it would be analogous to similar

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suggestions for $SeF_3^+NbF_6^-$[42] and $SeF_3^+Nb_2F_{11}^-$.[43] It is, however, questionable that the space available toward the center of the Te_4Cl_{16} cube is sufficient to keep four localized electron pairs. More probable is a (at least partial) delocalization, together with a possible involvement, of the "inert" 5s electron pairs in the bonding, as shown for the corresponding $a_{1g}\sigma^*$ electrons in $TeCl_6^{2-}$ and $TeBr_6^{2-}$ from the electronic spectra.[44] If the tellurium 6s orbitals are used for bonding in $TeCl_6^{2-}$ (in the form of a $5p^35d^26s$ hybridization) this would explain the unusually large difference between the observed bond length (2.54 Å) and the sum of the normal covalent radii of Te and Cl (about 2.34 Å).[36] To what extent and how there is tellurium s electron participation in bonding of $TeCl_4$ remains uncertain.

The structure of solid $TeCl_4$ can also be described as a somewhat distorted cubic close packing with one-fourth of the octahedral voids occupied by Te (see also ref 24). As shown in Table, IV all intermolecular Cl···Cl distances are equal to or larger than the sum of the van der Waals radii (3.60 Å).

TABLE IV

PACKING OF THE Cl ATOMS. INTERMOLECULAR NONBONDED DISTANCES BETWEEN NEIGHBORING CHLORINES

	No. of nonbonded Cl neighbors within Te_4Cl_{16} unit	—Additional intermolecular Cl neighbors—	
		No.	Cl···Cl distances, Å
Cl(1)	5	7	3.643–4.219
Cl(2)	5	7	3.685–4.219
Cl(3)	5	7	3.715–4.015
Cl(4)	9	3	3.702–4.015
Cl(5)	9	3	3.593–3.745
Cl(6)	5	7	3.644–3.963
Cl(7)	5	7	3.593–4.015
Cl(8)	5	7	3.745–3.904

The packing density of the Cl atoms in $TeCl_4$ (37.8 Å^3 per Cl atom) is smaller than, *e.g.*, in $CdCl_2$ (37.4 Å^3), $ZrCl_4$ (34.8 Å^3), LiCl (34.2 Å^3), and $CrCl_3$ (30.0 Å^3).[45]

Compounds with a cubane skeleton are known for a variety of elements, although there are only a few structure determinations reported in the literature.[46] Solid tellurium tetrachloride, or, correctly formulated tetra-μ_3-chloro-tetrakis[trichlorotellurium(IV)], is one of the few purely inorganic cubanes. It is the first example of a group VIa element (except oxygen) in a cubane, it is the first main group cubane with octahedral coordination (type I, according to ref 46a), and it is unique in being the only simple "binary" inorganic cubane.

With the knowledge of the structure of solid $TeCl_4$ much of the previous diverging results can be understood. Easy homolytic, heterolytic, or thermal fission which is to be expected from the weak bonding in the cubane skeleton may explain such properties as electric conductivity in the melt,[8] measured nonzero dipole moments in solution,[3] solubility in polar and nonpolar solvents, and observation of monomers up to tetramers in benzene solution[13,16–20] (presence of concentration-dependent oligomerization equilibria?). The nature of the fission products is determined by the polarity of the medium and seems to be especially sensitive to traces of moisture, thus complicating the results. Raman spectra indicate that the end product of homolytic fission in solution is the monomeric C_{2v} $TeCl_4$ molecule as in the gas phase.[20]

Raman[6,9,13] and infrared[6,11–14] spectra of solid $TeCl_4$, which could not be interpreted completely on the basis of previously proposed structural models, are possible to be assigned now in terms of the approximate T_d symmetry of the Te_4Cl_{16} unit. Qualitatively, there is a systematic decrease of the Te–Cl stretching vibration frequencies from the $TeCl_3^+$ ions in $TeCl_3^+AsF_6^-$ ($\nu_1(A_1)$ 412, $\nu_3(E)$ 385 cm^{-1})[47] and $TeCl_3^+AlCl_4^-$ (390, 367 cm^{-1})[9] to those which are observed in the $TeCl_4$ spectra between 342 and 376 cm^{-1} and which are concentrated mainly in the terminal $TeCl_3$ groups. For the pair $TeCl_3^+AlCl_4^-$–$TeCl_4$ this decrease is paralleled by an increase in the Te–Cl bond distances within the $TeCl_3$ groups (2.276–2.311 Å). According to the vibrational spectra, an even shorter Te–Cl bond distance is to be expected for $TeCl_3^+AsF_6^-$ (in this sense, the bonding in $TeCl_3^+AsF_6^-$ is closer to the "polar limiting case" than that in $TeCl_3^+AlCl_4^-$).

The ^{35}Cl nqr spectrum of $TeCl_4$[5] which shows two groups of three lines and which was previously interpreted in terms of a monomer C_{2v} structure is readily compatible with the observed tetrameric structure.

Cell constants, space groups, and intensity distribution on the X-ray photographs show that $SeCl_4$ and $TeBr_4$ are isostructural with $TeCl_4$ (see also ref 22–24).

Thermal Vibrations.—The thermal parameters (Table II) are reasonably consistent within groups of chemically equivalent atoms, the directions of largest vibration for all atoms being roughly tangential to the Te_4Cl_4 cube. Consequently, the rigid-body approximation could be applied remarkably well to the whole Te_4Cl_{16} molecular unit, yielding the following tensors describing the libration (deg^2) and translation (Å^2) referred to orthogonal axes parallel to a, b, and c^*

$$\omega = \begin{pmatrix} 4.78\ (54) & 0 & -1.69\ (37) \\ & 4.12\ (55) & 0 \\ & & 7.32\ (48) \end{pmatrix}$$

$$T = \begin{pmatrix} 0.0332\ (16) & 0 & -0.0047\ (11) \\ & 0.0393\ (16) & 0 \\ & & 0.0371\ (17) \end{pmatrix}$$

with principal rms librations of 2.8, 2.2, and 2.0°. Resulting bond length corrections are smaller than the error of the experimental bond lengths and were ignored.

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