CONTRIBUTION NO. 3031 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
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The Crystal Structures of Tetratellurium(2+) Tetrachloroaluminate and Heptachlorodialuminate, $Te_4^{2+}(AlCl_4^-)_2$ and $Te_4^{2+}(Al_2Cl_7^-)_2$[1]

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Received May 24, 1971

The crystal structures of the compounds $Te_4(AlCl_4)_2$ (A) and $Te_4(Al_2Cl_7)_2$ (B) have been determined from three-dimensional X-ray diffraction studies using peak height data collected with an automated diffractometer. Both structures were derived by Patterson and Fourier methods and were refined by full-matrix least-squares techniques with anisotropic temperature parameters being employed in the final stages. Compound A occurs in the orthorhombic space group *Pbca* with a = 10.746 (5), b = 14.112 (5), and c = 11.845 (5) Å and four $Te_4(AlCl_4)_2$ units per cell (d_{obsd} = 3.04 (6) g cm^{-3}, d_{calcd} = 3.135 g cm^{-3}). A total of 2616 independent reflections were used in the structure derivation, with 1501 data above background giving final conventional values of R = 0.073 and R_w = 0.077. The structure consists of planar and almost square Te_4^{2+} units [(d(Te–Te) = 2.6738 (17) and 2.6633 (16) Å; angles of 89.90 (4) and 90.10 (4)°] and approximately tetrahedral $AlCl_4^-$ anions. Compound B occurs in the monoclinic space group $P2_1/c$ with a = 9.113 (4), b = 11.151 (6), c = 13.096 (5) Å, β = 90.20 (2)°, d_{obsd} = 2.8 (2) g cm^{-3}, and d_{calcd} = 2.781 g cm^{-3} for two $Te_4(Al_2Cl_7)_2$ units per cell. A total of 4896 independent reflections were used for the structure determination, 1736 data above background giving final residuals of 0.090 and 0.081 (R_w). The compound also has nearly square Te_4^{2+} units [2.6599 (16) and 2.6610 (18) Å edges, 89.81 (4) and 90.19 (4)° angles] plus $(Cl_3AlClAlCl_3)^-$ anions in the staggered conformation with an Al–Cl–Al bridge angle of 110.8 (3)°. Chemical features of note are (1) the bonding within the Te_4^{2+} cation, (2) the coordination of anion chlorine to the cation in both structures to give substantially planar arrays, (3) a discernible interrelation of the two structures, and (4) the apparent interionic Al–Cl interactions which lead to interlocking chains of $Al_2Cl_7^-$ anions in B.

Introduction

A recent investigation of the ($TeCl_4$ + $4AlCl_3$)–Te system[2] revealed three reduced phases were formed, presumably tetrachloroaluminate salts of polytellurium cations. The present paper reports the results of crystallographic studies of two of these phases, namely, $Te_4^{2+}(AlCl_4^-)_2$ and $Te_4^{2+}(AlCl_7^-)_2$.

Experimental Section

Compound A [$Te_4^{2+}(AlCl_4^-)_2$] was prepared as described before[2] from a stoichiometric mixture of Te, $TeCl_4$, and $AlCl_3$ in a sealed Pyrex tube of 5-mm diameter and 30-mm length. Since slow cooling of the molten mixture generally gave only poorly formed crystals, the material used in the diffraction study was obtained by recrystallization of A from molten $NaAlCl_4$.

Compound B [$Te_4^{2+}(Al_2Cl_7^-)_2$] was obtained during a phase study of mixtures in which tellurium was less reduced than in compound A. Dark, rose-colored crystals of B were obtained after slow cooling of the molten mixture obtained by heating a 5-g mixture of Te, $TeCl_4$, and $AlCl_3$ in the molar proportions 3:1:4 to *ca.* 250° in a sealed evacuated Pyrex tube.

Single crystals of compounds A and B suitable for X-ray study were selected under the microscope in a drybox, mounted in thin-wall Lindemann glass capillaries, and sealed under an atmosphere of argon.

The crystal of compound A selected was a rectangular plate about 0.05 × 0.16 × 0.20 mm, which dimensions were parallel to a, c, and b, respectively, of the orthorhombic unit cell. The crystal of compound B used was approximated by a triangular plate 0.25 × 0.20 × 0.27 mm and 0.13 mm thick. The latter crystal had been removed from a solid matrix and developed faces were not evident. Equiinclination Weissenberg photographs of both compounds taken at room temperature with Cu Kα radiation (hkl, k = 0–4 for A, h = 0–6 for B) provided initial unit cell parameters and information for space group assignments. Better values for the cell constants were obtained by averaging those calculated from 2θ values measured at room temperature with Mo Kα radiation on an automated diffractometer. The intensity data for all reflections up to θ = 30° were collected from the same crystals with Zr-filtered Mo radiation on a Hilger–Watts four-circle diffractometer interfaced to an SDS 910/1401 computer. The intensities of three standard reflections were checked after measurement of each 30 reflections and were found to show no significant or systematic variations in intensities. In both cases only the peak heights were measured for each reflection and these were subsequently converted to integrated intensities using peak height:integrated intensity ratios measured for about 100 reflections over the range of θ studied.[3]

The intensities of the individual reflections were corrected first for background and then for Lorentz–polarization and absorption effects. The standard deviations were based on the expression

$$\sigma(I) = \{I_T + I_B + (E_T I_T)^2 + (E_B I_B)^2 + (E_A I_N)^2\}^{1/2}A$$

where I_T is the total count, I_B the background count, and I_N the net count. The terms including E_T, E_B, and E_A represent systematic errors in I_T, I_B, and the transmission coefficient A, respectively.[4] For both structures reported here values of 0.03 for E_T and E_N and 0.06 for E_A were employed.

Crystal Data.—Compound A forms deep purple crystals which are crystallographically orthorhombic with lattice dimensions a = 10.746 (5), b = 14.112 (5), and c = 11.845 (5) Å. The systematic absences ($hk0$, $h \neq 2n$; $0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$) uniquely characterize the space group as *Pbca* (no. 61). A cast rod of composition $Te_4^{2+}(AlCl_4^-)_2$ (which exhibited small shrinkage cracks) had a density of 3.04 (6) g cm^{-3} compared with 3.135 g cm^{-3} calculated assuming four $Te_4^{2+}(AlCl_4^-)_2$ units per cell. A total of 2616 independent reflections were collected over one octant at room temperature. Transmission coefficients, evaluated by numerical integration, varied from 0.28 to 0.66 (μ = 83 cm^{-1} for Mo Kα radiation).

Compound B.—The deep rose-purple crystals found embedded in the other phase of the mixture ($TeCl_4 \cdot AlCl_3$) were shown to be monoclinic with lattice constants a = 9.113 (4), b = 11.151 (6), c = 13.096 (5) Å, and β = 90.20 (2)°. The systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) unambiguously establish the space group as $P2_1/c$ (no. 14). A cast rod of the mixture of 60 mol % B and 40 mol % $TeCl_4 \cdot AlCl_3$ had a density of 2.6 (2) g cm^{-3}. The density of B was estimated by approximating the density of the $TeCl_4 \cdot AlCl_3$ therein as the average of the densities of $TeCl_4$ and of $AlCl_3$. The result, 2.8 (2) g cm^{-3}, is in good agreement with a value of 2.781 g cm^{-3} calculated for two $Te_4^{2+}(Al_2Cl_7^-)_2$ units per cell.

A total of 4896 independent reflections in the hkl and $hk\bar{l}$

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14, 1970.

[2] D. J. Prince, J. D. Corbett, and B. Garbisch, *Inorg. Chem.*, **9**, 2731 (1970).

[3] L. E. Alexander and G. S. Smith, *Acta Crystallogr.*, **15**, 983 (1962).

[4] S. A. Lawton and R. A. Jacobson, *Inorg. Chem.*, **7**, 2125 (1968).

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $Te_4^{2+}(AlCl_4^-)_2$[a]

Atom	x/a	y/b	z/c	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te(1)	0.01034 (11)	0.07418 (7)	0.36796 (8)	1.453 (15)	0.583 (6)	0.655 (7)	0.153 (8)	0.005 (8)	0.069 (5)
Te(2)	0.39208 (12)	0.40989 (8)	0.43435 (9)	1.440 (15)	0.597 (6)	0.737 (8)	−0.258 (8)	−0.054 (8)	−0.004 (6)
Al(1)	0.3892 (5)	0.3587 (3)	0.0844 (3)	1.10 (6)	0.54 (2)	0.59 (3)	0.02 (3)	−0.07 (3)	−0.05 (2)
Cl(1)	0.3823 (6)	0.1222 (5)	0.4093 (4)	2.40 (10)	1.44 (5)	0.60 (3)	−0.18 (6)	0.10 (4)	−0.15 (3)
Cl(2)	0.0694 (5)	0.3308 (4)	0.3532 (5)	1.17 (6)	1.01 (4)	1.53 (6)	0.26 (4)	0.22 (4)	0.13 (4)
Cl(3)	0.3128 (4)	0.4788 (3)	0.1716 (3)	1.47 (6)	0.59 (2)	0.96 (3)	0.22 (3)	−0.21 (4)	−0.18 (2)
Cl(4)	0.2764 (5)	0.2396 (3)	0.1264 (4)	1.49 (6)	0.62 (2)	1.44 (5)	−0.04 (3)	0.39 (5)	−0.09 (3)

[a] Standard deviations of the least significant figures are given in parentheses. [b] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The thermal parameters have been multiplied by 10^2.

octants were measured. Refinement of the unit cell parameters using the diffractometer data showed that the original choice of axes made the angle β less than 90°. The orientation of the coordinate system was transformed into the standard form with $\beta > 90°$ by reversing the direction of the positive a and b axes and converting the indices of the intensity data from hkl and $hk\bar{l}$ to $\bar{h}\bar{k}l$ and $\bar{h}\bar{k}\bar{l}$, respectively. Transmission coefficients varied from 0.415 to 0.636 (μ = 60 cm^{-1} for Mo Kα radiation).

Structure Determination

Atomic scattering factors for the refinement of both structures were taken from Hanson, *et al.*[5] Correction for the real and imaginary part of anomalous dispersion were applied to the tellurium atoms.[6] All calculations were carried out on the IBM 360/65 computer at the Iowa State University Computer Center with the following programs: ABCOR[7] for absorption corrections, ALF[8] for Fourier summation, ORFLS[9] for least-squares parameter refinement, ORFFE[10] for estimations of errors, and ORTEP[11] for figure illustrations.

Compound A.—A three-dimensional Patterson function was generated from all the intensity data collected. Interpretation of the vector map unambiguously yielded trial coordinates for two independent tellurium atoms occupying eightfold general positions of the space group *Pbca*. Positional parameters for one aluminum and four chlorine atoms in general positions were determined from Fourier syntheses in which the tellurium atoms had been subtracted. The 28 positional and isotropic thermal parameters for all atoms in the asymmetric unit were adjusted in a full-matrix least-squares refinement using all 2616 independent reflections. Three cycles of refinement produced values of 0.186 and 0.190 for R and R_w, respectively, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = \{\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2\}^{1/2}$ with $w = \sigma_F^{-2}$. At this point a difference map showed no spurious peaks of significance. Therefore it was concluded that the model was complete and had the correct symmetry. Full matrix refinement now using anisotropic thermal parameters and all data resulted in an R of 0.104 and an R_w of 0.086.

The 1501 reflections for which $|F_o| > 3\sigma_F$ were used in two more cycles of refinement which converged at R = 0.073, R_w = 0.077. Further refinement produced no significant changes in either the reliability indices or the estimated standard deviations of the parameters. A final difference Fourier map indicated that all atoms had been successfully located since the largest feature on the map had a peak density of only 1 e Å^{-3} and this occurred in the neighborhood of tellurium atoms.

Compound B.—A three-dimensional Patterson function was generated from the intensity data. Interpretation of this map yielded trial coordinates for two nonrelated tellurium atoms occupying the fourfold general positions of the space group $P2_1/c$. One cycle of a full-matrix least-squares refinement of their positional and isotropic thermal parameters (*ca.* 27 of the total electron density) was run using all 4896 independent reflections. A difference Fourier map calculated with phases determined by the tellurium atoms then revealed several peaks, some of which could be interpreted as an aluminum atom approximately tetrahedrally surrounded by four chlorine atoms, all in general positions. A difference Fourier map generated after two more cycles of isotropic least-squares refinement which included the five lighter atoms just deduced indicated several peaks which could be interpreted as four more independent atoms in general positions. A model suggested that the remaining four atoms could be one aluminum and three chlorine atoms which, along with the four chlorines and one aluminum already located, would form a singly bridged $Al_2Cl_7^-$ anion. Assuming this trial structure and stoichiometry were correct, three cycles of isotropic least-squares refinement with all data reduced the R to 0.262 and R_w to 0.256. Despite the rather large residual values an electron difference map revealed no peaks of significance.

Of the 4896 independent reflections which had been used up to this point, 3092 could be rejected on the basis that $|F_o| < 3\sigma_F$ (including those for which F_o = 0 by extinction for the chosen space group). The remaining 1804 reflections were used in two cycles of least-squares refinement with the residuals converging at R = 0.198 and R_w = 0.191. Three more cycles using anisotropic thermal parameters for all atoms reduced R to 0.109 and R_w to 0.104. A difference map revealed no peak larger than 1 e Å^{-3}.

An examination of F_o and F_c revealed 68 high-angle reflections ($\theta \geq 25°$) which were weak ($10|F_o| < |F_o|$(max)) and for which $|F_c|$ was greater than $10|F_o|$. The indices of these questionable reflections showed no systematic occurrences. Further refinement without the 68 data reduced R to 0.090 and R_w to 0.081, during which the estimated standard deviations for the positional parameters and for the bond lengths both decreased by about 0.001 Å and the anisotropic thermal parameters changed from 1 to 10 parts in 10^4. Since for all the 68 discarded reflections $|F_o|$ was within 15% of $3\sigma_F$, small changes in the assigned errors in the definition of $\sigma(I)$ (*vide supra*) could have eliminated these reflections *a priori*. A final difference map calculated using the remaining 1736 reflections had no residual greater than 1 e Å^{-3} and the larger of the remaining features occurred in the neighborhood of the heavy atoms. A comparison of F_o and F_c for the 3092 reflections rejected on a statistical basis revealed no major discrepencies; *i.e.*, $||F_o| - |F_c|| < 3\sigma_{F_o}$.

Results and Discussion

Compound A. $Te_4(AlCl_4)_2$.—The final atomic and thermal parameters for the compound together with their estimated standard deviations are given in Table I.[12] Since all aspects of the structure appear to justify a description in terms of Te_4^{2+} and $AlCl_4^-$ ions, the distances and angles within the Te_4 and $AlCl_4$ moieties have been designated *intraionic* parameters in Table II. The *inter*ionic distances less than 4.1 Å are listed in Table III and a stereoscopic view of the structure is shown in Figure 1.

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(5) H. P. Hanson, F. Herman, J. D. Lea, and S. Skellman, *Acta Crystallogr.*, **17**, 1040 (1964).

(6) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(7) D. J. Wehe, W. R. Busing, and H. A. Levy, "Fortran Program for Single Crystal Orienter Absorption Corrections," USAEC Report ORNL-TM-299, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(8) J. Rodgers and R. A. Jacobson, USAEC Report IS-2155, Ames Laboratory, Iowa State University, Ames, Iowa, 1967.

(9) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(10) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program," USAEC Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(11) C. K. Johnson, "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration," USAEC Report ORNL-3764, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(12) A table of the observed and calculated structure factors 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 author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

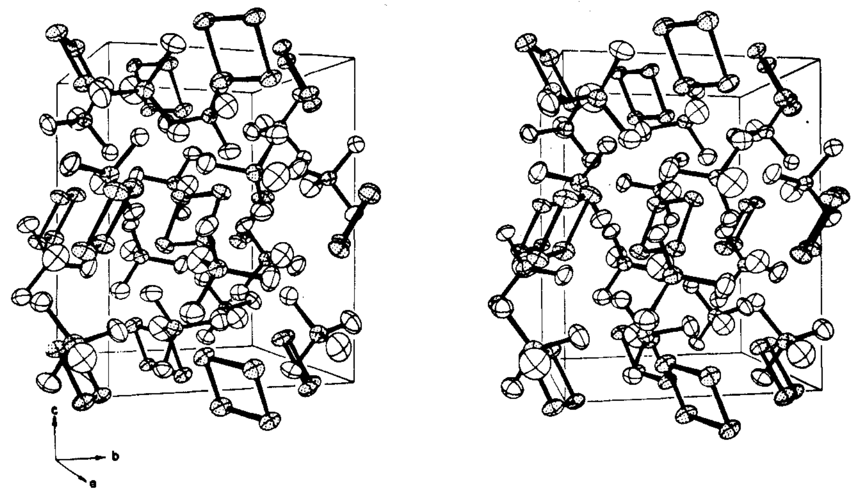

Figure 1.—Stereographic view of the structure of $Te_4^{2+}(AlCl_4^-)_2$ looking down the *a* axis.

TABLE II
INTRAIONIC DISTANCES (Å) AND ANGLES (DEG) IN $Te_4^{2+}(AlCl_4^-)_2$

Te(1)–Te(2)	2.6738 (17)[a]	Te(1)–Te(1′)	3.771 (2)
Te(1)–Te(2′)	2.6633 (16)	Te(2)–Te(2′)	3.777 (2)
Al–Cl(1)	2.093 (6)	Cl(1)–Cl(3)	3.499 (6)
Al–Cl(2)	2.110 (7)	Cl(1)–Cl(4)	3.421 (7)
Al–Cl(3)	2.149 (6)	Cl(2)–Cl(3)	3.472 (7)
Al–Cl(4)	2.130 (6)	Cl(2)–Cl(4)	3.410 (7)
Cl(1)–Cl(2)	3.522 (8)	Cl(3)–Cl(4)	3.440 (6)
Te(1)–Te(2)–Te(1′)	89.90 (4)	Cl(1)–Al–Cl(4)	108.2 (3)
Te(2)–Te(1)–Te(2′)	90.10 (4)	Cl(2)–Al–Cl(3)	109.2 (3)
Cl(1)–Al–Cl(2)	113.8 (3)	Cl(2)–Al–Cl(4)	107.1 (3)
Cl(1)–Al–Cl(3)	111.2 (3)	Cl(3)–Al–Cl(4)	107.0 (3)

[a] Equation of Te_4 plane centered at $^1/_2$, $^1/_2$, $^1/_2$ is $-1.2457x + y + 0.6627z - 0.2085 = 0$.

TABLE III
INTERIONIC DISTANCES (Å) IN $Te_4^{2+}(AlCl_4^-)_2$ <4.1 Å

	Distance	Angle[b]
Cl(2)–Cl(4)	3.717 (8)	
Cl(3)–Cl(4)	3.844 (7)	
Te(2)–Cl(3) }[a]	3.292 (4) }[a]	5.3
Te(1)–Cl(3) }	3.370 (4) }	
Te(2)–Cl(4) }	3.343 (5) }	9.4
Te(1)–Cl(4) }	3.434 (4) }	
Te(1)–Cl(1)	3.625 (5)	30.8
Te(1)–Cl(2)	3.687 (4)	42.5
Te(1)–Cl(3) }	3.753 (5) }	67.3
Te(2)–Cl(3) }	3.900 (5) }	
Te(2)–Cl(2)	3.768 (5)	23.2
Te(2)–Cl(2)	4.059 (6)	55.1
Te(2)–Cl(1)	4.078 (6)	35.9
Te(1)–Cl(1)	4.083 (7)	58.0

[a] Brace designates chlorine atom bridging edge of the Te_4^{2+} unit and distance therefrom. [b] Angle (deg) that the line between designated atoms makes with the plane of the Te_4^{2+} cation.

The compound contains approximately square Te_4^{2+} and tetrahedral $AlCl_4^-$ ions. The Te_4^{2+} unit occurs about a center of symmetry and is therefore planar. The two edges of the cation differ by 0.010 Å or about 6 times the standard deviation of either, while the angles differ from 90° by only 0.1°, or 2.5 times the standard deviation in each. The Al–Cl distances in the anion average 2.12 Å, the range from 2.09 to 2.15 Å being 10 times the individual deviations, while the Cl–Al–Cl angles vary from 107 to 114° and average 109.1°. The longer Al–Cl distances (and to a lesser extent the smaller thermal parameters) occur for those chlorines which also have the closer tellurium neighbors (Table III). This aspect will be considered later when the interionic interactions and packing in the two structures are treated together. The Al–Cl distances found here are quite similar to those which occur in $Se_8^{2+}(AlCl_4^-)_2$.[13]

Compound B. $Te_4(Al_2Cl_7)_2$.—This compound contains a very similar Te_4^{2+} cation together with a clear example of the oft-postulated anion $Al_2Cl_7^-$. The final positional and thermal parameters for the compound are given in Table IV.[12] The intraionic distances and angles are given in Table V, and the interionic distances less than 4.1 Å, in Table VI. A stereoscopic view of the packing is shown in Figure 2.

The Te_4^{2+} cation again occurs at a center of symmetry. In this case the independent edges of the cation differ by only 0.0011 Å, or less than a single standard deviation, whereas the angles deviate from 90° by 0.19° or 5σ. The $Al_2Cl_7^-$ ion occurs in the staggered conformation and contains an approximate plane of symmetry, as shown in Figure 3. The terminal Al–Cl distances average 2.10 Å, with a range of 2.08–2.13 Å or 7σ. The two longer Al–Cl distances again occur for those chlorine atoms which have the closer tellurium neighbors, Cl(1) and Cl(5). Inspection of the figure will confirm that the terminal Al–Cl bonds are bent toward the bridging Cl(4) so that the angles Cl(x)–Al–Cl(4) average 105.1° (with a range of 5.7°) whereas those angles which do not involve Cl(4) average 8.4° larger (with a 5.5° range). The largest angle in the former set occurs for Cl(6) which has an additional nonbonding chlorine contact across the bridge.

The distances within the $Al_2Cl_7^-$ anion seem quite reasonable, with the chlorine–chlorine contacts around the outside of the molecule, 3.47–3.59 Å, when both are bonding to the same aluminum, being reasonably close to twice the standard van der Waals radius of chlorine (3.6 Å). The chlorine neighbors of the bridging Cl(4) occur at distances up to ~0.1 Å less than just noted, which is plausible since a divalent chlorine atom should have a smaller van der Waals radius. This may also account for the bending of the terminal aluminum–chlorine bonds toward the bridge noted above although packing interactions may also be involved (*vide infra*).

The independent tellurium–tellurium distances found in the Te_4^{2+} cations, 2.662 Å in three cases and 2.67 Å in the fourth, seem quite appropriate as far as can be

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[13] R. K. McMullan, D. J. Prince, and J. D. Corbett, *Inorg. Chem.*, **10**, 1749 (1971).

TABLE IV

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $Te_4^{2+}(Al_2Cl_7^-)_2$[a]

Atom	x/a	y/b	z/c	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te(1)	0.5643 (2)	0.8441 (1)	0.0329 (1)	1.31 (2)	0.65 (1)	0.77 (1)	0.02 (1)	−0.52 (1)	0.04 (1)
Te(2)	0.6800 (1)	0.0626 (1)	0.0455 (1)	1.08 (2)	0.82 (1)	0.88 (1)	−0.11 (1)	−0.63 (1)	−0.02 (1)
Al(1)	0.8818 (6)	0.8221 (5)	0.2946 (4)	0.91 (8)	0.91 (6)	0.39 (4)	−0.03 (6)	−0.37 (4)	0.02 (4)
Al(2)	0.2613 (6)	0.9222 (5)	0.3446 (4)	0.93 (8)	0.74 (5)	0.45 (4)	0.02 (6)	−0.28 (5)	−0.02 (4)
Cl(1)	0.9073 (6)	0.8282 (5)	0.1332 (3)	1.53 (9)	1.16 (6)	0.39 (3)	0.05 (6)	−0.45 (4)	−0.00 (4)
Cl(2)	0.6727 (6)	0.8777 (5)	0.3371 (5)	0.96 (8)	1.22 (6)	1.01 (5)	0.13 (6)	−0.15 (5)	−0.19 (5)
Cl(3)	0.9524 (6)	0.6650 (4)	0.3677 (4)	1.29 (8)	0.83 (5)	0.50 (3)	0.00 (5)	−0.34 (4)	0.10 (3)
Cl(4)	0.0256 (5)	0.9714 (4)	0.3554 (4)	1.09 (7)	0.72 (4)	0.62 (4)	0.05 (5)	−0.24 (4)	−0.12 (3)
Cl(5)	0.3131 (7)	0.8630 (5)	0.4939 (4)	2.1 (1)	0.94 (5)	0.52 (4)	0.41 (6)	−0.54 (5)	0.02 (3)
Cl(6)	0.2814 (6)	0.7829 (5)	0.2384 (4)	1.54 (9)	1.06 (6)	0.51 (4)	−0.10 (6)	−0.14 (5)	−0.23 (4)
Cl(7)	0.3686 (6)	0.0806 (5)	0.3010 (5)	1.25 (8)	0.77 (5)	1.16 (5)	−0.07 (5)	−0.45 (5)	0.20 (4)

[a] Standard deviations of the least significant figures are given in parentheses. [b] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The thermal parameters have been multiplied by 10^2.

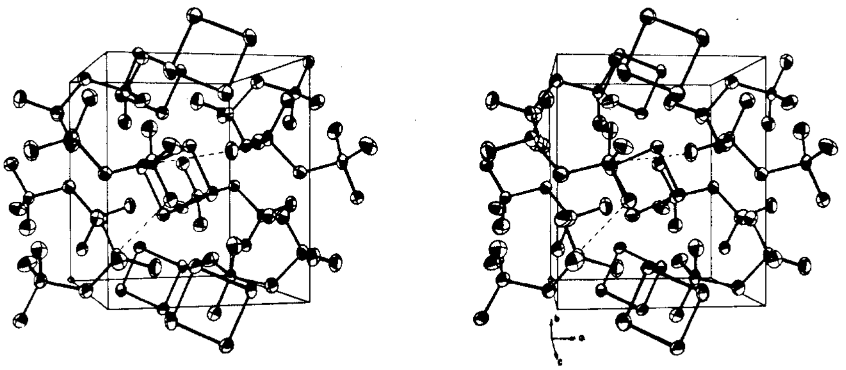

Figure 2.—Stereographic view of the structure of $Te_4^{2+}(Al_2Cl_7^-)_2$ looking down the c axis.

TABLE V

INTRAIONIC DISTANCES (Å) AND ANGLES (DEG) IN $Te_4^{2+}(Al_2Cl_7^-)_2$

Te(1)–Te(2)	2.6599 (16)[a]	Te(1)–Te(1′)	3.769 (2)
Te(1)–Te(2′)	2.6610 (18)	Te(2)–Te(2′)	3.756 (2)
Cl(1)–Al(1)	2.128 (7)	Cl(5)–Al(2)	2.115 (7)
Cl(2)–Al(1)	2.081 (8)	Cl(6)–Al(2)	2.094 (7)
Cl(3)–Al(1)	2.097 (7)	Cl(7)–Al(2)	2.099 (7)
Cl(4)–Al(1)	2.262 (7)	Cl(4)–Al(2)	2.222 (7)
Te(1)–Te(2)–Te(1′)	89.81 (4)	Al(1)–Cl(4)–Al(2)	110.8 (3)
Te(2)–Te(1)–Te(2′)	90.19 (4)	Cl(1)–Al(1)–Cl(2)	111.0 (3)
Cl(4)–Al(1)–Cl(1)	105.2 (3)	Cl(1)–Al(1)–Cl(3)	116.5 (3)
Cl(4)–Al(1)–Cl(2)	102.5 (3)	Cl(2)–Al(1)–Cl(3)	114.0 (3)
Cl(4)–Al(1)–Cl(3)	106.1 (3)	Cl(5)–Al(2)–Cl(6)	111.3 (3)
Cl(4)–Al(2)–Cl(5)	103.4 (3)	Cl(5)–Al(2)–Cl(7)	114.3 (3)
Cl(4)–Al(2)–Cl(6)	108.2 (3)	Cl(6)–Al(2)–Cl(7)	113.7 (3)
Cl(4)–Al(2)–Cl(7)	105.1 (3)		
Nonbonding <5.5 Å			
Al(1)–Al(2)	3.690 (8)	Cl(3)–Cl(4)	3.485 (7)
Al(1)–Cl(6)	3.743 (7)	Cl(3)–Cl(5)	4.287 (7)
Cl(1)–Cl(2)	3.469 (8)	Cl(3)–Cl(6)	3.691 (8)
Cl(1)–Cl(3)	3.592 (6)	Cl(4)–Cl(5)	3.404 (7)
Cl(1)–Cl(4)	3.487 (6)	Cl(4)–Cl(6)	3.498 (7)
Cl(1)–Cl(6)	3.708 (7)	Cl(4)–Cl(7)	3.432 (7)
Cl(2)–Cl(3)	3.504 (7)	Cl(5)–Cl(6)	3.474 (7)
Cl(2)–Cl(4)	3.389 (7)	Cl(5)–Cl(7)	3.540 (7)
		Cl(6)–Cl(7)	3.510 (7)

[a] Equation of plane of Te_4^{2+} cation centered at $^1/_2$, $^1/_2$, $^1/_2$ is $3.0512x + y - 10.696z + 3.3224 = 0$.

judged. In the element the distance within the spiral chain is 2.864 Å, with four more neighbors in adjacent chains at 3.468 Å.[14] An interesting comparison can be made using the covalent radii given by Pauling, 2.74 Å for the single bond and 2.54 Å for the double.[15] If these are used to calibrate the familiar Pauling bond order equation, the distance observed in Te_4^{2+} corresponds to a bond order of 1.3. The number of bonds per edge according to the MO[16] is a relatively unambiguous 1.25 for such a species $(a_{1g})^2(b_{2g})^2(e_u)^4(a_{2u})^2(e_g)^4$ although the numerical agreement with the Pauling bond order must be considered largely coincidental because of the substantial differences in the two approaches. (A MO bond order of 1.5 given[17] for the analogous Se_4^{2+} is an

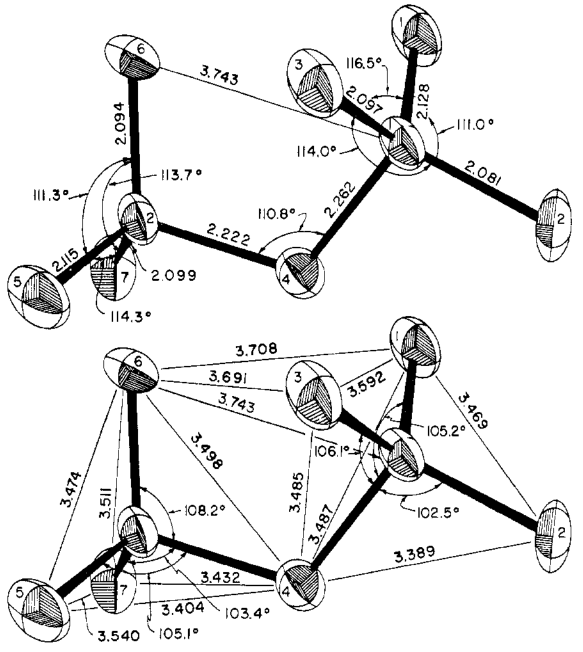

Figure 3.—Parameters of the $Al_2Cl_7^-$ ion in $Te_4^{2+}(Al_2Cl_7^-)_2$.

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TABLE VI
INTERIONIC DISTANCES (Å) IN $Te_4^{2+}(Al_2Cl_7^-)_2$ <4.1 Å

	Distance		Distance		Distance	Angle[b]
Cl(1)–Cl(3)	3.504 (7)	Cl(1)–Cl(7)	3.835 (8)	Te(1)–Cl(5)[a]	3.290 (5)	3.6
Cl(5)–Cl(6)	3.603 (7)	Cl(4)–Cl(4)	3.869 (7)	Te(2)–Cl(5)	3.390 (5)	1.9
Cl(2)–Cl(7)	3.608 (7)	Cl(2)–Cl(5)	3.876 (8)	Te(1)–Cl	3.392 (5)	6.6
Cl(3)–Cl(4)	3.639 (7)	Cl(2)–Cl(6)	3.934 (7)	Te(2)–Cl(1)	3.525 (5)	4.9
Cl(2)–Cl(5)	3.644 (7)	Cl(6)–Cl(7)	3.942 (8)	Te(1)–Cl(2)	3.699 (6)	52.8
Cl(3)–Cl(6)	3.691 (7)	Cl(1)–Cl(3)	3.967 (8)	Te(1)–Cl(7)	3.706 (6)	26.5
Cl(7)–Al(1)	3.743 (6)	Cl(5)–Cl(7)	3.999 (7)	Te(1)–Cl(7)	3.714 (6)	4.2
Cl(3)–Cl(7)	3.779 (7)	Cl(1)–Cl(4)	4.028 (8)	Te(2)–Cl(3)	3.764 (5)	48.9
Cl(2)–Al(2)	3.784 (6)			Te(2)–Cl(6)	3.793 (6)	58.1
Cl(2)–Cl(7)	3.792 (7)			Te(1)–Cl(6)		

[a] Brace denotes chlorine atom bridging edge of the Te_4^{2+} cation. [b] Angle (deg) that the line between designated atoms makes with the plane of the Te_4^{2+} cation.

energy parameter based on coefficients of occupied orbitals and so is not comparable.)

It is interesting to note that the more distorted cation found in $Te_4(AlCl_4)_2$ shows a slight splitting (9 cm^{-1}) of the otherwise degenerate (e_u) ir frequency near 130 cm^{-1}, whereas $Te_4(Al_2Cl_7)_2$, with the evidently more symmetric cation, does not show a discernible splitting. The splittings of ν_3 and ν_4 for $AlCl_4^-$ in the former compound[2] are not inconsistent with the distortions found.

Two features of the packing in the two structures are of interest: (1) the apparent secondary interaction of the $Al_2Cl_7^-$ ions to form chains and (2) some unique features of the chloride–tellurium contacts in both structures. There are no interionic chlorine–chlorine contacts which are particularly short, but the $Al_2Cl_7^-$ anions pack in such a way as to give each aluminum atom an additional chloride neighbor at 3.74–3.78 Å, which is comparable to the Al(1)–Cl(6) distance already present within the $Al_2Cl_7^-$ anion (Figure 3). Thus Cl(7) rather symmetrically approaches the Cl(1)–Cl(2)–Cl(3) face of another anion to rather normal van der Waals distances (3.78–3.84 Å), while Cl(2) is situated over the Cl(5)–Cl(6)–Cl(7) face similarly but somewhat less symmetrically (3.61–3.93 Å). The net result is to give interlocking chains of anions throughout the structure, though the interaction forces must be relatively weak. The location of these two types of interactions is marked by dashed lines in Figure 2.

The chlorine–tellurium interactions in both structures appear to have some significance. It is obvious from an inspection of Tables III and VI that the effective contact radius of tellurium in the Te_4^{2+} cation is extremely anisotropic, the ion being substantially "fatter" in the normal or π direction than it is in or near the plane of the cation. For example, in the structure of $Te_4^{2+}(AlCl_4^-)_2$ the cation is "sandwiched" approximately between the faces of two $AlCl_4^-$ anions (Figure 1), with Te–Cl distances of 3.6–3.7 Å; similar Te–Cl distances are also found in compound B more or less normal to the plane of the cation. The resultant van der Waals contact radius of 1.8–1.9 Å for tellurium compares reasonably well with 1.72 Å for the secondary neighbors in the element, and 1.7–1.8 Å derived from the Te–I bridging distances in $TeMe_2I_2$;[18,19] however it is not immediately obvious that such a correlation should be particularly significant. In contrast to the distances found for chlorine atoms at large angles to the plane, those which are positioned in or near the plane of the Te_4^{2+} cation (Table III and VI) occur at distances as low as 3.29 Å, or 0.3 Å less. Furthermore, *these closer atoms at lower angles are in both structures positioned so as to bridge all edges of the Te_4^{2+} ions*, the eight independent Te–Cl distances ranging from 3.29 to 3.52 Å.

The bridging interaction would appear to be rather specific, and inspection of the molecular orbitals involved[16] suggests that this planar coordination is quite reasonable in a bonding sense. The lowest empty MO which is not buried in the already filled π cloud of the cation is of e_u symmetry and derives from radial and tangential p orbitals lying in the plane of the cation; the resultant MO has positive π (but negative σ) overlap which would give a distribution appropriately disposed for the observed coordination. The apparent specificity of this interaction, in spite of what must be an extremely low basicity for chloroaluminate anions, suggests that the absence of coordinative bonding may in some cases be as important as an electrostatic basis for the concept of "acid stabilization."[20] In other words, the present structures appear to give a glimpse of the coordination which would precede decomposition when such an electrophilic cation might form in a more basic system.

The packing found in the two structures is sufficiently similar that it is possible to describe their interrelationship rather simply using the views of the structure shown in Figure 4. First, half of the Te_4^{2+} units are removed from the $Te_4^{2+}(AlCl_4^-)_2$ arrangement (bottom), specifically all of those centered on the *b* and *c* axes or along the left and right sides of the unit cell shown. The $AlCl_4^-$ ions occur in this projection almost as pairs and do so in space if those with *x* coordinates ~0.1 and 0.9 are translated by $\pm c/2$. The $Al_2Cl_7^-$ dimers then can be easily generated by rotation of the $AlCl_4^-$ units, elimination of one chloride between them, and translation of these parallel to *a* (left and right) partly out of the unit cell, again to fill space left by the cations eliminated. The remainder of the structure (Figure 2) is generated by unit translations of the dimeric anions.

As far as can be deduced the $Al_2Cl_7^-$ anion found in the present study seems relatively unperturbed by the cation and as such should serve as a good model for interpretation of melt spectra attributed to it.[21] The apparent sharpness of the spectra reported suggests there may not be a great deal of conformational mobility in-

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(19) The 2.2-Å value commonly given for the contact radius of tellurium is that derived for Te^{2-} and is again[2] quite inappropriate.

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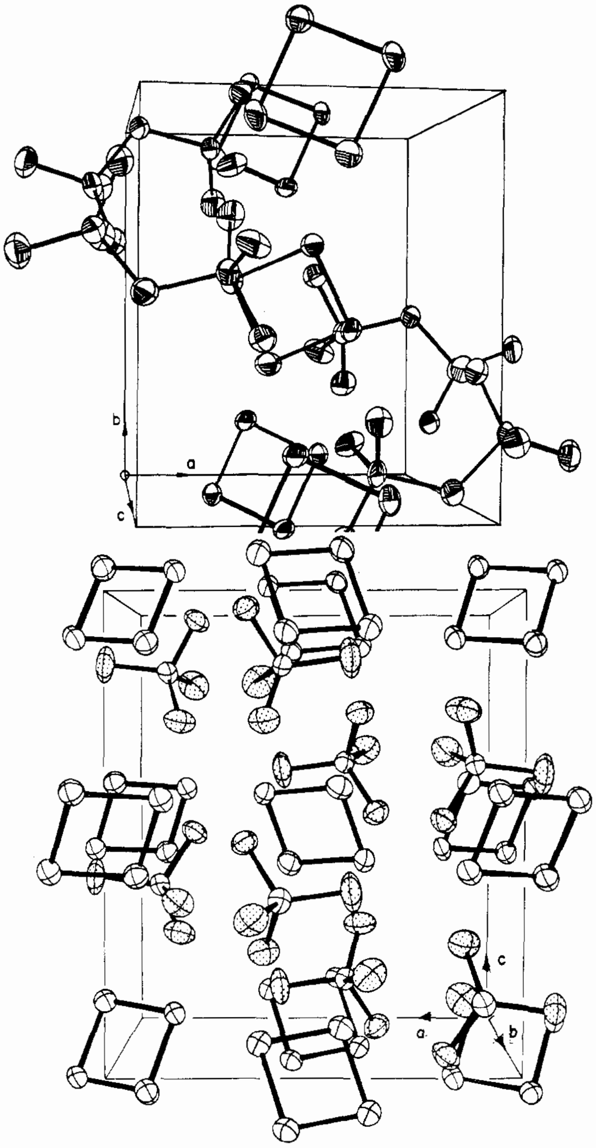

Figure 4.—A comparison of the packing in $Te_4^{2+}(AlCl_4^-)_2$ (bottom) and $Te_4^{2+}(Al_2Cl_7^-)_2$ (top) looking down the *b* and *c* axes, respectively. Anions related by unit translations have been omitted.

volved. The assumption of a linear chlorine bridge, although a great simplification for vibration assignments, is not reasonable for either $Al_2Cl_7^-$ or $Ga_2Cl_7^-$.[22]

The crystal structure of another compound apparently containing an $Al_2Cl_7^-$ anion was reported a short time ago, namely, in the compound $Pd_2(C_6H_6)_2(Al_2Cl_7)_2$,[23] although the uniqueness of the discovery was evidently not recognized. Since the original paper did not report all of the pertinent parameters for the anion, those recalculated from their positional data are shown in Figure 5 for comparison with Figure 3. The most remarkable feature of this anion is its occurrence in the *eclipsed* conformation. However, there is evidently a relatively strong coordination of Cl(1) to Pd since the Al(1)–Cl(1) distance is approximately 0.04 Å longer than the other Al–Cl distances, while the Cl(1)–Cl(2) nonbonding distance is only 3.28 Å, about 0.1 Å less than found in the present work when only one of the chlorine atoms is bridging. In the eclipsed form the bridge angle is about 5° greater and the chlorine–chlorine contacts across the bridge are almost 0.2 Å larger than in the structure reported here. (Average standard deviations were reported as 0.01 Å in Al–Cl distances and 0.5° in angles at aluminum.) It is not at all obvious why the eclipsed conformation should be more stable in the palladium compound since the staggered arrangement would obviously suffer fewer nonbonded interactions. The principal difference in the environment, the evidently strong coordination of one chlorine to the $Pd_2(C_6H_6)_2$ unit, may be indirectly responsible.

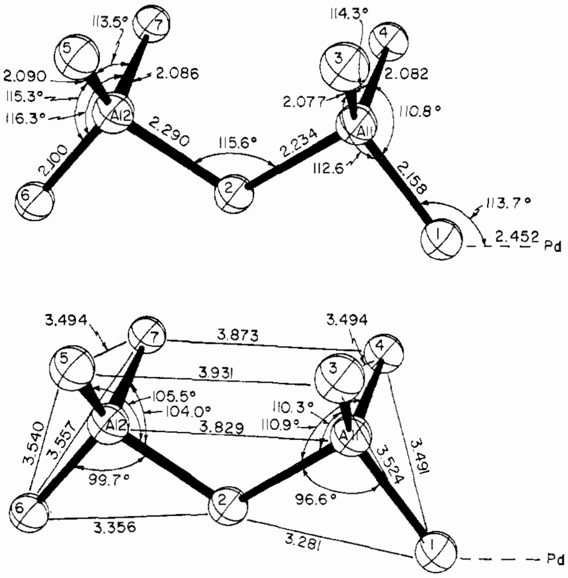

Figure 5.—Parameters of the $Al_2Cl_7^-$ ion in $Pd_2(C_6H_5)_2(Al_2Cl_7)_2$ (calculated from data in ref 23).

Acknowledgments.—The authors are particularly indebted to Dr. D. J. Prince for preliminary work on sorting out the crystalline phases and their unit cell parameters. Jim Benson and Drs. R. M. Friedman, J. C. Clardy, and R. A. Jacobson provided valuable advice with various aspects of the crystallographic work.

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