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Preparation, Spectroscopic Properties, and Crystal Structures of $Te_6(AsF_6)_4\cdot 2AsF_3$ and $Te_6(AsF_6)_4\cdot 2SO_2$: A New Trigonal-Prismatic Cluster Cation, Te_6^{4+}

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The compounds $Te_6(AsF_6)_4\cdot 2AsF_3$ and $Te_6(AsF_6)_4\cdot 2SO_2$ have been prepared by the reaction of elemental tellurium with AsF_5 in AsF_3 or SO_2 as solvent. Crystal structures of both compounds have been determined by three-dimensional X-ray counter measurements. Crystals of $Te_6(AsF_6)_4\cdot 2AsF_3$ are monoclinic with $a = 14.832$ (9) Å, $b = 12.242$ (8) Å, $c = 15.301$ (9) Å, and $\beta = 96.59$ (7)°. The structure has been refined in the space group $C2/c$ to final agreement indices $R_1 = 0.082$ ($R_2 = 0.099$) for 1720 observed ($I > 3\sigma(I)$) data and $R_1 = 0.096$ ($R_2 = 0.109$) for all 2114 independent reflections. Crystals of $Te_6(AsF_6)_4\cdot 2SO_2$ are triclinic with $a = 9.962$ (3) Å, $b = 10.681$ (4) Å, $c = 16.599$ (4) Å, $\alpha = 107.69$ (7)°, $\beta = 92.40$ (7)°, and $\gamma = 120.10$ (7)°. The structure of this compound has been refined in the space group $P\bar{1}$ to a final agreement index R_1 of 0.093 for 1829 reflections with $I > 3\sigma(I)$ and a weighted index R_2 of 0.087 for 2708 independent reflections. Both compounds contain the novel trigonal-prismatic Te_6^{4+} species and consist of Te_6^{4+} and AsF_6^- ions and either AsF_3 or SO_2. The cation in the SO_2 adduct is quite regular, within experimental error, but in the AsF_3 adduct it is slightly distorted. The Te–Te bond distances in the triangular faces range from 2.662 to 2.694 Å, while those between the faces are considerably longer, ranging from 3.062 to 3.148 Å. Electronic spectroscopic studies are also reported on the Te_6^{4+} cation and these have shown that the species, which was previously identified as "Te_n^{n+}" in highly acidic media, is actually the Te_6^{4+} cation.

Introduction

It has been known for a very long time that tellurium forms a deep red solution when dissolved in concentrated sulfuric acid.[1] Similarly, deep red solutions are also obtained when tellurium is dissolved in weak oleums or HSO_3F at room temperature.[2,3] Absorption spectra and conductometric and cryoscopic measurements on the solutions in HSO_3F led to the identification of the Te_4^{2+} cation in these media.[2,3] At the same time studies on the purple-red melts formed by the reaction of tellurium with $TeCl_4$ in molten $NaAlCl_4$ led Bjerrum and co-workers[4,5] to propose the presence of the species Te_{2n}^{n+}, which they believed to be Te_4^{2+}.

If the acid solutions described above are warmed or if the oleum is sufficiently strong (>~45% SO_3), then the colors of the solutions change from red to orange-yellow.[3,6] The same change may also be produced by addition of an oxidizing agent such as peroxydisulfate to the sulfuric acid solutions or $S_2O_6F_2$ to the HSO_3F solutions. Absorption spectra and conductometric, cryoscopic, and magnetic measurements on the solutions in HSO_3F suggested that the yellow species was tellurium in a 1+ oxidation state, and it was formulated as "Te_n^{n+}", where *n* is even as the cation was found to be diamagnetic. Furthermore, these studies also established that "Te_n^{n+}" could not be Te_2^{2+}, and was probably Te_4^{4+}, although higher molecular weight species such as Te_6^{6+} and Te_8^{8+} could not be ruled out.[3,6] In contrast, Paul and co-workers[7] concluded from similar studies in $H_2S_2O_7$ that the yellow species was Te_2^{2+}. Bjerrum[8] also concluded, from spectrophotometric measurements on solutions formed by the reduction of $TeCl_4$ with tellurium metal in $KAlCl_4$ melts buffered with KCl–$ZnCl_2$, that the species was Te_2^{2+}.

Solid compounds containing Te_4^{2+} and "Te_n^{n+}" are also well-known. It has been shown that oxidation of tellurium by $S_2O_6F_2$, AsF_5, and SbF_5 in SO_2 as solvent gives the compounds $Te_4(SO_3F)_2$, $Te_4(AsF_6)_2$, and $Te_4(Sb_2F_{11})_2$, respectively,[3] while the compounds $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$ have been

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prepared from Te–$TeCl_4$–$AlCl_3$ melts.[9,10] Yellow solids of reported empirical formula "$TeSbF_6$" and "$Te_2S_3O_{10}$", presumably containing the "Te_n^{n+}" cation, have been obtained by the reactions of tellurium with excess SbF_5 and SO_3 in SO_2, respectively.[3,6,7] One other polyatomic cation of tellurium has also been reported, Te_6^{2+}, and this has been prepared as both an AsF_6^- salt and an $AlCl_4^-$ salt.[3,9]

The structure of the Te_4^{2+} cation has been determined by crystallographic studies of both $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$.[10] In each compound the cation lies about a center of symmetry and is almost exactly square planar. It is, therefore, similar in structure to the analogous Se_4^{2+} cation.[11] However, no structural information is available on the "Te_n^{n+}" or Te_6^{2+} cations.

Recently, we have been able to prepare crystalline samples of two compounds thought to contain the "Te_n^{n+}" species. The structures of these compounds have shown that they are salts of the Te_6^{4+} cation, rather than the postulated "Te_n^{n+}" cation. Consequently, we have undertaken further electronic spectroscopic studies of these and related compounds and on solutions believed to contain "Te_n^{n+}" in order to investigate this inconsistency.

A preliminary account of the crystal structure of $Te_6(AsF_6)_4 \cdot 2AsF_3$ has already appeared in the literature.[12]

Experimental Section

Tellurium metal (99.7%) was obtained from ICN Pharmaceuticals Inc. (K & K) and was used as supplied. Arsenic pentafluoride (Ozark Mahoning Co.) was used directly from the cylinder. Antimony pentafluoride (Ozark Mahoning Co.) was doubly distilled in a Pyrex glass still, in an atmosphere of dry nitrogen. Sulfur trioxide (Allied Chemical Corp.) stabilized in a liquid form as "SULFAN" was doubly distilled under vacuum before use. Arsenic trifluoride (99%) was obtained from Research Organic/Inorganic Chemical Corp. (ROC/RIC) and was distilled under vacuum directly before use. Anhydrous sulfur dioxide (Matheson of Canada) was distilled from a glass vessel containing P_4O_{10}, over which it had been stored for at least 24 h. Sulfuric acid (95.5%, BDH) and 15–18, 20–23, and 30–33% oleums ("Baker Analyzed", J. T. Baker Chemical Co.) were used directly as supplied. The 65% oleum was prepared by distilling sulfur trioxide onto a weighed amount of commercial sulfuric acid.

$Te_6(AsF_6)_4 \cdot 2AsF_3$ and $Te_6(AsF_6)_4 \cdot 2SO_2$. In a typical experiment a large excess of arsenic pentafluoride (17.63 mmol, 3.00 g) was condensed onto tellurium metal (5.88 mmol, 0.75 g), in 30–40 cm^3 of frozen AsF_3 or SO_2 at −196 °C. Typical apparatus has been described previously.[13] The reaction mixtures were allowed to warm to room temperature. Reaction proceeded over a number of days to give a purple-red solution and a brown solid in both solvents. The color of the solution was primarily due to the presence of some Te_4^{2+}, and even when a very large excess of AsF_5 was used in these reactions, some Te_4^{2+} always formed. In both solvents the brown solid was much less soluble than the Te_4^{2+} species and so could be isolated by filtering and washing with the respective solvent until no trace of red appeared in the pale yellow solution above the brown solid. Rust brown $Te_6(AsF_6)_4 \cdot 2AsF_3$ was subsequently isolated by filtering and removal of the last traces of solvent under vacuum. Crystals of this compound were then mounted in quartz capillaries, inside a drybox equipped with a microscope. Isolation of dark brown $Te_6(AsF_6)_4 \cdot 2SO_2$ was a little more difficult as this compound easily loses SO_2 under vacuum. To overcome this difficulty, we did not completely remove the solvent so that the crystals were maintained in the presence of a little liquid SO_2. The ampule was then attached to the vacuum line and the remaining liquid SO_2 evaporated until the pressure of gaseous SO_2 inside the line and ampule was 1 atm. Pyrex capillaries were drawn off a short $^1/_4$ in. o.d. section of tube which was attached to the reaction vessel. In order to maintain constant pressure during this procedure, we opened the system to the atmosphere through a long, fine capillary in another part of the manifold. Crystals were manipulated inside the vessel until they were wedged in the capillaries. These were then sealed off, leaving the crystals in an atmosphere of SO_2.

The solid compounds of reported stoichiometry "$TeSbF_6$" and "$Te_2S_3O_{10}$" were prepared according to the published procedures.[3,6,7]

Spectra. Absorption spectra were recorded on a Cary 14 instrument using 0.5- and 1.0-cm rectangular silica cells, with a reference cell containing solvent. The solutions in oleum were made up in a Vacuum Atmospheres Corp. drybox, Model HE-43, equipped with a drying train, Model HD-373-3. Solutions in AsF_3 or SO_2 were made up in Pyrex or quartz apparatus by using conventional vacuum techniques.

Electronic diffuse reflectance spectra were recorded against MgO on a Beckman DK-2A ratio recording spectrophotometer or a Cary 14 instrument, both equipped with standard reflectance attachments. Samples were handled in the drybox and were loaded into airtight cells, similar to those described by Reid, Scaife, and Wailes.[14]

Crystal Data. $Te_6(AsF_6)_4 \cdot 2AsF_3$ is monoclinic with $a = 14.832$ (9) Å, $b = 12.242$ (8) Å, $c = 15.301$ (9) Å, $\beta = 96.59$ (7)°, $V = 2760.7$ Å^3, $Z = 4$, $d_{calcd} = 4.29$ g/cm^3, fw 1785.1, $F(000) = 3120$, λ(Mo K$\bar{\alpha}$) = 0.71069 Å and μ(Mo K$\bar{\alpha}$) = 142 cm^{-1}. The unit cell parameters were obtained from a least-squares refinement of 15 reflections in the region 20° < 2θ < 25°. Preliminary Weissenberg and precession photographs revealed the systematic absences hkl when $h + k = 2n + 1$ and $h0l$ when $l = 2n + 1$, characteristic of the space groups Cc and $C2/c$. The structure was refined successfully in the centrosymmetric space group $C2/c$ (No. 15, C_{2h}^6).[15]

$Te_6(AsF_6)_4 \cdot 2SO_2$ is triclinic with $a = 9.962$ (3) Å, $b = 10.681$ (4) Å, $c = 16.599$ (4) Å, $\alpha = 107.69$ (7)°, $\beta = 92.40$ (7)°, $\gamma = 120.10$ (7)°, $V = 1414.6$ Å^3, $Z = 2$, $d_{calcd.} = 3.87$ g/cm^3, fw 1649.4, $F(000) = 1448$, λ(Mo K$\bar{\alpha}$) = 0.71069 Å and μ(Mo K$\bar{\alpha}$) = 116 cm^{-1}. The unit cell parameters were obtained from a least-squares refinement of 15 reflections in the region 20° < 2θ < 25°. The structure was refined successfully in the centrosymmetric space group $P\bar{1}$ (No. 2, C_i^1).[15]

X-ray Intensity Measurements. $Te_6(AsF_6)_4 \cdot 2AsF_3$. A needle-shaped crystal of approximate dimensions 0.12 × 0.10 × 0.28 mm with the 0.28-mm edge, which was approximately perpendicular to the b axis, coincident with the ϕ axis of the diffractometer was examined on a Syntex P$\bar{1}$ automatic diffractometer equipped with a fine-focus Mo-anode tube and graphite monochromator. Intensities were measured by using a θ–2θ scan, the scan rate varying from 8.0 to 24.0°/min in 2θ, so that the weaker reflections were examined more slowly to minimize counting errors. Stationary-background counts, with a time equal to half the scan time for each reflection, were made at each end of the scan range. One standard reflection was checked every 50 reflections to monitor the stability and alignment of the crystal, but no significant variations were observed. A total of 2423 reflections were measured within a unique quadrant with 2θ < 50°. Subsequent averaging resulted in a total of 2141 independent reflections, 1747 of which had intensities greater than 3 times their standard error, based on counting statistics. Lorentz and polarization corrections were applied to the observed intensities.

$Te_6(AsF_6)_4 \cdot 2SO_2$. The crystal, which was a slightly irregularly shaped cube of side 0.24 mm, was mounted on the diffractometer with the c^* axis coincident with the ϕ axis of the diffractometer and the intensities were measured as described above. One standard reflection was checked every 50 reflections to monitor the stability and alignment of the crystal, but no variations were observed. A total of 2838 reflections were measured in several shells up to 2θ < 50°, resulting in 2708 reflections after averaging, of which 1829 had intensities greater than 3 times their standard error, based on counting statistics. Lorentz and polarization corrections were applied to the observed intensities.

Structure Determinations. $Te_6(AsF_6)_4 \cdot 2AsF_3$. The structure factors were put on an absolute scale by calculating accurately the statistical distribution of the E values for all intensities. The resulting reflection statistics were of the type usually found in hypercentric crystal structures. The average computed values were $|E|_{av} = 0.813$, $|E|^2_{av} = 1.002$, $|E^2 - 1|_{av} = 0.993$, $|E^2 - 1|^2_{av} = 2.099$, and $|E^2 - 1|^3_{av} = 9.372$. A total of 146 reflections had E values above 1.6. The most consistent set of signs for 137 of these was determined by using the direct-methods programs SINGEN and PHASE of the X-ray 71 system.[16] An E map, computed with the calculated phases, revealed the positions of six independent heavy atoms, three of which were at the corners of a triangle of side ~2.7 Å. These three atoms were assumed to be tellurium and the other atoms arsenic. The scattering curves for the neutral heavy atoms were corrected for anomalous dispersion by using values for the real and imaginary parts.[17] Full-matrix least-squares refinement of positional and isotropic thermal parameters gave a conventional agreement index, R_1, of 0.21. Subsequent electron density maps revealed the positions of all the light atoms. An absorption correction was applied and anisotropic temperature factors were introduced for the heavy atoms. Several cycles of least-squares

Table I. Positional and Thermal Parameters (×10^3) for $Te_6(AsF_6)_4 \cdot 2AsF_3$ [a]

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te(1)	89.1 (1)	67.3 (1)	311.4 (1)	59 (1)	32 (1)	34 (1)	1 (1)	−11 (1)	3 (1)
Te(2)	137.0 (1)	253.9 (2)	238.8 (1)	42 (1)	49 (1)	53 (1)	−6 (1)	2 (1)	5 (1)
Te(3)	49.0 (1)	259.1 (1)	380.9 (1)	68 (1)	39 (1)	27 (1)	3 (1)	−11 (1)	−8 (1)
As(1)	387.5 (2)	223.5 (2)	109.0 (2)	60 (2)	39 (1)	67 (2)	12 (1)	13 (1)	13 (1)
As(2)	391.5 (2)	47.4 (2)	367.4 (2)	56 (2)	36 (1)	46 (1)	−8 (1)	−18 (1)	1 (1)
As(3)	168.2 (2)	43.3 (2)	589.4 (2)	55 (2)	41 (1)	28 (1)	−1 (1)	−7 (1)	3 (1)

atom	x/a	y/b	z/c	B, Å^2	atom	x/a	y/b	z/c	B, Å^2
F(1)	402 (1)	270 (2)	6 (1)	72 (5)	F(9)	372 (2)	−61 (2)	429 (2)	115 (8)
F(2)	288 (2)	286 (2)	110 (2)	104 (7)	F(10)	114 (1)	156 (2)	549 (1)	81 (6)
F(3)	443 (1)	334 (2)	155 (1)	72 (5)	F(11)	162 (1)	88 (1)	693 (1)	62 (4)
F(4)	293 (2)	109 (2)	378 (2)	99 (7)	F(12)	271 (2)	98 (2)	592 (2)	94 (6)
F(5)	443 (2)	116 (2)	452 (1)	89 (6)	F(13)	171 (1)	−5 (1)	487 (1)	57 (4)
F(6)	419 (1)	149 (2)	300 (1)	88 (6)	F(14)	65 (1)	−18 (2)	595 (1)	80 (5)
F(7)	489 (1)	−17 (2)	357 (1)	87 (6)	F(15)	215 (2)	−73 (2)	633 (2)	91 (6)
F(8)	354 (2)	−23 (3)	274 (2)	139 (11)					

[a] Anisotropic temperature factors U_{ij} are expressed in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Table II. Positional and Thermal Parameters (×10^3) for $Te_6(AsF_6)_4 \cdot 2SO_2$ [a]

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te(1)	43.9 (4)	824.7 (4)	282.4 (2)	36 (2)	35 (2)	52 (2)	5 (2)	17 (2)	23 (2)
Te(2)	124.6 (4)	854.5 (4)	105.2 (2)	41 (2)	34 (2)	32 (2)	11 (2)	6 (2)	8 (2)
Te(3)	203.7 (4)	136.1 (4)	358.0 (2)	51 (2)	39 (2)	49 (2)	34 (2)	18 (2)	12 (2)
Te(4)	283.3 (4)	166.7 (4)	181.2 (2)	44 (2)	33 (2)	69 (2)	29 (2)	24 (2)	34 (2)
Te(5)	357.3 (4)	−10.6 (4)	354.3 (2)	50 (2)	89 (3)	51 (2)	54 (2)	21 (2)	43 (2)
Te(6)	439.3 (4)	22.1 (4)	179.5 (2)	34 (2)	59 (2)	61 (2)	36 (2)	26 (2)	33 (2)
As(1)	270.9 (6)	552.0 (6)	918.1 (4)	38 (3)	30 (3)	57 (3)	13 (3)	11 (3)	12 (3)
As(2)	188.3 (6)	−13.9 (6)	885.2 (4)	39 (3)	63 (3)	51 (3)	39 (3)	25 (2)	32 (3)
As(3)	251.8 (6)	−0.4 (7)	594.4 (4)	50 (3)	86 (4)	54 (3)	54 (3)	28 (3)	42 (3)
As(4)	305.7 (6)	525.9 (6)	600.8 (4)	31 (3)	35 (3)	55 (3)	8 (3)	7 (3)	7 (3)

atom	x/a	y/b	z/c	B, Å^2	atom	x/a	y/b	z/c	B, Å^2
F(1)	239 (4)	383 (4)	843 (2)	102 (11)	F(16)	353 (4)	−9 (4)	675 (2)	83 (11)
F(2)	283 (4)	712 (4)	990 (2)	110 (11)	F(17)	145 (5)	5 (6)	512 (3)	125 (16)
F(3)	158 (5)	431 (5)	970 (3)	107 (14)	F(18)	87 (4)	−141 (4)	610 (2)	67 (9)
F(4)	371 (5)	660 (5)	860 (3)	115 (13)	F(19)	294 (5)	378 (5)	523 (3)	104 (13)
F(5)	444 (5)	601 (5)	976 (3)	111 (13)	F(20)	327 (5)	690 (5)	680 (3)	101 (14)
F(6)	99 (4)	498 (5)	859 (3)	126 (13)	F(21)	422 (5)	645 (5)	551 (3)	102 (13)
F(7)	198 (4)	−156 (4)	813 (2)	87 (11)	F(22)	486 (4)	573 (4)	662 (2)	95 (10)
F(8)	169 (4)	127 (4)	954 (2)	80 (10)	F(23)	187 (4)	407 (4)	651 (2)	98 (10)
F(9)	74 (4)	−20 (4)	802 (2)	76 (10)	F(24)	141 (4)	491 (4)	541 (2)	84 (11)
F(10)	300 (5)	−12 (5)	968 (3)	108 (13)	S(1)	410 (2)	607 (2)	170 (1)	69 (4)
F(11)	354 (4)	117 (4)	866 (2)	60 (9)	S(2)	91 (2)	459 (2)	344 (2)	62 (4)
F(12)	21 (4)	−144 (4)	906 (2)	81 (11)	O(1)	332 (5)	694 (5)	186 (3)	69 (11)
F(13)	283 (5)	−127 (5)	523 (3)	102 (13)	O(2)	319 (6)	465 (7)	172 (4)	119 (18)
F(14)	235 (5)	133 (5)	669 (3)	90 (12)	O(3)	180 (5)	388 (5)	329 (2)	51 (12)
F(15)	423 (6)	138 (6)	589 (3)	123 (16)	O(4)	145 (6)	560 (6)	328 (3)	84 (17)

[a] Anisotropic temperature factors U_{ij} are expressed in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

refinement using the program CRYLSQ[16] converged to a final agreement index R_1 of 0.082 and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ of 0.099 for 1720 observed reflections. Refinement using all 2114 reflections gave an R_1 of 0.096 and an R_2 of 0.109 and resulted in an improvement in the standard deviations of the model. The weights in the final refinement were given by $w = xy$ where $x = 160/F$ if $F_o > 160$ and $y = (\sin\theta)/0.18$ if $\sin\theta < 0.18$; otherwise $x = y = 1.0$. This scheme gave unit weights to the majority of the data. Prior to the final cycle of refinement 27 reflections which were assumed to be suffering from extinction ($F_o <<< F_c$) were removed. In the final cycle of refinement the largest Δ/σ was 0.1 and a final difference Fourier map was featureless except for several peaks up to 2.7 e/Å^3 and troughs up to 1.6 e/Å^3 close to the tellurium atoms. A final comparison of the average $w||F_o| - |F_c||^2$ as a function of F_o and $\sin\theta$ revealed no systematic trends. The final positional and thermal parameters from the refinement using all of the data are given in Table I.

$Te_6(AsF_6)_4 \cdot 2SO_2$. The structure factors were put on an absolute scale by calculating the statistical distribution of the E values for all the intensities. The resulting reflection statistics were of the type usually found in hypercentric crystal structures. The average computed values were $|E|_{av} = 0.791$, $|E|^2_{av} = 0.997$, $|E^2 - 1|_{av} = 1.002$, $|E^2 - 1|^2_{av} = 2.431$, and $|E^2 - 1|^3_{av}\ 1|^3_{av} = 9.776$. A total of 173 reflections had E values above 1.4 and the most consistent set of signs for 149 of these reflections was determined as before. The E map, computed with the calculated phases, revealed the positions of six heavy atoms having a trigonal-prismatic arrangement. These atoms were assigned neutral tellurium scattering curves which were corrected for anomalous dispersion as before. Full-matrix least-squares refinement of the positional and isotropic thermal parameters gave an R_1 index of 0.36. The positions of the remaining atoms were located from subsequent difference electron density maps. An absorption correction was applied and anisotropic temperature factors were introduced for the tellurium and arsenic atoms. Refinement, with the locally written program CUDLS, led to a final agreement index R_2 of 0.087 for 2708 reflections where $w^{1/2} = (456.6 - 5.32F_o + 0.017F_o^2)^{-1}$ and an R_1 of 0.093 for the 1829 observed reflections. The largest shift Δ/σ was 0.1 in the final cycle and a final difference electron density map contained no significant features. The final positional and thermal parameters are given in Table II and the observed and calculated structure factors for both structures are available.[18]

Results and Discussion

The Te_6^{4+} cation represents the first reported example of an isolated hexaatomic trigonal-prismatic species. Only two

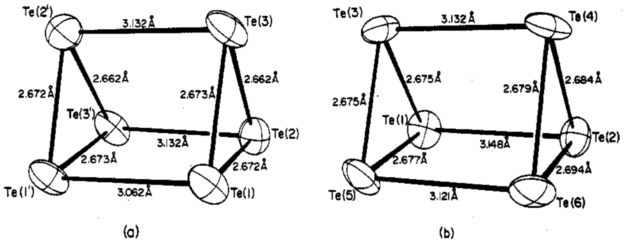

Figure 1. Structure of the Te_6^{4+} cation in (a) $Te_6(AsF_6)_4 \cdot 2AsF_3$ and (b) $Te_6(AsF_6)_4 \cdot 2SO_2$.

related molecules are known: hexamethylprismane (and related derivatives of the hypothetical prismane)[19] and the Bi_9^{5+} cation, which has a tricapped trigonal-prismatic structure.[20,21]

The bond lengths and angles found for $Te_6(AsF_6)_4 \cdot 2AsF_3$ and $Te_6(AsF_6)_4 \cdot 2SO_2$ are given in Tables III and IV, respectively, and the structures of the two cations are shown in Figure 1. The cation in the SO_2 adduct possesses no crystallographically imposed symmetry but is, within the crystallographic limits of error, quite regular. The end triangular faces are parallel to within 0.60°, while the deviations of the atoms in each of the rectangular faces from their calculated least-squares planes are ±0.006, ±0.005, and ±0.003 Å for the planes containing atoms 5346, 1562, and 3124, respectively. In the AsF_3 adduct the Te_3 group in the asymmetric unit is situated about the twofold axis, thereby giving rise to the Te_6^{4+} cation. The cation is genuinely distorted in this structure. Not only are the end triangular faces not quite parallel with a small but significant angle of 1.75° between their planes but they are also twisted relative to each other with an average twist angle of 2.72°. This results in a deviation of ±0.032 (1) Å for the atoms in the rectangular faces from their least-squares planes and this distortion is well-shown from a consideration of the angles within the rectangular faces themselves (Table III).

The Te–Te bond distances in the end faces of the cations range from 2.662 to 2.694 Å, with an average of 2.675 Å. The long bonds between the end faces range from 3.121 to 3.148 Å, with an average of 3.133 Å, excluding the slightly shorter bond in the AsF_3 adduct, which has a length of 3.062 Å and is significantly shorter (0.070 Å, 35σ) than the other long bonds. In solution the Raman spectrum is consistent with a regular trigonal-prismatic species,[22] while a recent ^{125}Te NMR study of this cation gave a $^{125}Te-^{123}Te$ coupling pattern that was also consistent with a regular trigonal-prismatic species.[23] It should be noted, however, that neither of these techniques would be expected to be sensitive enough to detect the small deviations of the prism from a regular structure that is observed in the solid state, should they also occur in solution. It seems probable, however, that the cation has a regular prismatic structure in solution and that the slight distortion of the cation in the solid state is caused by packing considerations.

Table III. Interatomic Bond Lengths (Å) and Bond Angles (deg) for $Te_6(AsF_6)_4 \cdot 2AsF_3$

	Cation		
Te(1)–Te(1')	3.062 (2)	Te(2)–Te(3)	2.662 (3)
Te(2)	2.672 (2)	Te(3')	3.132 (2)
Te(3)	2.673 (2)	Te(3)–Te(2')	3.132 (2)
Te(1')–Te(1)–Te(2)	89.8 (1)	Te(1)–Te(3)–Te(2)	60.1 (1)
Te(1')–Te(1)–Te(3)	91.6 (1)	Te(1)–Te(3)–Te(2')	88.3 (1)
Te(2)–Te(1)–Te(3)	59.7 (1)	Te(2)–Te(3)–Te(2')	90.2 (1)
Te(1)–Te(2)–Te(3)	60.2 (1)		
Te(1)–Te(2)–Te(3')	90.1 (1)		
Te(3)–Te(2)–Te(3')	89.8 (1)		
	Anions		
As(2)–F(4)	1.66 (3) [a]	As(3)–F(10)	1.68 (2) [b]
F(5)	1.65 (2)	F(11)	1.68 (2)
F(6)	1.70 (2)	F(12)	1.66 (2)
F(7)	1.68 (2)	F(13)	1.69 (2)
F(8)	1.71 (3)	F(14)	1.71 (2)
F(9)	1.67 (3)	F(15)	1.69 (2)
F(4)–As(2)–F(5)	91 (1)	F(10)–As(3)–F(11)	90 (1)
F(6)	90 (1)	F(12)	95 (1)
F(7)	179 (1)	F(13)	90 (1)
F(8)	96 (1)	F(14)	89 (1)
F(9)	95 (1)	F(15)	176 (1)
F(5)–As(2)–F(6)	89 (1)	F(11)–As(3)–F(12)	89 (1)
F(7)	89 (1)	F(13)	178 (1)
F(8)	171 (1)	F(14)	87 (1)
F(9)	93 (1)	F(15)	88 (1)
F(6)–As(2)–F(7)	91 (1)	F(12)–As(3)–F(13)	93 (1)
F(8)	86 (1)	F(14)	175 (1)
F(9)	174 (1)	F(15)	89 (1)
F(7)–As(2)–F(8)	83 (1)	F(13)–As(3)–F(14)	90 (1)
F(9)	84 (1)	F(15)	91 (1)
F(8)–As(2)–F(9)	91 (1)	F(14)–As(3)–F(15)	87 (1)
	AsF_3 Molecule		
As(1)–F(1)	1.71 (2)	As(1)–F(6)	3.04 (2)
F(2)	1.67 (3)	F(5)	3.08 (2)
F(3)	1.70 (2)	F(6')	3.18 (2)
		F(15)	3.20 (2)
F(1)–As(1)–F(2)	93.8 (11)	F(3)–As(1)–F(5)	95.3 (8)
F(3)	90.8 (9)	F(6)	79.9 (8)
F(5)	70.6 (8)	F(6')	71.0 (8)
F(6)	163.8 (8)	F(15)	140.0 (8)
F(6')	107.2 (8)	F(5)–As(1)–F(6)	97.0 (6)
F(15)	118.8 (8)	F(6')	44.1 (6)
F(2)–As(1)–F(3)	90.8 (11)	F(15)	118.7 (6)
F(5)	163.2 (10)	F(6)–As(1)–F(6')	57.3 (6)
F(6)	99.5 (10)	F(15)	75.9 (6)
F(6')	152.0 (10)	F(6')–As(1)–F(15)	118.5 (6)
F(15)	62.9 (10)		
	Interionic Distances Less Than 3.5 Å		
Te(1)–F(14)	2.90 (2)	Te(3)–F(7)	2.89 (2)
F(11)	2.92 (2)	F(10)	2.92 (2)
F(3)	2.95 (2)	F(1)	3.08 (2)
F(13)	2.95 (2)	F(12)	3.18 (2)
F(4)	3.13 (2)	F(14)	3.45 (2)
F(15)	3.48 (2)	As(1)–F(9)	3.38 (3)
Te(2)–F(8)	2.75 (4)	F(7)	3.47 (2)
F(2)	3.17 (3)		
F(12)	3.32 (2)		
F(9)	3.41 (3)		
F(4)	3.46 (2)		

[a] Mean = 1.68 Å. [b] Mean = 1.69 Å.

The Te–Te bond lengths within the triangular faces of the Te_6^{4+} cation are slightly shorter than twice the covalent radius for tellurium, 2.74 Å,[24] and may be directly compared with the Te–Te single bond lengths of 2.712 (2) Å in diphenyl ditelluride[25] and 2.703 (10) Å in *p,p'*-dichlorodiphenyl ditelluride.[26] Other Te–Te bond distances are those of 2.692 (5) and 2.720 (4) Å for the Te_3^{2-} anion in $(2,2,2\text{-crypt-}K^+)_2Te_3^{2-} \cdot NH_2CH_2CH_2NH_2$,[27] 2.802 and 2.805 Å for the Te_3^{2-} anion in K_2Te_3,[28] and 2.70 (1) and 2.74 (3) Å for the Te_2^{2-} anion in $MgTe_2$[29] and $MnTe_2$,[30] respectively. Comparison with the nearest-neighbor bond distance in tellurium metal (2.835 (2) Å) is not really justified because in this structure there are long-range interactions (3.495 (3) Å) to other atoms in neighboring helical chains, which serve to lengthen the directly bonded distances.[31] Of more importance, for comparative purposes, are the structures of the $Te_3S_3^{2+}$ and $Te_2Se_4^{2+}$ cations, both of which have boat-shaped six-membered rings with a Te–Te cross-ring bond forming a Te_3 or Te_2Se triangle.[32] The cross-ring bonds in $Te_3S_3(AsF_6)_2$, $Te_2Se_4(SbF_6)_2$, and $Te_2Se_4(AsF_6)_2$ are 2.787 (4), 2.786 (7), and 2.82 (2) Å, respectively, while the other Te–Te bonds which complete the Te triangle in $Te_3S_3^{2+}$ are 2.684 (4) and 2.665 (6) Å. The slightly longer cross-ring bonds in $Te_3S_3^{2+}$

Table IV. Interatomic Bond Lengths (Å) and Bond Angles (deg) for $Te_6(AsF_6)_4 \cdot 2SO_2$

Cation

Te(1)-Te(2)	3.148 (6)	Te(3)-Te(4)	3.132 (6)
Te(3)	2.675 (5)	Te(5)	2.675 (7)
Te(5)	2.677 (5)	Te(4)-Te(6)	2.679 (7)
Te(2)-Te(4)	2.684 (5)	Te(5)-Te(6)	3.121 (6)
Te(6)	2.694 (5)		

Te(2)-Te(1)-Te(3)	89.6 (2)	Te(2)-Te(4)-Te(3)	89.8 (2)
Te(2)-Te(1)-Te(5)	88.9 (2)	Te(2)-Te(4)-Te(6)	60.3 (1)
Te(3)-Te(1)-Te(5)	60.0 (2)	Te(3)-Te(4)-Te(6)	90.2 (2)
Te(1)-Te(2)-Te(4)	90.0 (1)	Te(1)-Te(5)-Te(3)	60.0 (2)
Te(1)-Te(2)-Te(6)	90.5 (1)	Te(1)-Te(5)-Te(6)	91.4 (2)
Te(4)-Te(2)-Te(6)	59.8 (1)	Te(3)-Te(5)-Te(6)	90.5 (2)
Te(1)-Te(3)-Te(4)	90.6 (1)	Te(2)-Te(6)-Te(4)	59.9 (1)
Te(1)-Te(3)-Te(5)	60.1 (2)	Te(2)-Te(6)-Te(5)	89.2 (1)
Te(4)-Te(3)-Te(5)	89.6 (2)	Te(4)-Te(6)-Te(5)	89.8 (2)

Anions

As(1)-F(1)	1.71 (4)	[a]	As(3)-F(13)	1.67 (5)	[b]
F(2)	1.70 (4)		F(14)	1.68 (5)	
F(3)	1.72 (5)		F(15)	1.63 (5)	
F(4)	1.70 (5)		F(16)	1.70 (5)	
F(5)	1.70 (5)		F(17)	1.74 (6)	
F(6)	1.66 (5)		F(18)	1.68 (3)	
As(2)-F(7)	1.67 (5)	[c]	As(4)-F(19)	1.65 (5)	[d]
F(8)	1.69 (4)		F(20)	1.75 (5)	
F(9)	1.71 (4)		F(21)	1.70 (5)	
F(10)	1.72 (6)		F(22)	1.77 (4)	
F(11)	1.67 (3)		F(23)	1.71 (4)	
F(12)	1.69 (4)		F(24)	1.68 (5)	

F(1)-As(1)-F(2)	174 (2)	F(13)-As(3)-F(14)	176 (2)
F(3)	84 (2)	F(15)	87 (2)
F(4)	93 (2)	F(16)	88 (2)
F(5)	94 (2)	F(17)	92 (2)
F(6)	84 (2)	F(18)	94 (2)
F(2)-As(1)-F(3)	94 (2)	F(14)-As(3)-F(15)	90 (2)
F(4)	89 (2)	F(16)	89 (2)
F(5)	91 (2)	F(17)	91 (2)
F(6)	91 (2)	F(18)	89 (2)
F(3)-As(1)-F(4)	176 (2)	F(15)-As(3)-F(16)	88 (2)
F(5)	93 (2)	F(17)	93 (2)
F(6)	86 (2)	F(18)	173 (2)
F(4)-As(1)-F(5)	90 (2)	F(16)-As(3)-F(17)	179 (2)
F(6)	90 (2)	F(18)	86 (2)
F(5)-As(1)-F(6)	178 (2)	F(17)-As(3)-F(18)	93 (2)

Anions (*Continued*)

F(7)-As(2)-F(8)	177 (2)	F(19)-As(4)-F(20)	176 (2)
F(9)	89 (2)	F(21)	89 (2)
F(10)	91 (2)	F(22)	92 (2)
F(11)	89 (2)	F(23)	92 (2)
F(12)	92 (2)	F(24)	89 (2)
F(8)-As(2)-F(9)	88 (2)	F(20)-As(4)-F(21)	87 (2)
F(10)	92 (2)	F(22)	88 (2)
F(11)	93 (2)	F(23)	92 (2)
F(12)	87 (2)	F(24)	91 (2)
F(9)-As(2)-F(10)	178 (2)	F(21)-As(4)-F(22)	87 (2)
F(11)	91 (2)	F(23)	179 (2)
F(12)	90 (2)	F(24)	90 (2)
F(10)-As(2)-F(11)	91 (2)	F(22)-As(4)-F(23)	94 (2)
F(12)	89 (2)	F(24)	177 (2)
F(11)-As(2)-F(12)	179 (2)	F(23)-As(4)-F(24)	89 (2)

SO_2 Molecules

S(1)-O(1)	1.45 (6)	O(1)-S(1)-O(2)	120 (3)
O(2)	1.33 (6)	O(3)-S(2)-O(4)	114 (4)
S(2)-O(3)	1.41 (6)		
O(4)	1.43 (7)		

Interionic Distances Less Than 3.5 Å (for SO_2 Less Than 3.0 Å)

Te(1)-F(1)	2.77 (3)	Te(4)-F(22)	2.91 (3)
F(23)	2.98 (4)	O(2)	3.05 (8)
F(6)	3.06 (5)	F(9)	3.15 (4)
F(14)	3.11 (5)	F(12)	3.18 (5)
O(4)	3.26 (7)	F(4)	3.21 (5)
F(9)	3.44 (5)	O(3)	3.44 (4)
Te(2)-F(3)	2.76 (3)	Te(5)-F(16)	2.86 (5)
F(2)	3.07 (6)	F(21)	3.14 (4)
F(8)	3.16 (5)	F(15)	3.33 (7)
F(10)	3.19 (5)	F(13)	3.37 (5)
F(9)	3.40 (5)	O(1)	3.41 (4)
F(12)	3.42 (4)	O(4)	3.43 (5)
Te(3)-F(19)	2.84 (4)	F(17)	3.45 (5)
O(3)	2.98 (5)	Te(6)-F(20)	2.89 (3)
F(18)	3.00 (4)	F(11)	3.09 (4)
F(9)	3.19 (4)	F(7)	3.13 (4)
F(21)	3.22 (4)	O(1)	3.16 (5)
F(17)	3.22 (6)	F(16)	3.20 (5)
F(22)	3.24 (4)	F(4)	3.25 (5)
		F(2)	3.38 (4)
		S(1)-F(11)	2.99 (4)

[a] Mean = 1.70 Å. [b] Mean = 1.68 Å. [c] Mean = 1.69 Å. [d] Mean = 1.71 Å.

and $Te_2Se_4^{2+}$ are probably caused by the tendency of the bond angles at sulfur and selenium to open up toward the values found in their elemental structures. It is apparent, therefore, that the bond distances within the triangular faces of Te_6^{4+} are slightly shorter than expected for a Te–Te single bond and are comparable to the bond distances in the Te_3 triangle of $Te_3S_3^{2+}$, excluding the slightly longer cross-ring bond. Interestingly, the average Te–Te bond distance found in the Te_4^{2+} cation,[10] which has a formal bond order of 1.25,[33] is 2.665 Å, close to the values found in the triangular faces of the Te_6^{4+} cation.

The bonds linking the triangles are appreciably longer than the bonds within the triangular faces and are much longer than twice the covalent radius for tellurium. They are, however, shorter than the long-range interactions which are observed in tellurium metal.

In terms of simple valence bond terminology, Te_6^{4+} can be described by the three resonance structures types 1–3. There

1

2

3

are three resonance structures of type 1, six resonance structures of type 2, in which there is a double bond in one of the triangular rings giving the bonds ~17% double-bond character, and six of type 3. The long interfacial bonds can be rationalized in terms of a large contribution from the three no-bond structures (type 1). The "short" bond distances in the triangular faces, which are comparable to those found in Te_4^{2+}, might suggest that they have some double-bond character and that resonance structures of type 2 also make some contribution to a valence bond description of the cation. However, it must be noted that in view of the very small angles of approximately 60° in the Te_3 triangles, the bonds are very likely to be bent. This would lead to slightly shorter interatomic distances. The third resonance structure (type 3) would appear to be unimportant from a consideration of the observed bond distances, so that the three resonance structures of type 1 adequately describe the structure. A regular trigonal-prismatic structure for Te_6^{4+} has also been found to give a closed-shell MO scheme on the basis of an extended-Hückel MO treatment.[34] This treatment included all overlap and employed a 5s and 5p orbital basis set. The ordering of the molecular orbitals was calculated to be (a_1') (a_2'') (e') (e'') ($2a_1'$) ($2e'$) ($3a_1'$) ($2a_2''$) ($2e''$) ($3e'$) ($3a_2''$) (a_2') ($3e''$) (a_1'') ($4e'$) ($4e''$), with the HOMO as ($3a_2''$) and the LUMO as (a_2') and a 1.52-eV gap between these levels.

The AsF_6^- anions in both structures are fairly regular octahedra, with mean As–F distances of 1.68 and 1.70 Å for

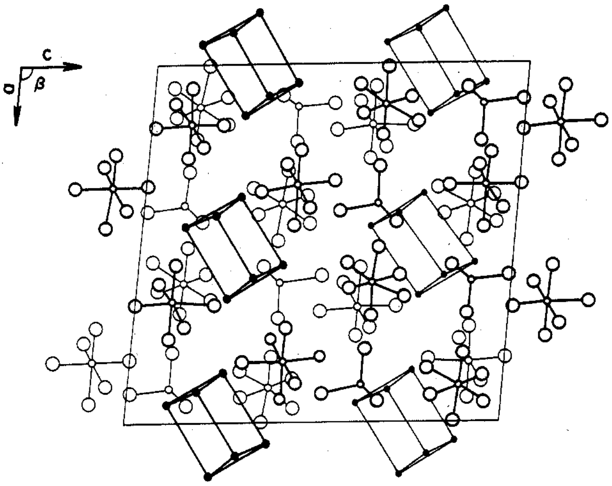

Figure 2. View of the structure of $Te_6(AsF_6)_4 \cdot 2AsF_3$ looking down the *b* axis: (solid circle) Te; (small open circle) As; (large open circle) F.

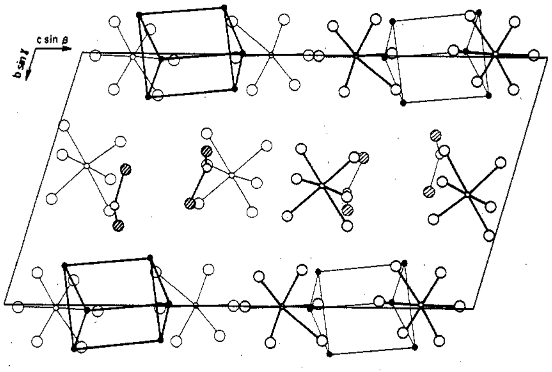

Figure 3. View of the structure of $Te_6(AsF_6)_4 \cdot 2SO_2$ looking down the *a* axis: (solid circle) Te; (small open circle) As; (large open circle) F; (medium open circle) S; (shaded circle) O.

the AsF_3 and SO_2 adducts, respectively (Tables III and IV). These distances are comparable to those found in other species containing this anion.

The AsF_3 molecule in the AsF_3 adduct has the expected AX_3E geometry,[35] with a mean As–F bond length of 1.69 (2) Å and a mean F–As–F angle of 92 (1)°. These values may be compared with values of 1.706 (2) and 1.7089 (16) Å for the bond length and 96.2 (2) and 95.9 (4)° for the bond angle obtained in two independent gas-phase electron diffraction studies of AsF_3.[36,37] Thus it seems that the bonds have the same length within experimental error but the bond angle appears to be significantly larger in the gas phase than in the present crystal structure. The overall coordination around the arsenic atom of the AsF_3 molecule is completed by four long contacts (3.05–3.20 Å) to fluorine atoms of the AsF_6^- ions, which are shorter than the sum of the van der Waals radii for arsenic and fluorine (3.35 Å).[24] The presence of these additional weak interactions is no doubt responsible for the bond angle in the solid state being significantly smaller than that found in the gas phase. The bond lengths and angles in the SO_2 molecules in the SO_2 adduct are comparable to those in $Te_2Se_8(AsF_6)_2 \cdot SO_2$ [38] and in crystalline SO_2.[39]

The packing diagrams for the two structures are shown in Figures 2 and 3. All of the interionic distances in the AsF_3 adduct are greater than 3.00 Å, with the exception of four short contacts of 2.90, 2.92, 2.95, and 2.95 Å to Te(1) and Te(1′), the atoms involved in the short bond between the triangular faces, one short contact of 2.75 Å to Te(2) and Te(2′), and two short contacts of 2.89 and 2.92 Å to Te(3) and Te(3′). In the SO_2 adduct, all interionic distances are greater than 2.95 Å, except for one short contact to each Te atom. These range from 2.76 to 2.91 Å. All interionic distances less than 3.5 Å in both structures have also been listed in Tables III and IV. To a good approximation, the structures may be regarded as consisting of discrete ions, although many of the contacts between the cations and fluorine atoms are considerably shorter than the sum of the van der Waals distances (3.55 Å). These contacts probably correspond to weak interactions and may play a role in determining the small distortions of the cation in the solid state from a perfectly regular geometry. However, in view of the uncertainties in the atomic positions of the fluorine atoms in both structures, it does not seem justifiable to discuss these short contacts in any more detail.

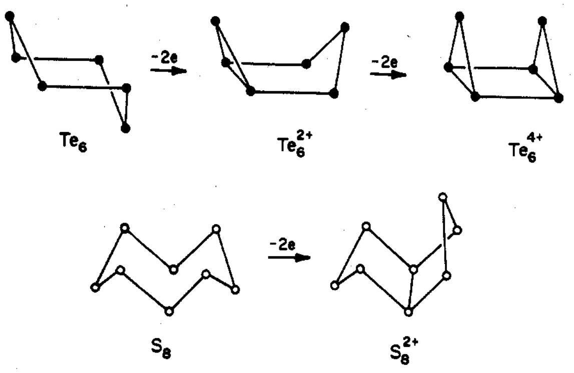

Figure 4. Comparison of structural changes in the oxidation of Te_6 and S_8 (or Se_8).

It is of interest to look at the relationship between the Te_6 molecule which, although unknown, may be assumed to have a six-membered ring in the chair formation like S_6,[40] and the $Te_3S_3^{2+}$ and $Te_2Se_4^{2+}$ cations and the Te_6^{4+} cation (Figure 4). Removal of a pair of electrons from a Te_6 type system would lead to the formation of a cross-ring bond and the adoption of a boat conformation as in the case of the $Te_3S_3^{2+}$ and $Te_2Se_4^{2+}$ cations. A similar conformational change is observed when a pair of electrons is removed from the exo–exo S_8 or Se_8 molecules[41,42] to form the S_8^{2+} and Se_8^{2+} cations,[43,44] respectively, both of which have exo–endo type structures (Figure 4). Removal of a second pair of electrons would be expected to give another cross-ring bond and the boat-shaped structure (Figure 4) which would be expected to have one Te–Te distance (the nonbonded interaction) considerably longer than the other two. In fact the molecule has the regular trigonal prism structure described above, with the 4+ charge presumably delocalized over the entire structure.

Electronic Spectra of the Te_6^{4+} Cation and the Identity of the "Te_n^{n+}" Species

It was somewhat surprising to find that the two compounds, discussed above, were salts of the Te_6^{4+} cation rather than the "Te_n^{n+}" cation. Electronic spectroscopic studies on these and the compounds of reported stoichiometry "$TeSbF_6$" and "$Te_2S_3O_{10}$" and on solutions thought to contain the "Te_n^{n+}" cation were therefore undertaken.

The band maxima and some molar extinction coefficients of the absorption spectra of solutions and the diffuse reflectance spectra of solids containing the Te_6^{4+} cation and the proposed "Te_n^{n+}" cation are given in Table V. Some of the spectra are reproduced in Figures 5 and 6. In most cases it was found impossible to prepare a solution of Te_6^{4+} free from Te_4^{2+}, even in the presence of a large excess of oxidizing agent (see Figure 5). Possible reasons for this behavior are discussed below. Even the purified solid compounds appeared to show some Te_4^{2+} contamination although this may have arisen from handling prior to their spectral examination. It is also possible that the Te_6^{4+} ion has a rather weak absorption band at ~475 nm which is, however, obscured if any Te_4^{2+} is present. Despite

Table V. Electronic Absorption and Diffuse Reflectance Spectra of Solutions and Solids Containing the Te_6^{4+} and the Proposed "Te_n^{n+}" Species[a]

sample	band max, nm (molar extinction coeff, dm^3 mol^{-1} cm^{-1})[b]					
			Absorption Spectra			
Te in ~15% oleum	248	~310 sh[f]	357	416	512 s[i]	*g*
Te in ~20% oleum	250	~310 sh	357	416	490 m[i]	*g*
Te in ~30% oleum	251	~310 sh	356	418	475 w, sh[i]	*g*
Te in ~65% oleum	252	~310 sh	356	418	~470 w, sh[i]	*g*
$Te_6(AsF_6)_4$ in SO_2	*h*	*h*	358	418	~475 w, sh[i]	*g*
$Te_6(AsF_6)_4$ in AsF_3	251 (6090)	300 (1177)	357 (413)	417 (292)	~475 w, sh[i]	*g*
"Te_n^{n+}" in HSO_3F[c]	250 (6300)	*g*	360	420	*g*	*g*
"Te_n^{n+}" in $H_2S_2O_7$ (45% oleum)[d]	280 (940)		380 (760)		480 (1120)[i]	*g*
			Reflectance Spectra			
$Te_6(AsF_6)_4\cdot 2AsF_3$	275 br		363	419	475	~550 sh
$Te_6(AsF_6)_4$[e]	275 br		365	417	472	~550 sh
"$TeSbF_6$"	270 br		363	417	470	550 sh
"$Te_2S_3O_{10}$"	270 br		365	420	~475 sh	~550 sh

[a] All spectra recorded at room temperature. [b] Molar extinction coefficients expressed in terms of concentration in g-atom of Te/L. [c] References 3 and 6. [d] Reference 7. [e] Prepared from $Te_6(AsF_6)_4\cdot 2SO_2$ by isolation under vacuum. See text. [f] Key: s = strong, m = medium, w = weak, sh = shoulder, br = broad. [g] Not reported or not observed. [h] Masked by absorption from the solvent. [i] Attributed to Te_4^{2+}; see text. The higher energy band of Te_4^{2+} at ~440 nm is not observed because of its relative intensity and overlap with bands from Te_6^{4+}.

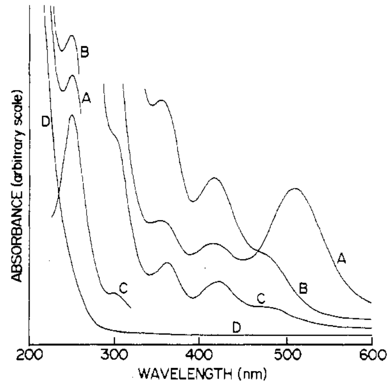

Figure 5. Absorption spectra of solutions containing the Te_6^{4+} cation and related tellurium-containing species: (A) Te dissolved in ~15% oleum; (B) Te dissolved in ~30% oleum; (C) Te_6^{4+} in AsF_3; (D) TeO_2 in ~30% oleum. Note the relative decrease in intensity of the band from Te_4^{2+} (~510 nm) between A and B and its apparent appearance in C (see text).

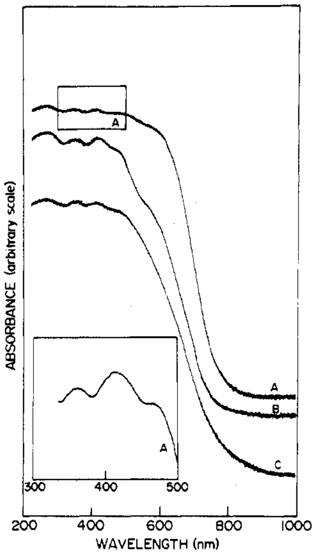

Figure 6. Electronic diffuse reflectance spectra of (A) $Te_6(AsF_6)_4\cdot 2AsF_3$, (B) "$TeSbF_6$", and (C) "$Te_2S_3O_{10}$".

the probable presence of a small amount of Te_4^{2+} in most of the solutions, the extinction coefficients of Te_6^{4+} are believed to be accurate to ±3%.

The shoulder at 300 nm in the spectrum of Te_6^{4+} in AsF_3 solution (Figure 5C), which has not been reported previously, is, in fact, present in the spectra of solutions Barr et al.[2,3] obtained by oxidizing Te in HSO_3F and in the spectra of oleum solutions where it is somewhat obscured by the absorption band due to the reduction product SO_2. Furthermore, in the solid-state spectra, a broad shoulder appears in each case at ~550 nm, and this is also attributed to the Te_6^{4+} cation.

Comparison of the solid-state and solution spectra indicates that the same species is responsible for the bands in each case. In particular, the absorption and reflectance spectra of species thought to contain "Te_n^{n+}" are identical with the absorption spectrum of Te_6^{4+} in AsF_3 and SO_2 and with the reflectance spectra of $Te_6(AsF_6)_4\cdot 2AsF_3$ and $Te_6(AsF_6)_4$—the SO_2 is lost from $Te_6(AsF_6)_4\cdot 2SO_2$ on isolation under vacuum—the crystal structures of which have been described above. The only discrepancy is with the spectral work of Paul and co-workers[7] in disulfuric acid (45% oleum). Their band maxima of "Te_n^{n+}" are somewhat different from our results in oleum. It is clear, however, that their spectrum of "Te_n^{n+}" is actually a composite of the spectra of Te_4^{2+}, Te_6^{4+}, and probably the reduction product SO_2. Also, a recent report on the electronic spectra and conductometric properties of tellurium in HSO_3Cl shows the bands characteristic of Te_6^{4+} in these solutions, not Te_4^{4+} as assumed by these authors.[45]

The original evidence for the formulation of "Te_n^{n+}" relied on a quantitative investigation of the oxidation of tellurium metal by $S_2O_6F_2$ in HSO_3F using spectroscopic procedures[3,6] and on the analytical compositions of "$TeSbF_6$" and "$Te_2S_3O_{10}$".[3,6,7] Our spectroscopic studies in oleum solutions and in SO_2 or AsF_3 with added oxidant give information on the formation and stability of Te_6^{4+} in these media, which now enables us to reinterpret the original results.

Crystalline tellurium is initially oxidized to a solution of purple-red Te_4^{2+} in oleum and in SO_2 or AsF_3, with AsF_5, SbF_5, or SO_3 as oxidizing agents (eq 1). This reaction is

$$Te(c) \xrightarrow{\text{fast}} Te_4^{2+}(s) \qquad (1)$$

relatively fast in each of these systems. In the presence of excess oxidizing agent, Te_4^{2+} is then oxidized to yellow-brown

Te_6^{4+}. There appears to be an equilibrium (eq 2) between

$$3Te_4^{2+} + \text{oxidizing agent} \rightleftarrows 2Te_6^{4+} \qquad (2)$$

Te_4^{2+} and Te_6^{4+} which is dependent on the concentration and strength of the oxidant. Thus in oleum solution, the Te_6^{4+}/Te_4^{2+} ratio increases with increasing SO_3 concentration, as shown in Figure 5, and when the SO_3 concentration is $>\sim 30\%$, the equilibrium lies far to the right and very little Te_4^{2+} is present. In SO_2 and AsF_3, with AsF_5 or SbF_5 as oxidants, Te_4^{2+} is always found together with Te_6^{4+}, even if a very large excess of oxidant is used. With the much stronger oxidant SO_3 in SO_2 some Te_4^{2+} is present if only a slight excess of oxidant is used, but with a large excess of SO_3 almost no Te_4^{2+} can be observed.

In oleum solution Te_6^{4+} is slowly oxidized to a soluble Te(IV) species, with the result that both red and yellow oleum solutions become colorless on standing for several weeks.

It should be noted that solutions of tellurium in 100% H_2SO_4 also form both Te_4^{2+} and Te_6^{4+} at ambient temperatures. After these solutions stand, however, a precipitate of TeO_2 forms, probably because of the higher concentration of water and lower solubility of the Te(IV)–oxy species under these conditions. Furthermore, if the solutions are heated to 50–60 °C, the Te_6^{4+} quickly disappears and the precipitate of TeO_2 forms considerably faster than at room temperature.[46]

The absorption spectrum of a solution formed by adding sparingly soluble TeO_2 to $\sim$30% oleum is shown in Figure 5D, in which the tail of a strong absorption band may be observed at $<\sim$270 nm. The spectra of solutions of tellurium in oleums (A and B) have the same absorption, which is consistent with the formation of a Te(IV)–oxy species in solution. This absorption is not present in the spectrum of Te_6^{4+} in AsF_3 as solvent (C).

The oxidation of Te_6^{4+} to Te(IV) does not appear to proceed in SO_2 or AsF_3 with AsF_5 or SbF_5, probably because they are not powerful enough oxidants. Somewhat surprisingly, there is no evidence for the oxidation of Te_6^{4+} to Te(IV) by SO_3 in SO_2 although in oleum, where SO_3 is the formal oxidant, oxidation is observed. This difference in behavior, which seems to be highly solvent dependent, could be kinetic in nature. Because of the equilibrium and continuous oxidation of the cationic tellurium species to Te(IV), no reliable extinction coefficients could be obtained in the oleum solutions. For this reason the extinction coefficients in disulfuric acid quoted by Paul and co-workers,[7] which are significantly different from the values originally obtained by Barr et al.[3] in HSO_3F and from our results in AsF_3, are not reliable.

If there is an equilibrium between Te_6^{4+} and Te_4^{2+} in HSO_3F, then in the original work in HSO_3F more oxidant ($S_2O_6F_2$) would have been required to give an apparently pure sample of Te_6^{4+} than the stoichiometric reaction would require, leading to the higher postulated oxidation state of 1+, that is, to the formulation of the yellow-brown species as "Te_n^{n+}".

The second line of evidence for the identification of "Te_n^{n+}" relied on the preparation of solid compounds of reported stoichiometry "$TeSbF_6$"[2,3,6] and "$Te_2S_3O_{10}$".[6,7] Both of these compounds were prepared in the presence of a large excess of their respective oxidizing agents. It is well-known that in the presence of excess SbF_5, $Sb_2F_{11}^-$ salts are usually formed rather than SbF_6^- salts. The material of stoichiometry "$TeSbF_6$" corresponds fairly closely to a compound of formula $Te_6(Sb_2F_{11})_2(SbF_6)_2$, i.e., $TeSbF_{5.67}$. However, this agreement may only be fortuitous and the material could be a mixture of several compounds. Furthermore, it has been our experience that in the reaction of tellurium with SbF_5 in SO_2, depending on the amount of SbF_5, a varying amount of the reduction product SbF_3 can be sublimed out of the solid reaction product, suggesting that some of the SbF_3 is combined with SbF_5 as $SbF_3{\cdot}SbF_5$ or in an anionic species such as $Sb_3F_{14}^-$.[47] The presence of large, bulky anions such as $Sb_2F_{11}^-$ and $Sb_3F_{14}^-$ would also explain why "$TeSbF_6$" is so insoluble in SO_2, while the AsF_6^- salt, $Te_6(AsF_6)_4$, is fairly soluble.

In the case of "$Te_2S_3O_{10}$", the $S_3O_{10}^{2-}$ anion is only one member of a series of polysulfates of general formula $(S_nO_{3n+1})^{2-}$. The material of stoichiometry "$Te_2S_3O_{10}$" probably contains a mixture of compounds but would appear to be predominantly $Te_6(S_5O_{16})_2$ on the basis of the analytical results. The anion $S_5O_{16}^{2-}$ has previously been identified by an X-ray crystallographic study of $K_2S_5O_{16}$.[48]

While the true composition of substances described as "$TeSbF_6$" and "$Te_2S_3O_{10}$" are not certain, the spectroscopic studies described above show that they both contain the Te_6^{4+} cation, with tellurium in the $^2/_3$+ oxidation state, not the 1+ state as previously thought. Of course, it is nevertheless possible that the 1+ oxidation state of tellurium can be stabilized under appropriate conditions. Bjerrum,[8] for example, has obtained evidence for a species Te_2^{2+} in $KAlCl_4$ melts buffered with KCl–$ZnCl_2$ which has an absorption spectrum quite unlike that of the Te_6^{4+} cation in highly acid media or in SO_2 or AsF_3 as solvents.

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Registry No. $Te_6(AsF_6)_4{\cdot}2AsF_3$, 62087-62-1; $Te_6(AsF_6)_4{\cdot}2SO_2$, 71076-35-2; $Te_6(Sb_2F_{11})_2(SbF_6)_2$, 71076-36-3; $Te_6(S_5O_{16})_2$, 71076-38-5; $TeSbF_6$, 53337-03-4; $Te_2S_3O_{10}$, 12503-97-8.

Supplementary Material Available: Listings of structure factor amplitudes for $Te_6(AsF_6)_4{\cdot}2AsF_3$ and $Te_6(AsF_6)_4{\cdot}2SO_2$ (29 pages). Ordering information is given on any current masthead page.

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Stability and Thermodynamics of Ligand-Free Germanium–Gold Clusters[1]

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The equilibria involving gaseous species above the condensed Au–Ge–Cu system have been investigated by the high-temperature mass spectrometric technique. The molecules Au_2, AuCu, AuGe, Au_2Ge, $AuGe_2$, Au_2Ge_2, $AuGe_3$, $AuGe_4$, Ge_2, Ge_3, and Ge_4 were shown to exist in the vapor phase above the liquid solution. Second- and third-law enthalpy changes have been determined from the experimental data for the following gaseous reactions: AuCu = Au + Cu, AuCu + Au = Au_2 + Cu, AuGe = Ge + Au, AuGe + Au = Ge + Au_2, AuGe + Cu = AuCu + Ge, Au_2Ge = Ge + 2Au, Au_2Ge + Ge = 2AuGe, $AuGe_2$ = 2Ge + Au, $AuGe_2$ + Au = 2AuGe, Ge_2 = 2Ge, Ge_2 + Au = Ge + AuGe. In addition, third-law enthalpy changes were evaluated for the following gaseous reactions: Au_2Ge_2 = 2AuGe, $AuGe_3$ + 2Au = 3AuGe, $AuGe_4$ + 3Au = 4AuGe, Ge_3 + Ge = $2Ge_2$, Ge_4 = 2Ge. The values of these reaction enthalpies have then been combined with ancillary literature data to give the dissociation energies, $D°_{298}$, of the diatomic molecules, and the atomization energies, $\Delta H°_{a,298}$, of the various polyatomic molecules assuming different molecular configurations. A preferred molecular structure along with the resulting atomization energy, $\Delta H°_{a,298}$ (kJ mol^{-1}), and the corresponding standard heat of formation, $\Delta H°_{f,298}$ (kJ mol^{-1}), respectively, are presented for the following previously unreported gaseous molecules: Au_2Ge (bent, 538 ± 12, 573 ± 12), $AuGe_2$ (bent, 535 ± 10, 581 ± 10), Au_2Ge_2 (linear, 934 ± 14, 551 ± 14), $AuGe_3$ (linear, 903 ± 20, 582 ± 20), $AuGe_4$ (trigonal bipyramid, 1307 ± 30, 559 ± 30). The previously known molecules AuCu, Ge_2, Ge_3, and Ge_4 have also been evaluated in this investigation, yielding the atomization energies of 227 ± 5, 260 ± 10, 637 ± 20, and 989 ± 22 kJ mol^{-1}, respectively. These values are within the error limits of the reported literature values. Finally, a thorough evaluation of the dissociation energy (referenced to 298 K) 272.6 ± 5.0 kJ mol^{-1} and the standard heat of formation 470.0 ± 5.0 kJ mol^{-1} has been performed on the molecule AuGe(g).

Introduction

Investigation into the physical and chemical properties of small atomic and molecular aggregates, particularly metal clusters, has been quite intensive over the last 2 decades. This interest stems from recognizing the key role these small aggregates play in such areas as homogeneous nucleation and crystal growth.[2-5] Experimental knowledge of binding energies and structures of microscopic clusters may aid the theoretician in the estimation of configurational entropies.[6] Also, small atomic metal aggregates are important in photographic systems. These dispersed metal clusters[7-10] are found to be better or worse catalysts because of size effects and geometrical arrangement of atoms. Thus an estimation of cluster geometry may assist in producing a theory that may predict the catalytic effect beforehand.

We have previously reported[11] on the stability of the molecules AuSn, Au_2Sn, $AuSn_2$, Au_2Sn_2, and $AuSn_3$ derived from Knudsen cell mass spectrometric measurements. Therefore, in keeping with this current interest in gaseous heteronuclear polyatomic molecules of gold, we have examined the gaseous molecules above the gold–germanium system. Since germanium and tin are known to form similar gaseous homonuclear polyatomic molecules, similar gaseous intermetallic molecules could be expected for the Ge–Au system, as for the Au–Sn system.[11] The Au–Ge system was also expected to offer the optimum experimental conditions for observing even higher polyatomic molecules, because of the similar vaporization enthalpies and equilibrium pressures of the component elements gold and germanium. Concomitant to this objective was the independent redetermination of the atomization energies of Ge_2, Ge_3, and Ge_4. Also, an improved evaluation of the gaseous diatomic molecule AuCu was performed, due to the incorporation of a small amount of elemental copper within the condensed mixture.

A preliminary account of the atomization energies of the four- and five-atom germanium–gold molecules has been given elsewhere.[12]

Experimental Section

The mass spectrometer employed for this investigation is a single-focusing, 12-in. radius, magnetic deflection, 90° sector, Knudsen cell, high-temperature instrument. The spectrometer[13] and the experimental procedure[13,14] have been discussed elsewhere.

The sample used in the present investigation was 0.49–0.49–0.02 M Au–Ge–Cu alloy. Commercially purchased 99.9+% germanium was obtained from Alfa Inorganics and pure reference standard copper and gold from the National Bureau of Standards. The sample was contained in a graphite cell that was inserted in a tantalum Knudsen cell, both cells having centric, close to knife-edge orifices of 1 mm diameter.

The instrument was standardized at an emission current of 1 mA, which was sustained throughout the experiment. The ions were

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