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The Poly(heptatellurium) Dication: A New Twist

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Introduction

Polyatomic main group cations are a very old and fascinating class of compounds. In the case of tellurium, Klaproth, in the late eighteenth century, noted the purple color of the element when it was dissolved in oleum, but the nature of these solutions was not understood for over 150 years.[1] The structures of a number of these tellurium cation clusters were first discovered in the 1970s.[2,3] Crystalline salts were isolated from acidic melts[4] (eq 1) or by oxidation of the element in sulfur dioxide[5] (eq 2).

$$7\mathrm{Te} + \mathrm{TeCl_4} + 4\mathrm{AlCl_3} \rightarrow 2[\mathrm{Te_4}][\mathrm{AlCl_4}]_2 \qquad (1)$$

$$6\mathrm{Te} + \text{excess } \mathrm{AsF_5} \rightarrow [\mathrm{Te_6}][\mathrm{AsF_6}]_4 \qquad (2)$$

These cationic clusters are very sensitive to nucleophiles and are only stable in the presence of weakly coordinating anions and nonbasic solvents. More recently, use of weaker Lewis acid melts[6] led to the isolation of several new polytellurium cations (eq 3), including $[\mathrm{Te_7}][\mathrm{WOBr_5}]$[7] and $[\mathrm{Te_8}][\mathrm{WCl_6}]_2$.[8]

$$8\mathrm{Te} + 2\mathrm{WCl_6} \rightarrow [\mathrm{Te_8}][\mathrm{WCl_6}]_2 \qquad (3)$$

In the course of our study of the reactions of cationic clusters with metal carbonyls,[9] we discovered a novel polymeric chain, $\{[\mathrm{Te_7}][\mathrm{AsF_6}]_2\}_\infty$, formed through an entirely different route. The synthesis and structure of this unusual cationic chain are reported here. Powder diffraction studies also confirm that a compound originally identified as "$[\mathrm{Te_6}][\mathrm{AsF_6}]_2$" in 1971 is actually the title compound as well.

Experimental Section

The starting material, $[\mathrm{Te_4}][\mathrm{AsF_6}]_2$, was prepared using literature methods.[10] Iron pentacarbonyl was purchased from Aldrich and used without further purification. Sulfur dioxide, purchased from Matheson Gas Products, was distilled onto phosphorus pentoxide and allowed to stand for 24 h before use. The reaction was carried out using a modification of the glassware and techniques described previously.[10] Infrared spectra were taken in sealed polyethylene bags. Powder patterns were determined using a Scintag XDS/2000 $\theta-\theta$ diffractometer equipped with an air-sensitive sample cell.

In a drybox, the starting material, $[\mathrm{Te_4}][\mathrm{AsF_6}]_2$ (0.407 g), was loaded into one side of a double-ampule flask containing a stir bar. One equivalent of $\mathrm{Fe(CO)_5}$ (0.060 mL) was syringed into the other side of the flask and frozen in liquid $\mathrm{N_2}$. The entire system was evacuated, and sulfur dioxide was distilled onto the $\mathrm{Fe(CO)_5}$ under static vacuum at −196 °C. The flask was flame-sealed and the frozen mixture warmed to room temperature under running water. *Caution!* Sulfur dioxide melts rather vigorously. The $\mathrm{SO_2}$ solution was then filtered onto the tellurium cation salt. There was an immediate reaction with bubbling and the formation of a brown solution, which was then stirred for 45 min. After stirring, the solution was filtered away from the large amount of elemental tellurium precipitate and allowed to stand undisturbed for 1 week. Black, lustrous, air- and moisture-sensitive polyhedra were deposited in modest yield (0.10 g, 20%). IR (Nujol): 396 (s), 126 (w), 65 (w) $\mathrm{cm^{-1}}$.

Table 1. Crystallographic Data for $\{[\mathrm{Te_7}][\mathrm{AsF_6}]_2\}_\infty$

empirical formula	$\mathrm{Te_7As_2F_{12}}$
fw	1271.02
color; habit	black polyhedra
size, mm	0.1 × 0.12 × 0.25
space group	*Pnma*
a, Å	16.208(6)
b, Å	11.300(4)
c, Å	9.620(4)
V, Å^3	1761(1)
Z	4
D_calc, g/cm^3	4.791
T, K	203
λ, Å	0.710 73
μ, cm^{-1}	15.254
R^a	0.038
$R_w{}^b$	0.044

$^a\ R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b\ R_w = \{(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)\}^{1/2}$.

Crystallographic Study

A crystal was isolated and mounted at low temperature using techniques described previously.[9] Intensity data were collected at 203 K on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation using an $\omega-2\theta$ mode. Accurate cell dimensions and a crystal orientation matrix were determined by a least-squares refinement of 25 reflections in the range $38.0 < 2\theta < 45.2°$. The crystallographic data and structure refinement are summarized in Table 1. A total of 3429 reflections were collected to a maximum 2θ value of 50°, 1827 of which were unique and 1329 of which were observed ($I > 3\sigma(I)$). The structure was solved by TEXSAN[11] /direct methods (SHELXS-86)[12] and refined using full-matrix least-squares techniques. All atoms were refined anisotropically, and an empirical absorption correction (0.583−1.000) was applied. The maximum and minimum peaks on the final difference Fourier map corresponded to 4.773 and −1.401 e Å^{-3}. Positional and isotropic thermal parameters for all atoms are listed in Table 2. A more complete list of the crystallographic data is reported in the Supporting Information.

Results and Discussion

The polymeric structure of $\{[\mathrm{Te_7}][\mathrm{AsF_6}]_2\}_\infty$ was determined via low-temperature X-ray analysis. The infinite chains of the polycation consist of six-membered tellurium rings connected through bridging tellurium atoms, in the 1- and 4-positions (Figure 1). The ring system is in the chair conformation, having an inversion center at the centroid position of the ring. The bridging tellurium, Te4, lies on a mirror plane, which is parallel to the six-membered rings, relating the rings through mirror symmetry. In this $[\mathrm{Te_7}]^{2+}$ cation, there is a range of tellurium bond distances (Table 3). The shortest bond distance in the polymer is 2.688(2) Å, which occurs between Te2 and Te3 and is slightly shorter than the sum of the covalent radii of tellurium (2.74 Å).[13] This bond distance is significantly shorter than the

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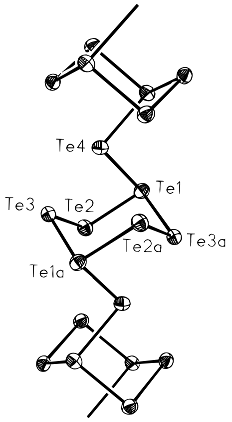

Figure 1. ORTEP diagram (70% probability ellipsoids) of a section of $[Te7]^{2+}{}_\infty$.

Table 2. Positional Parameters and Isotropic Temperature Factors for $\{[Te_7][AsF_6]_2\}_\infty$

atom	*x*	*y*	*z*	*B*(eq),[a] Å^2
Te1	0.11625(5)	0.07623(8)	0.3546(1)	1.95(4)
Te2	−0.00185(6)	−0.07258(8)	0.2443(1)	2.07(4)
Te3	−0.13066(5)	0.02432(8)	0.3785(1)	1.94(4)
Te4	−0.00967(8)	$^1/_4$	0.3950(1)	1.89(5)
As1	0.3287(1)	$^1/_4$	0.5132(2)	1.96(9)
As2	0.1877(1)	$^1/_4$	0.9772(2)	2.05(9)
F1	0.2224(7)	$^1/_4$	0.527(1)	3.1(6)
F2	0.4334(7)	$^1/_4$	0.499(1)	4.0(7)
F3	0.3344(5)	0.1429(7)	0.638(1)	3.6(4)
F4	0.3215(6)	0.3557(8)	0.387(1)	3.9(5)
F5	0.2361(8)	$^1/_4$	1.135(1)	3.5(6)
F6	0.1359(8)	$^1/_4$	0.819(1)	3.2(6)
F7	0.1208(7)	0.145(1)	1.039(1)	6.4(7)
F8	0.2512(7)	0.358(1)	0.917(1)	6.2(6)

[a] $B(\mathrm{eq}) = (8/3)\pi^2[a^2a^{*2}U_{11} + b^2b^{*2}U_{22} + c^2c^{*2}U_{33} + aba^*b^*(\cos\gamma)U_{12} + aca^*c^*(\cos\beta)U_{13} + bcb^*c^*(\cos\alpha)U_{23}]$.

Table 3. Selected Bond Distances (Å) and Angles (deg)

Te1−Te2	2.760(1)	Te2−Te3	2.688(2)
Te1−Te3	2.817(2)	Te3−Te4	3.221(2)
Te1−Te4	2.859(2)		
Te1−Te2−Te3	96.08(5)	Te2−Te1−Te3a	99.32(4)
Te1−Te4−Te1a	86.77(6)	Te2−Te1−Te4	88.60(5)
Te1a−Te3−Te2	102.06(4)	Te3a−Te1−Te4	102.26(5)

rest of the Te−Te distances in the six-membered-ring system. The Te1−Te2 distance of 2.760(1) Å and the Te1−Te3 distance of 2.817(2) Å are more typical of tellurium−tellurium bond distances. The 2.859(2) Å bond distance between the bridging tellurium, Te4, and the ring Te1 is the longest Te−Te distance in the structure. There is also a long contact between Te4 and Te3 (3.221(1) Å), which is significantly greater than a typical tellurium−tellurium bond but much less than the sum of the van der Waals radii of 4.40 Å.[13] These long interatomic distances are common in tellurium compounds, as noted previously in $[Te_8]^{2+}$ [8] and $[Te_6]^{2+}$.[14] The angles in the cationic strand are not out of the ordinary, ranging from 86 to 102° around the bonded tellurium atoms.

The two arsenic hexafluoride anions are almost perfect octahedra, with no significant pertubations in either angles or arsenic−fluorine bond distances. These distances range from 1.69 to 1.74 Å for the arsenic−fluorine bonds, and the angles vary from 89.3 to 91.3° for cis and 177.9 to 179.8° for trans positions. There are several close tellurium−fluorine contacts around the cation, creating an unusual pattern (Figure 2). The shortest of these is 2.993(9) Å (Te3−F4B), which is significantly shorter than the van der Waals sum of 3.55 Å.[13] It is apparent from the view that Te1, which is formally assigned a +1 charge, has the largest number of fluorine contacts shorter than van der Waals distances. However, the invocation of significant tellurium−fluorine bonding is probably not warranted due to the lack of variation in the As−F bond lengths in the anions. A packing diagram of $\{[Te_7][AsF_6]_2\}_\infty$, viewed down the *b* axis of the unit cell, reveals an interesting packing pattern of the cationic tellurium chains and the anions (Figure 3).

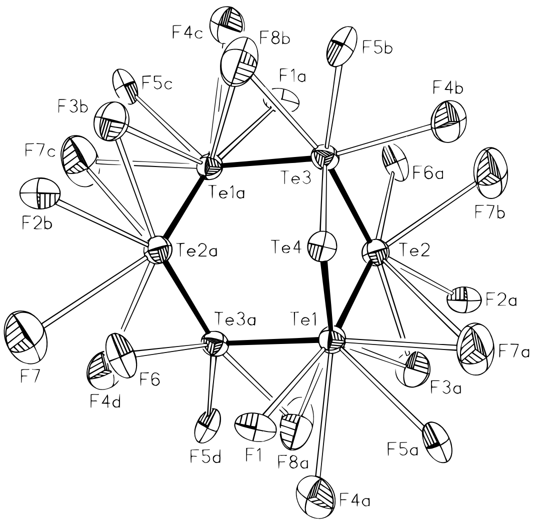

Figure 2. ORTEP diagram (50% probability ellipsoids) of anion−cation contacts in $\{[Te_7][AsF_6]_2\}_\infty$, where open bonds depict interactions less than the sum of van der Waals radii.

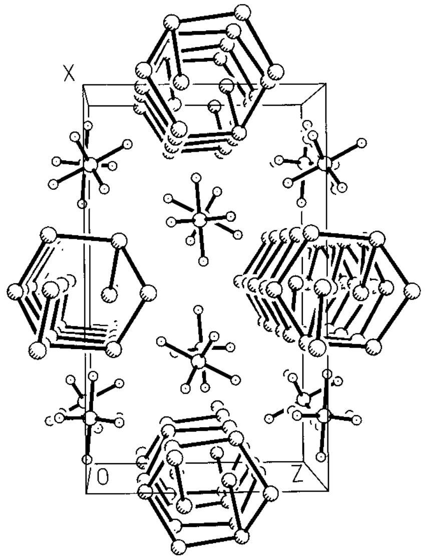

Figure 3. Packing diagram of $\{[Te_7][AsF_6]_2\}_\infty$ viewed down the *b* axis of the unit cell. Te atoms are highlighted spheres, As atoms are open spheres, and F atoms are dotted spheres.

The fate of the iron carbonyl is still not clear at this time. Infrared studies of the filtrate and the precipitate, reveal that there are at least two highly reactive iron carbonyl−tellurium cationic species present in the reaction products. Unfortunately, they have not been structurally characterized to date. It is not certain whether the title compound is formed through the reduction of $[Te_4]^{2+}$ to $[Te_7]^{2+}$ by the metal carbonyl or in a base-induced disproportionation such as eq 4. The low yield of

$$13[Te_4]^{2+} \rightarrow 7[Te_7]^{2+} + 3Te^{4+} \qquad (4)$$

the title compound and the number of uncharacterized reaction products preclude us from making a definitive proposal at this time. The title compound is insoluble in all solvents, including SO_2, AsF_3, CH_3CN, and CH_2Cl_2. It is also extremely reactive and immediately decomposes in the presence of even the

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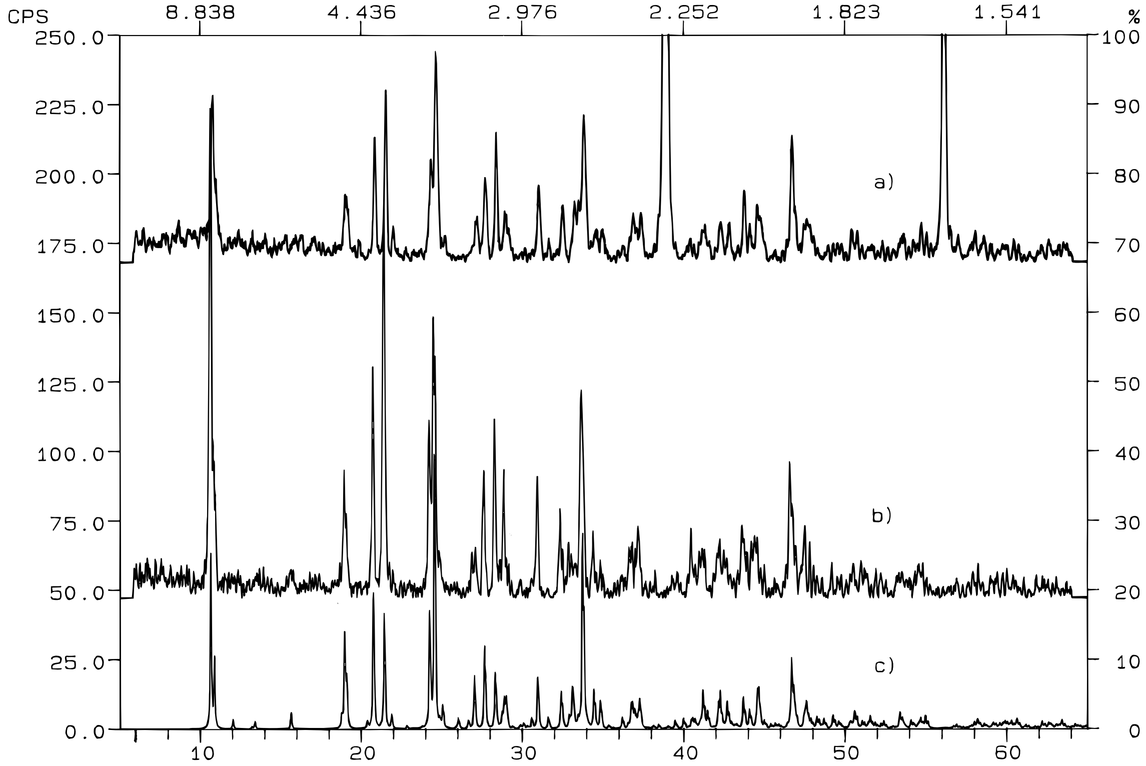

Figure 4. X-ray powder patterns of (a) $\{[Te_7][AsF_6]_2\}_\infty$ prepared as described in this paper, with NaF standard ($2\theta \approx 39$ and 56°), (b) "$[Te_6][AsF_6]_2$", prepared via literature synthesis, and (c) $\{[Te_7][AsF_6]_2\}_\infty$ generated from single-crystal parameters.

weakest nucleophile. The far-IR spectrum is dominated by the $[AsF_6]^-$ band at 396 cm^{-1}. However there are two weak bands at 127 and 65 cm^{-1}, which are most likely due to Te−Te stretching modes.

The structure of $\{[Te_7]^{2+}\}_\infty$ is somewhat reminiscent of the $[Se_6I]_n^+$ cation reported previously.[15] However, the selenium−iodine monocation contains 42 valence electrons, versus 40 for the $[Te_7]^{2+}$ cation. This difference is immediately apparent in the bridging iodine linking the selenium rings, where the bond angle at the iodine atom is 173°. This angle implies three lone pairs around the iodine center occupying equatorial positions, in a pseudo trigonal bypyramidal geometry. This coordination environment is in contrast to the linking tellurium atom (Te4) in $\{[Te_7]^{2+}\}_\infty$, which only has two lone pairs and an acute bonding angle of 86.77(6)°. The Se−I bonds in $[Se_6I]_n^+$ are also quite long, suggesting a bond order of approximately $^1/_2$. In contrast, the connecting Te−Te bond lengths in $[Te_7]^{2+}$ are all typical of single-bond distances. There is another complex $\{[Te_7][WOBr_5]\}_\infty$ containing a polymeric $\{[Te_7]^{2+}\}_\infty$ cation, previously reported, but the structure is very different from the one presented here.[7] The previous structure contains a square planar, four-coordinate, hypervalent tellurium center with a wide variation in the tellurium bond distances, ranging from 2.74 to 2.97 Å. This contrasts with the $\{[Te_7]^{2+}\}_\infty$ cation described in our paper, which contains no hypervalent centers.

Previous work on tellurium polycations indicated the presence of another insoluble phase generated from the oxidation of excess tellurium powder by AsF_5.[16]

$$6Te + 3AsF_5 \rightarrow \text{“}[Te_6][AsF_6]_2\text{”} + AsF_3 \qquad (5)$$

The intractability of this solid prevented its identification, but it was suggested that its formula was $[Te_6][AsF_6]_2$. A similar phase was also described in $Te/TeCl_4/AlCl_3$ melts.[17] We prepared this tellurium cation using the literature procedure[16] and determined its X-ray powder pattern. We also determined the powder pattern of the title compound. The observed diffraction patterns are identical with each other and with the pattern calculated from the data of the single-crystal determination[18] (Figure 4). Thus we suggest that the previously reported "$[Te_6][AsF_6]_2$" is in reality $\{[Te_7][AsF_6]_2\}_\infty$. However, the literature preparation is a better synthetic procedure, as it is simpler and results in higher yields.

Conclusions

The polymeric cation $\{[Te_7][AsF_6]_2\}_\infty$ has been prepared from reaction of $[Te_4][AsF_6]_2$ and iron carbonyl in SO_2. It has been characterized by single-crystal and powder X-ray diffraction and has an unusual structure of interconnected tellurium rings. It is substantially different from another isomer of $\{[Te_7][WOBr_5]_2\}_\infty$ prepared from a melt reaction. However, it is structurally similar to $[Se_6I]_\infty^+$ but has less two electrons, leading to significant bonding differences. The powder pattern of $\{[Te_7][AsF_6]_2\}_\infty$ is identical to that of the previously reported "$[Te_6][AsF_6]_2$", leading to the resolution of a longstanding mystery in tellurium cation chemistry. These results also strongly suggest that other, more complex tellurium cation systems may be discovered.

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Supporting Information Available: Complete tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, X-ray powder *d* spacings, and Te−F distances (5 pages). Ordering information is given on any current masthead page.

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