X-Ray Crystal Structure of $Te_6(AsF_6)_4\cdot 2AsF_3$. A New Trigonal Prismatic Cluster Cation Te_6^{4+}

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Summary A single crystal *X*-ray diffraction study has shown that $Te_6(AsF_6)_4\cdot 2AsF_3$ contains the novel trigonal prismatic cluster Te_6^{4+}.

In our earlier studies we have shown that tellurium can be oxidised by AsF_5 and by SbF_5 in SO_2 solution to give the cations Te_6^{2+}, Te_4^{2+}, and Te_n^{n+}.[1] In attempting to prepare a crystalline sample of $Te_n(AsF_6)_n$ we obtained the compound $Te_6(AsF_6)_4\cdot 2AsF_3$ and have determined its structure by *X*-ray crystallography.

The compound $Te_6(AsF_6)_4\cdot 2AsF_3$ may be prepared as a brown crystalline solid by the reaction of tellurium with AsF_5 in AsF_3 as the solvent. In liquid sulphur dioxide the similar compound, $Te_6(AsF_6)_4\cdot SO_2$ can be obtained but the crystals decompose slowly by losing SO_2. However, if this material is recrystallized from AsF_3 brown crystals, identical with those produced by the direct reaction, are obtained.

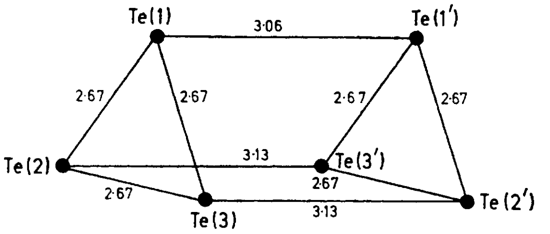

Figure 1. The structure of the Te_6^{4+} cation

Crystal data were obtained from precession and Weissenberg techniques using Mo-K_α radiation: $As_3F_{15}Te_3$, M 892·7; monoclinic, a = 14·832(9), b = 12·242(8), c = 15·30(1) Å, β = 96·56(8)°, U = 2760·7 Å^3, space group $C2/c$ (No. 15, C_{2h}^6),[2] $Z = 8$. Intensity data were collected using a Syntex P$\bar{1}$ automatic diffractometer with graphite monochromated Mo-K_α radiation giving 2384 independent reflections, 1747 of which had $I > 3\sigma(I)$. The positions of the 6 heavy atoms were located using direct methods and all the light atoms from an electron density map. Full-matrix least-squares refinement of positional and isotropic thermal parameters has led to an R factor of 0·10. Refinement is being continued.

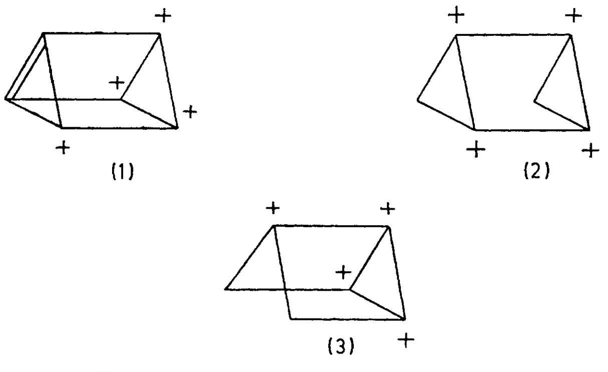

Figure 2. Resonance structures for Te_6^{4+}

The unit cell contains four discrete Te_6^{4+} cations, one of which is shown in Figure 1, sixteen discrete octahedral AsF_6^- anions, and eight AsF_3 molecules.

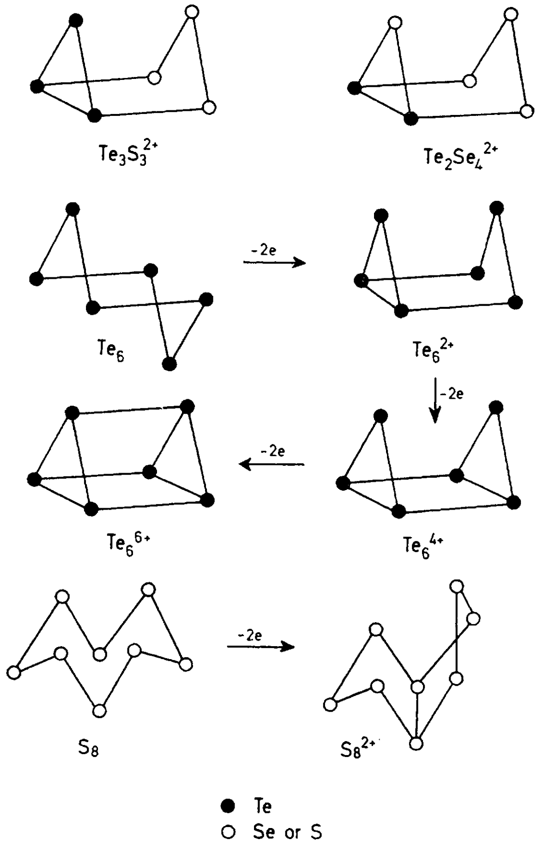

Figure 3. Structures related to Te_6^{4+}

The cation Te_6^{4+} represents the first example of a simple hexa-atomic trigonal prism molecule. The only two known related molecules are prismane C_6H_6[3] and the cluster cation Bi_9^{5+}.[4,5] which has a tricapped trigonal prism structure. A simple valence bond structure containing only single bonds can be written for prismane but Te_6^{4+} can only be described in valence bond terminology by several resonance structures. For example, there are six resonance structures of the type (**1**) (see Figure 2), in which there is a double bond in one of the triangular rings. Thus each of these bonds may be said to have 17% double bond character which is consistent with the observation that these bonds are shorter than the bonds linking the triangles. Indeed the bond lengths within the triangles are similar to those found in Te_4^{2+} which can be described as having 25% double bond character.[6] The bonds linking the triangles are appreciably longer than a Te–Te single bond, *e.g.* 2·74 Å for diphenyl ditelluride.[7] These long Te–Te bonds can be rationalized in terms of three no-bond structures such as (**2**). A third possible type of resonance structure (**3**) would appear, from the observed bond distances, to be unimportant.

The relationship between the structures of $Te_2Se_4^{2+}$, $Te_3S_3^{2+}$,[8] and possible structures for Te_n^{n+} and Te_6^{2+} is of interest. The first two have boat-shaped six-membered rings with one cross-ring bond forming a three-membered Te_3 or Te_2Se ring (Figure 3).[8] It seems reasonable to assume that Te_6^{2+} might have the same structure. Removal of an electron pair then leads to the formation of an additional bond to complete the second Te_3 triangle to give Te_6^{4+}. Removal of a second electron pair could plausibly lead to the formation of a third bond between the triangles, giving Te_6^{6+} the structure of which is not known. The trigonal prism has been suggested as a possible shape for Te_n^{n+} for which n has not yet been determined.

Comparison of the structure of Te_6^{4+} with the unknown Te_6 molecule, which may be assumed to have a six-membered ring in the chair formation like S_6,[9] is also of interest. Removal of a pair of electrons to give Te_6^{2+} leads to the formation of a cross-ring bond and the adoption of a boat conformation. A similar conformational change is observed when a pair of electrons is removed from S_8[10] to give S_8^{2+} [11] which has an *exo-endo* conformation.

The two crystallographically different AsF_6^- groups are regular octahedra with a mean As–F distance of 1·68 Å which is similar to that found in other AsF_6^- salts. The AsF_3 group has the expected AX_3E geometry with mean As–F bond lengths of 1·69 Å and mean F–As–F angles of 92°. The F–As–F angles are expected to be greater than the corresponding angles in SbF_3 (88·7°)[12] as the smaller electronegativity difference between arsenic and fluorine will lead to greater bond–bond repulsions.[13]

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