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Redetermination of Te$_6$[AsF$_6$]$_4$·2SO$_2$ at 125 K

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Key indicators

Single-crystal X-ray study
$T = 125$ K
Mean σ(S–O) = 0.005 Å
R factor = 0.029
wR factor = 0.077
Data-to-parameter ratio = 17.5

For details of how these key indicators were
automatically derived from the article, see
http://journals.iucr.org/e.

The crystal structure of the title compound, hexatellurium tetrakis(hexafluoroarsenate) sulfur dioxide disolvate, Te$_6$[AsF$_6$]$_4$·2SO$_2$, was first determined by Burns, Gillespie, Luk & Slim [*Inorg. Chem.* (1979), **18**, 3086–3094]. We present here a redetermination at low temperature and of improved precision, in which all atoms were refined with anisotropic displacement parameters.

Comment

Burns *et al.* (1979) presented the remarkable homopolyatomic cation Te$_6$$^{4+}$, made by oxidizing elemental tellurium with a large excess of arsenic pentafluoride in liquid sulfur dioxide or in arsenic trifluoride. Te$_6$$^{4+}$ is the only representative of a 32-electron cluster with a trigonal prismatic shape and the main group element cluster with the highest charge per atom known so far. The dark-brown crystals of Te$_6$[AsF$_6$]$_4$·2SO$_2$ and Te$_6$[AsF$_6$]$_4$·2AsF$_3$ are highly sensitive to air and moisture, and the SO$_2$-containing compound easily loses its sulfur dioxide when kept without an SO$_2$ atmosphere. Burns *et al.* (1979) performed the X-ray data collection at ambient temperature with crystals sealed in glass capillaries. The octahedral [AsF$_6$]$^-$ anions showed a tendency to extreme vibrations and to rotational disorder. A refinement with anisotropic displacement factors for the F, S and O atoms was not possible.

In our studies on heteronuclear main group element clusters, we obtained crystals of Te$_6$[AsF$_6$]$_4$·2SO$_2$ and redetermined the crystal structure. We used the cold-oil method of Kottke & Stalke (1993) for isolating and mounting the selected crystal and collected intensity data at low temperature with the crystal embedded in a drop of frozen glassy perfluorinated polyether. The precision of the crystal structure determination was thereby significantly enhanced. However, even at 125 K the displacement parameters of the F atoms
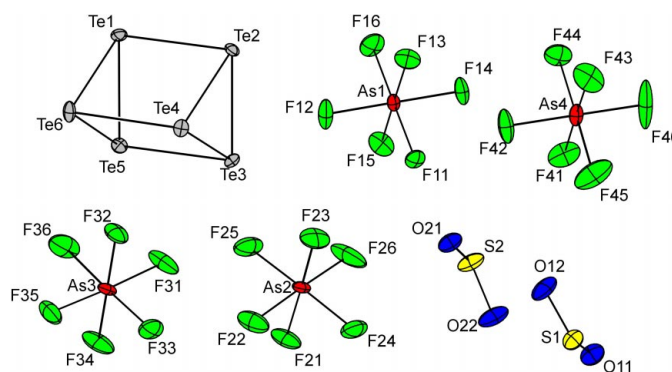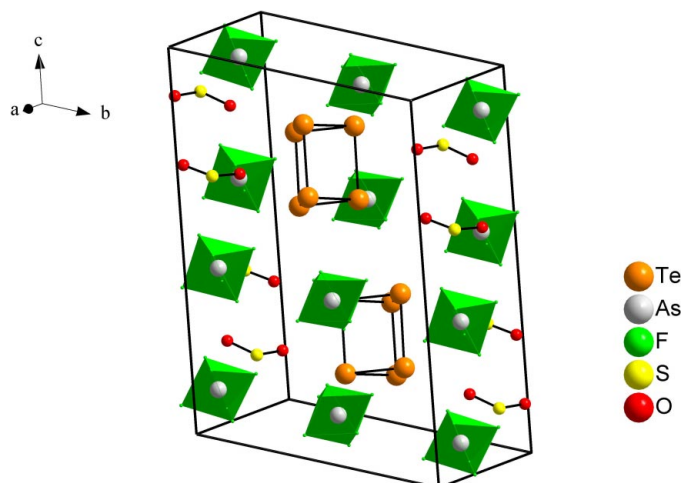

Figure 1
The trigonal prismatic Te$_6$$^{4+}$ ion, the octahedral [AsF$_6$]$^-$ ions and the sulfur dioxide molecules shown with 50% displacement ellipsoids and atom numbering.

Figure 2
The unit-cell contents of Te₆[AsF₆]₄.2SO₂

show large anisotropy. The overall precision of positional parameters, bond lengths and angles was improved by one order of magnitude. There is no substantial change in the unit cell constants or in the geometrical parameters of the ions. Bond lengths and angles of the trigonal prismatic Te_6^{4+} cationic cluster, the octahedral $[AsF_6]^-$ anions, and the SO_2 molecules are essentially identical to those determined by Burns *et al.* (1979). The bonding situation in this trigonal prismatic cluster was the focus of theoretical studies for some time; the long Te—Te bonds parallel to the pseudo-threefold axis of the Te_6 prism have been explained by a π^*–π^* six-center four-electron bond (Lyne *et al.*, 1992; Brownridge *et al.*, 2000)

Because of the high charge of the polycationic cluster, there are short intermolecular contacts present in the crystal structure. Between the Te atoms of the Te_6^{4+} cation and the O atoms of the SO_2 molecules and the F atoms of the $[AsF_6]^-$ anions distances as short as 2.857 Å are observed. Shorter secondary Te···F bonds, ranging from 2.80 Å, are observed only in the structure of $Te_4[SbF_6]_2$ (Cardinal *et al.*, 1982). Hexafluoroarsenates of other polycations show intermolecular contacts that are slightly longer: $Te_4[AsF_6]_2$·SO_2 (Beck *et al.*, 2003): shortest Te···F = 3.00 Å, shortest Te···O = 3.11 Å; $Te_7[AsF_6]_2$ (Drake *et al.*, 1996): shortest Te···F = 2.99 Å; $Te_2Se_8[AsF_6]_2$·SO_2 (Collins *et al.*, 1987): shortest Te···F = 2.99 Å, shortest Te···O = 3.29 Å.

Although the cation almost fulfills D_{3h} symmetry there are some slight distortions which were attributed by Burns *et al.* (1979) to crystal packing forces. Since the Te_6^{4+} cation has a non-degenerate fully occupied HOMO (Lyne *et al.*, 1992), no Jahn–Teller distortion is expected. Since these distortions are again observed in the redetermined crystal structure, it is very likely that the strong cation–anion interactions are responsible for the distortions and the symmetry reduction.

Experimental

The reactions were carried out in 'H-tube' vessels as previously described (Cardinal *et al.*, 1982). Sulfur dioxide was dried by storing

Crystal data

$Te_6[AsF_6]_4$·$2SO_2$	$Z = 2$
$M_r = 1649.4$	$D_x = 3.962$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.9163$ (1) Å	Cell parameters from 12 374
$b = 10.593$ (1) Å	reflections
$c = 16.375$ (1) Å	$\theta = 2.0$–$27.5°$
$\alpha = 106.92$ (1)°	$\mu = 11.32$ mm^{-1}
$\beta = 93.83$ (1)°	$T = 125$ (1) K
$\gamma = 119.716$ (2)°	Prism, light brown
$V = 1382.4$ (2) Å^3	$0.30 \times 0.20 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer	6359 independent reflections
ω and φ scans	6036 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{int} = 0.070$
($HABITUS$; Herrendorf &	$\theta_{max} = 27.5°$
Bärnighausen, 1993)	$h = -12 \rightarrow 12$
$T_{min} = 0.083$, $T_{max} = 0.104$	$k = -13 \rightarrow 13$
12 374 measured reflections	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$+ 6.4919P]$
$wR(F^2) = 0.077$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{max} = 0.012$
6331 reflections	$\Delta\rho_{max} = 1.25$ e Å^{-3}
361 parameters	$\Delta\rho_{min} = -1.62$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Te1—Te5	2.6946 (4)	Te3—Te4	2.6892 (4)
Te1—Te6	2.6963 (4)	Te3—Te5	3.1340 (4)
Te1—Te2	3.1493 (4)	Te4—Te6	3.1027 (4)
Te2—Te4	2.7019 (4)	Te5—Te6	2.6895 (4)
Te2—Te3	2.7021 (4)		
Te5—Te1—Te6	59.853 (11)	Te3—Te4—Te2	60.161 (11)
Te5—Te1—Te2	89.735 (11)	Te3—Te4—Te6	90.196 (11)
Te6—Te1—Te2	88.730 (12)	Te2—Te4—Te6	89.605 (11)
Te4—Te2—Te3	59.687 (11)	Te6—Te5—Te1	60.105 (11)
Te4—Te2—Te1	90.276 (11)	Te6—Te5—Te3	89.527 (11)
Te3—Te2—Te1	89.938 (11)	Te1—Te5—Te3	90.400 (11)
Te4—Te3—Te2	60.152 (11)	Te5—Te6—Te1	60.042 (11)
Te4—Te3—Te5	89.804 (11)	Te5—Te6—Te4	90.466 (12)
Te2—Te3—Te5	89.921 (11)	Te1—Te6—Te4	91.380 (12)

The largest difference peak is 1.25 Å from Te5 and the largest difference hole is 0.85 Å from Te4.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *COLLECT* and *DENZO* (Otwinowski & Minor, 1997); data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure:

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*SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Berndt *et al.*, 2001); software used to prepare material for publication: *PARST* (Nardelli, 1995).

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