Triiodotelluronium Hexafluoroarsenate $TeI_3[AsF_6]$.
The Crystal Structure of the Hemi SO_2 Solvate and
the Structure Relation to the Unsolvated Form

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$TeI_3[AsF_6]$ is formed from Te, I_2, and AsF_5 in liquid SO_2. At room temperature light red crystals of the hemi SO_2 solvate $TeI_3[AsF_6] \cdot 0.5\ SO_2$ are obtained from a saturated solution. The crystal structure (orthorhombic, *Pnnm*, $a = 1107.41(2)$, $b = 1866.58(3)$, $c = 1207.00(2)$ pm at 123 K, $Z = 8$) consists of pyramidal TeI_3^+ cations (Te-I = 267 pm), almost regular octahedral $[AsF_6]^-$ anions and of SO_2 molecules which show disorder for the O atom positions. A remarkable feature of the crystal structure is the arrangement of the TeI_3^+ ions that are pairwise associated, facing each other with the I atoms and forming large voids between each other. This causes the significantly lower density of $TeI_3[AsF_6] \cdot 0.5\ SO_2$ (3.88 Mgm^{-3}) in comparison to the unsolvated form (4.20 Mgm^{-3}, Passmore 1981).

Key words: Triiodotelluronium(+), Hexafluoroarsenate(V)(–), Sulfurdioxide Solvate,
      Crystal Structure

Introduction

Chalcogen tetrahalides EX_4 (E = S, Se, Te; X = F, Cl, Br, I) can act both as Lewis bases and as Lewis acids. Strongly acidic halide ion acceptors withdraw halide ions and transform EX_4 to EX_3^+ ions. Salt like compounds containing EX_3^+ cations have been prepared and characterized with various counterions [1 – 3, and references therein]. Iodides, however, are rare and only $SeI_3[AsF_6]$ [4], $SeI_3[SbF_6]$ [4], $TeI_3[AsF_6]$ [5], $TeI_3[SbF_6]$ [4], $TeI_3[AlI_4]$ [6], $TeI_3[GaI_4]$ [7], and $TeI_3[InI_4]$ [7] are known. With the aim to obtain cationic species with a high chalcogen content, *e.g.* the Te analogue of Se_6I_2 $[AsF_6]_2$ [8], we performed reactions of Te, I_2, and AsF_5 in liquid sulfur dioxide and succeeded in the isolation of a new crystalline phase, the SO_2 solvate of $TeI_3[AsF_6]$. Its crystal structure and the structure relation to the already known unsolvated form are presented here.

Experimental Section

Preparation of $TeI_3[AsF_6] \cdot 0.5\ SO_2$

The reactions were carried out in "H-tube" vessels as previously described [9, 10]. Sulfur dioxide was stored for several days over P_4O_{10} and freshly condensed into the reaction vessel. Iodine was mortared with P_4O_{10} and sublimated; tellurium was sublimated in a closed quartz vacuum ampoule. All glassware was flame dried in vacuum before use, and handling of the starting materials was performed in an argon filled glove box to exclude humidity.

In a typical experiment, 540 mg of I_2 (4.26 mmol) and 352 mg of Te (2.75 mmol) were filled in one bulb of a H-tube vessel in a glove box. 400 mg of AsF_5 (2.35 mmol) and 40 ml of liquid SO_2 were condensed onto the solids using a cold bath. The closed vessel was allowed to warm to room temperature. After 15 min the solution obtained a reddish-brown colour. After 2 h of stirring the solution was filtered from the solids through the glass frit into the second bulb. Keeping the solution for 3 d at room temperature caused a precipitation of light-red, dark red and light-brown crystals.

Crystal structure determination

A light-red crystal was selected from the precipitate using the cold-oil method [11]. A crystal of the dimensions $0.22 \times 0.17 \times 0.10$ mm³ was used for all crystallographic measurements embedded in a drop of frozen, glassy perfluorinated ether. The data set was collected with a BRUKER-NONIUS Kappa-CCD diffractometer at 150 K. Examination of the reciprocal lattice revealed the crystal class *mmm*. The absence of integral extinctions and the presence of zonal

Table 1. Crystallographic data, data collection and refinement for TeI$_3$[AsF$_6$]·0.5SO$_2$.

Formula	As$_2$F$_{12}$I$_6$O$_2$STe$_2$
M$_r$ per formula unit	1458.5
Crystal system, space group	orthorhombic, *Pnnm*
Lattice constants	$a = 1107.41(2)$ pm
	$b = 1866.58(3)$ pm
	$c = 1207.00(4)$ pm
Unit cell volume	$V = 2494.95(7) \cdot 10^6$ pm^3
Number of formula units	$Z = 4$
Density (calc.)	$\rho = 3.883$ Mg·m^{-3}
Absorption coefficient	$\mu = 125.6$ cm^{-1}
Temperature	$T = 150$ K
2θ Range	$4° < 2\theta < 55°$
Measured reflections	29086,
	$-14 < h < 14$,
	$-24 < k < 24$,
	$-15 < l < 15$
Unique reflections; R$_{int}$	2999; 8.6%
Refined parameters	138
Ratio reflections/parameters	21.7
R Factors	$wR(F^2) = 6.97\%$
	$R(|F|) = 4.61$ % for all
	reflections
	$R(|F|) = 3.67$ % for 2624
	reflections with $I > 2\sigma(I)$
Goodness of fit	1.122
Residual electron density (max/min.)	$+1.78/-0.98$ e/10^6 pm^3

extinctions ($0kl : k + l = 2n$, $h0l : h + l = 2n$) led to the space groups *Pnn*2 and *Pnnm*, of which the centrosymmetric group was confirmed by the refinement. The structure was solved by direct methods [12] and refined on F^2 with anisotropic displacement parameters except for the O atom of the SO$_2$ molecule [13]. This atom was treated as disordered over four positions. The refined occupation factors give a sum of 1.02(4), thus representing a complete SO$_2$ molecule. A numerical absorption correction was applied to the data set. The shape of the crystal with 9 faces was optimised using the program HABITUS [14]. Table 1 contains the crystallographic data and details of data collection and structure refinement, Table 2 the positional parameters of the atoms. Further details of the crystal structure determination have been deposited with the Fachinformationszentrum Karlsruhe, D-76334 Eggenstein-Leopoldshafen (crysdata@fiz-karlsruhe@email.de) from where they can be obtained by referring to the deposit number CSD-391236.

Results and Discussion

Synthesis of TeI$_3$[AsF$_6$]·0.5 SO$_2$

The reaction of Te and I$_2$ with AsF$_5$ in liquid SO$_2$ at room temperature using an excess of Te yields a variety of products, which can be crystallized from the solution. Examination of the hand-separated crystals by X-ray diffraction showed the presence of light-brown

Table 2. Positional parameters and equivalent isotropic displacement parameters /10^4 pm^2 of the atoms in the structure of TeI$_3$[AsF$_6$]·0.5 SO$_2$. Additionally, the site occupation factors of the split positions for the oxygen atoms O(A)–O(D) are given. Standard deviations in brackets refer to the last significant digit.

Atom	x	y	z	B_{eq}	sof
Te	0.24843(4)	0.59198(2)	0.21139(3)	1.588(9)	
I(1)	0.19954(4)	0.47186(2)	0.32354(4)	2.46(1)	
I(2)	0.44980(4)	0.63009(3)	0.31745(4)	2.59(1)	
I(3)	0.08958(4)	0.67764(3)	0.31239(4)	2.66(1)	
As(1)	0.5	0.5	0	1.86(2)	
As(2)	0	0.5	0	1.67(2)	
As(3)	0.26940(9)	0.77172(5)	0	1.75(2)	
F(11)	0.4466(6)	0.5867(3)	0	3.0(1)	
F(12)	0.6037(4)	0.5211(2)	0.1012(3)	2.7(1)	
F(21)	0.0150(4)	0.5649(2)	0.1010(4)	2.7(1)	
F(22)	-0.1531(5)	0.5115(3)	0	2.6(1)	
F(31)	0.3549(6)	0.7346(3)	0.1010(5)	5.6(1)	
F(32)	0.1797(6)	0.8091(3)	0.0992(7)	7.4(2)	
F(33)	0.3551(5)	0.8488(3)	0	2.8(1)	
F(34)	0.1841(7)	0.6953(3)	0	4.3(1)	
S	0.7727(6)	0.6682(3)	0	8.1(1)	
O(A)	0.666(6)	0.680(3)	0.030(5)	4(2)	0.09(2)
O(B)	0.743(9)	0.666(3)	0.103(6)	9(2)	0.22(6)
O(C)	0.807(4)	0.6846(15)	0.122(3)	6(1)	0.37(5)
O(D)	0.858(3)	0.7050(15)	0.050(3)	8(1)	0.34(3)

Table 3. Selected bond lengths /pm and angles /° in the structure of TeI$_3$[AsF$_6$]·0.5 SO$_2$.

Te-I(1)	267.45(6)	As(2)-F(22)	170.9(5)
Te-I(2)	266.79(6)	As(3)-F(31)	169.2(5)
Te-I(3)	267.16(6)	As(3)-F(32)	170.5(6)
As(1)-F(11)	172.3(5)	As(3)-F(33)	172.3(6)
As(1)-F(12)	172.2(5)	As(3)-F(34)	171.0(6)
As(2)-F(21)	172.6(4)		
I(1)-Te-I(2)	98.62(2)	I(1)-Te-I(3)	97.90(2)
I(2)-Te-I(3)	99.90(2)		

Te$_6$[AsF$_6$]$_4$·2 SO$_2$ [15], dark red Te$_4$[AsF$_6$] · x SO$_2$ ($x = 1,4$) [10], the already known unsolvated form of TeI$_3$[AsF$_6$] [5], and of light-red crystals of the new, solvated form TeI$_3$[AsF$_6$]·0.5 SO$_2$.

TeI$_3^+$ and [AsF$_6$]$^-$ ions are formed from Te, I$_2$ and AsF$_5$ according to eq. (1):

$$2Te + 3I_2 + 3AsF_5 \rightarrow 2TeI_3^+ + 2[AsF_6]^- + AsF_3 \quad (1)$$
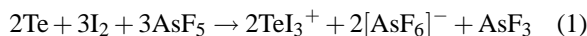
Crystal structure of TeI$_3$[AsF$_6$]·0.5 SO$_2$ and the relation to the solvate free form

The crystal structure of TeI$_3$[AsF$_6$]·0.5 SO$_2$ consists of TeI$_3^+$ and [AsF$_6$]$^-$ ions, and of SO$_2$ molecules. Fig. 1 depicts the structure of the molecules, Fig. 2 shows the unit cell. All four atoms of the TeI$_3^+$
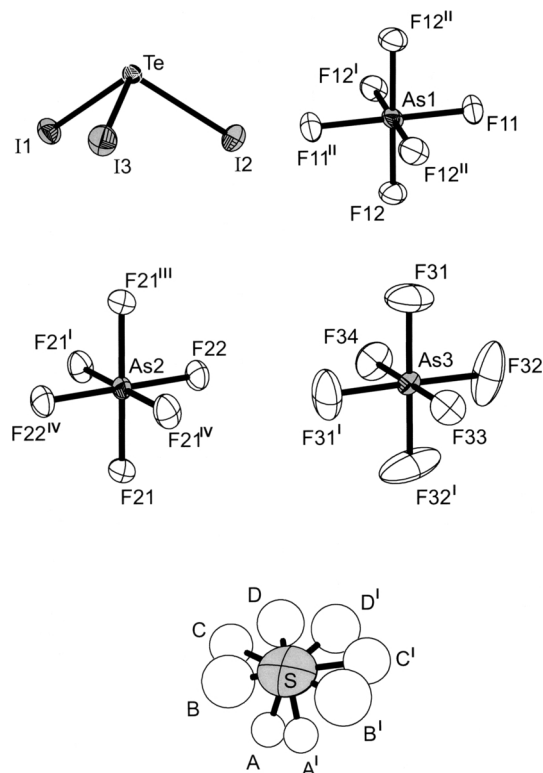
Fig. 2. The unit cell of TeI$_3$[AsF$_6$]·0.5 SO$_2$. [AsF$_6$]$^-$ ions are depicted as grey octahedra.

Fig. 1. The TeI$_3{}^+$ ion, the three independent [AsF$_6$]$^-$ ions and the disordered SO$_2$ molecule in the structure of TeI$_3$[AsF$_6$]·0.5 SO$_2$. Displacement ellipsoids represent a probability density of 50%. Symmetry operators: I = $x, y, -z$; II = $-x+1, -y+1, z$; III = $-x, -y+1, -z$; IV = $-x, -y+1, z$.

a	**b**
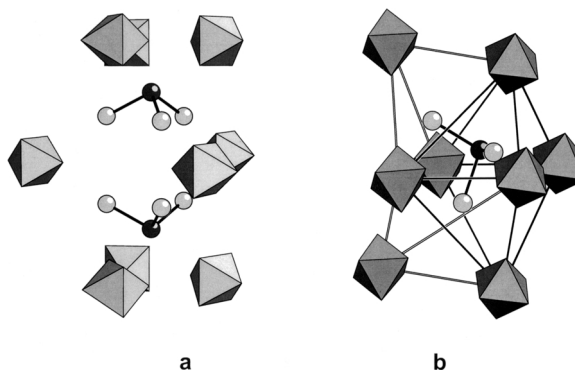
Fig. 3. The TeI$_3{}^+$ ions and their coordination environment in the structures of TeI$_3$[AsF$_6$]·0.5 SO$_2$ (**a**) and TeI$_3$[AsF$_6$] (**b**). [AsF$_6$]$^-$ ions are shown as grey octahedra. The lines in Fig. **b** connect six AsF$_6$ octahedra to from a big octahedron filled with a TeI$_3{}^+$ ion. Two adjacent tetrahedral voids are also shown.

cation occupy crystallographically independent positions. The Te-I distances are in average 267 pm and differ less than 1 pm, the I-Te-I angles are in average 99° and differ less than 2° (Table 3). The ion thus approximately fulfils the C_{3v} symmetry. The three independent As atoms occupy special positions. As(1) and As(2) are both located on the position $2/m$, two F atoms of each anion are located on mirror planes giving the ions crystallographic C_{2h} symmetry. As(3), F(33), and F(34) are occupying special positions on mirror planes, giving the anion overall symmetry C_s. Despite the crystallographic symmetry is lower, all three ions are almost regular octahedra with As-F bond lengths between 169.2 and 172.6 pm, and F-As-F angles between 88.1(3) and 92.2(3)°. The sulfur atom of the neutral SO$_2$ molecule is located on a mirror plane. The two oxygen atoms are distributed by a rotational disorder over 8 sites.
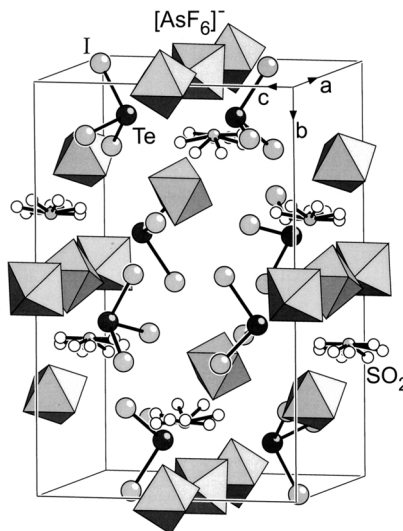
A typical feature of compounds containing trigonal-pyramidal EX$_3{}^+$ ions is the completion of the coordination environment of the chalcogen atom to give a distorted 3+3 octahedron by halogen atoms of the surrounding halometalate anions [1, 3]. This feature is not distinctly present in the structure of TeI$_3$[AsF$_6$]·0.5 SO$_2$. Within a sphere of radius 350 pm seven F atoms of neighbouring [AsF$_6$]$^-$ ions coordinate the Te atom of the TeI$_3{}^+$ ion with Te-F distances between 295 and 337 pm. The SO$_2$ molecules do not play a coordinating role in the crystal structure since all S-Te, O-Te, S-I, O-I, S-F, and O-F distances are larger than 300 pm.

Besides the presence of SO_2 molecules the structures of the solvated and solvate free form of $TeI_3[AsF_6]$ show outstanding differences in the arrangement of the ions. The volume of a molecule of SO_2 is about $55 \cdot 10^6$ pm^3 [16]. The comparison of the unit cell volumes of $TeI_3[AsF_6] \cdot 0.5$ SO_2 and $TeI_3[AsF_6]$ show an increase in volume of $290 \cdot 10^6$ pm^3 [17]. Since four SO_2 molecules are present in the unit cell of the solvated form a volume increase of about $220 \cdot 10^6$ pm^3 would be expected. The observed increase is higher indicating a less dense packing in the solvated form. This is reflected by the lower density (3.88 Mgm^{-3}) of $TeI_3[AsF_6] \cdot 0.5$ SO_2 with respect to $TeI_3[AsF_6]$ (4.20 Mgm^{-3}) [5]. A remarkable feature of the crystal structure of the solvated form is the arrangement of the TeI_3^+ ions which are pairwise associated, facing each other with the I atoms in an ecliptic configuration and forming large voids between each (Fig. 3a). From the point of view of electrostatic balance in a ionic crystal structure such an arrangement is unfavourable, since the negatively polarized ends of the two TeI_3^+ ions come close (shortest I-I contact 426 pm). In contrast to this, the structure of the unsolvated form can be regarded as a closest packing of $[AsF_6]^-$ ions with the TeI_3^+ ions for a large part in octahedral voids. Fig. 3b shows a section of this NaCl-type arrangement. One iodine atom of the TeI_3^+ cation sticks out of the octahedral void made up by six $[AsF_6]^-$ anions into the adjacent tetrahedral void. This gives the structure of the solvate free form of $TeI_3[AsF_6]$ the significantly higher density with respect to the solvated form.

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