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Commensurate and incommensurate structures of the hexabromotellurate(IV) bis{dibromodiselenate(I)} ion – $[(C_2H_5)_n(C_6H_5)_{4-n}P]_2[TeBr_6(Se_2Br_2)_2]$, *n* = 0,1

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Structure analysis of $[(C_2H_5)_n(C_6H_5)_{4-n}P]_2[TeBr_6(Se_2Br_2)_2]$ is presented for $n = 1$ and 0 [hereafter (I) and (II)]. Crystal (I) has been synthesized from elemental selenium, tellurium tetrabromide, ethyltriphenylphosphonium bromide and bromine. It has a standard monoclinic structure, space group $P2_1/c$, and has been solved and refined to $R = 0.0357$ for 4803 observed X-ray reflections by traditional techniques. Crystal (II), which has been prepared from elemental selenium, tellurium tetrabromide, tetraphenylphosphonium bromide and bromine, is an incommensurately one-dimensionally modulated structure with planar monoclinic superspace group. (II) has been refined to $R = 0.0501$ for 4247 observed reflections. The modulation of the atoms that belong to the anion switches between two different basic positions, which are described by the crenel function algorithm. The modulation of the phenyl groups is much weaker and it could be refined within the rigid-body approximation. The $TeBr_6$ octahedron is nearly regular in both structures. The two Br atoms of the octahedron have a bond to one of the Se atoms in an Se_2Br_2 molecule. For (I) both bonded Br atoms are *trans* positioned, while for (II) they can be either *trans* or *cis* positioned. The alternations of those arrangements are caused by modulation. The point group of the anion is -1 for crystal (I) and $2/m$ for the average structure of crystal (II).

1. Introduction

In contrast to monoselenium dibromide $SeBr_2$, which has not been isolated but which makes a series of complexes with bromide (Krebs & Ahlers, 1990), the binary compound of Se(I) with bromine Se_2Br_2 is stable as a pure liquid or solid. It exists in α- and β-Se_2Br_2 polymorphic modifications, which have been characterized by crystal structure analysis at 165 K (Kniep *et al.*, 1983). In 1998 the first two complexes of Se_2Br_2 with the bromide ion were reported. The hexabromotetraselenate(I) $[Se_4Br_6]^{2-}$ ion consists of two Br—Se—Se—Br units bonded together by two bromide-ion bridges between the Se atoms in such a way that a chair-shaped six-membered ring is formed (Hauge *et al.*, 1998). The dianion $[SeBr_6(Se_2Br_2)_2]^{2-}$ forms a nearly regular $SeBr_6$ octahedron with two *trans* positioned Br atoms that are weakly bonded to one of the Se atoms in an Se_2Br_2 molecule (Hauge *et al.*, 1998). The dianion $[SeBr_6(Se_2Br_2)_2]^{2-}$ was the first example of a bromoselenate ion that contains a selenium ion in the two oxidation states +1 and +4.

The binary compound of Te(IV) with bromine, $TeBr_4$, is very stable and like other tellurium(IV) halides has been characterized structurally (Shoemaker & Abrahams, 1965; Büscher, 1978). It forms a series of complexes with bromide: the anions $[TeBr_6]^{2-}$ (Krebs & Ahlers, 1990; Krebs *et al.*, 1991;

Hauge & Marøy, 1998), $[TeBr_5]^-$ (Reich *et al.*, 1996), $[Te_2Br_{10}]^{2-}$ (Krebs & Büscher, 1980; Reich & Krebs, 1994), $[Te_2Br_9]^-$ (Reich *et al.*, 1998) and $[Te_3Br_{13}]^-$ (Krebs *et al.*, 1991). All of these complexes are based on $TeBr_6$ octahedra, and in the oligomeric species the octahedra are connected by common edges.

The dianion $[SeBr_6(Se_2Br_2)_2]^{2-}$ was isolated as the phenyltrimethylammonium salt by reaction between elemental selenium and bromine in the presence of phenyltrimethylammonium bromide (Hauge *et al.*, 1998). The amounts of reactants used were in accordance with the equation

$$5Se + 4Br_2 + 2Br^- = [SeBr_6(Se_2Br_2)_2]^{2-}.$$

In this work we used elemental selenium and $TeBr_4$ in addition to bromine and ethyltriphenylphosphonium or tetraphenylphosphonium bromide in an attempt to produce a similar complex that contained selenium and tellurium. The amounts of reactants used were in accordance with the equation

$$TeBr_4 + 4Se + 2Br_2 + 2Br^- = [TeBr_6(Se_2Br_2)_2]^{2-},$$

if we take into consideration the fact that the product of the reaction of selenium with bromine in acetonitrile is mainly Se_2Br_2 when the Se/Br_2 ratio is 2.0 (Hauge *et al.*, 1998):

$$2Se + Br_2 \rightleftharpoons Se_2Br_2.$$

This work reports the first complex that contains one chalcogen atom (selenium) in oxidation state +1 and another (tellurium) in oxidation state +4.

2. Experimental

2.1. Preparation

2.1.1. Crystal I. 2.4 mmol (0.384 g) of bromine were added to 4.8 mmol (0.379 g) of selenium, 1.2 mmol (0.537 g) of tellurium tetrabromide and 2.4 mmol (0.891 g) of ethyltriphenylphosphonium bromide in 4.0 g of acetonitrile. The mixture was stirred and heated to boiling point for 45 min. Then 10 g of acetonitrile were added to the mixture under stirring and heating to boiling point, and the resulting dark solution was set aside at room temperature. After a few hours 0.67 mmol (0.80 g) of orange crystals of ethyltriphenylphosphonium hexabromotellurate(IV) $[C_2H_5(C_6H_5)_3P]_2[TeBr_6]$ were isolated. The filtrate was placed in a refrigerator (271 K) for 6 h, and 0.33 mmol (0.60 g) of red short prisms of $[C_2H_5(C_6H_5)_3P]_2[TeBr_6(Se_2Br_2)_2]$ were isolated. Found: Se 17.06%, Te 6.89%. Calculated from the formula: Se 17.30%, Te 6.99%.

The filtrate was further cooled and then held at 251 K for several days. The remaining concentration of $[C_2H_5(C_6H_5)_3P]_2[TeBr_6]$ was insufficient to coordinate residual Se_2Br_2, and therefore the resulting product was a mixture of orange crystals of $[C_2H_5(C_6H_5)_3P]_2[TeBr_6]$ and red crystals of $[C_2H_5(C_6H_5)_3P]_2[TeBr_6(Se_2Br_2)_2]$, all of which were contaminated with the 'oil' of Se_2Br_2.

2.1.2. Crystal II. 2.4 mmol (0.384 g) of bromine were added to 4.8 mmol (0.379 g) of selenium, 1.2 mmol (0.537 g) of tellurium tetrabromide and 2.4 mmol (1.006 g) of tetraphenylphosphonium bromide in 4.0 g of acetonitrile. The mixture was stirred and heated to boiling point for 45 min. Then 6 g of acetonitrile were added under stirring and heating to boiling point. A small amount of selenium did not react and was filtered off. The dark solution was set aside at room temperature. After 8 h, 0.70 mmol (1.35 g) of red crystals of $[(C_6H_5)_4P]_2[TeBr_6(Se_2Br_2)_2]$ were isolated. Found: Te 6.45%. Calculated for the formula: Te 6.64%.

Selenium and tellurium were determined by atomic absorption spectrometry ('Perkin-Elmer' −503). The density was measured by flotation; a mixture of trichloromethane and tribromomethane was used.

2.2. Crystal structure analysis

2.2.1. $[C_2H_5(C_6H_5)_3P]_2[TeBr_6(Se_2Br_2)_2]$ – regular structure. All measurements were carried out on a KUMA four-circle diffractometer equipped with a CCD detector. The structure was solved by direct methods using *SHELXS*97 (Sheldrick, 1997) and further refined by *Jana*2000 (Petříček & Dušek, 2000). The crystal data, conditions for data collection and refinement are summarized in Table 1.[1] The H atoms were found in the difference-Fourier map and refined isotropically. All non-H atoms were refined anisotropically.

Final atomic coordinates and equivalent isotropic displacement parameters are listed in the supplementary material. Bond lengths and angles of the $[TeBr_6(Se_2Br_2)_2]^{2-}$ ion are listed in Table 2.

2.2.2. $[(C_6H_5)_4P]_2[TeBr_6(Se_2Br_2)_2]$ – modulated structure. Preliminary X-ray investigations using a KUMA CCD four-circle diffractometer revealed a diffraction pattern typical for modulated crystals with clearly visible first-order satellites. All the reflections that were observed on the collected frames were indexed by four integers *hklm* with respect to the four-dimensional base (de Wolff, 1974) $\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$, where $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ are the reciprocal axes of the basic structure and $\mathbf{q}$ is the modulation vector (see Table 1). The crystal was found to be incommensurately modulated.

The integration of the main reflections and first-order satellites was performed with the *KUMA* software (KUMA Diffraction, 2000), which allows the integration of satellite reflections. The higher-order satellites were not detected. Data were corrected for Lorentz and polarization factors and for absorption. The Laue class ($2/m$) and reflection conditions ($hklm$, $h + k = 2n$) and ($h0lm$, $m = 2n$) lead to two possible superspace groups, $C2/m(\alpha, 0, \gamma)0s$ and $Cm(\alpha,0,\gamma)s$. The subsequent refinements were consistent with the existence of a center of symmetry.

The average structure was solved by *SHELXS*97 (Sheldrick, 1997) and refined using *Jana*2000 (Petříček & Dušek, 2000). There are two clearly distinguishable positions of the

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: SN0022). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$[C_2H_5(C_6H_5)_3P]_2$-$[TeBr_6(Se_2Br_2)_2]$	$[(C_6H_5)_4P]_2$-$[TeBr_6(Se_2Br_2)_2]$
Chemical formula weight	912.6	960.6
Cell setting, space group	Monoclinic, $P2_1/c$	Monoclinic, $C2/m(\alpha 0\gamma)0s$
a, b, c (Å)	10.363 (2), 12.830 (3), 19.666 (4)	11.261 (2), 24.543 (4), 10.814 (2)
β (°)	92.43 (3)	102.84 (3)
V (Å^3)	2612.4 (10)	2913.9 (10)
Z	4	4
D_x (Mg m^{-3})	2.32	2.189
D_m (Mg m^{-3})	2.25	–
Density measured by	Flotation method	–
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	11.094	9.952
Temperature (K)	120 (2)	120 (2)
Crystal form, colour	Prism, dark red	Parallelepiped, dark red
Crystal size (mm)	0.20 × 0.15 × 0.10	0.22 × 0.20 × 0.12
Modulation wavevector	–	$\mathbf{q}$ = 0.7363 (5) $\mathbf{a}^*$ + 0.5452 (4) $\mathbf{c}^*$
Data collection		
Diffractometer	KUMA CCD	KUMA CCD
Data collection method	Integration scans	Integration technique scans
Absorption correction	Empirical, Ψ scan	Gaussian
T_{min}	0.1680	0.159
T_{max}	0.2869	0.337
No. of measured, independent and observed reflections	18202, 6065, 4803	17374, 8052, 4247
No. of main reflections	–	1851
No. of satellite reflections	–	2396
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R_{int}	0.0578	0.0604
θ_{max} (°)	28.43	28.53
Range of h, k, l, m	$-13 \rightarrow h \rightarrow 13$ $-16 \rightarrow k \rightarrow 17$ $-25 \rightarrow l \rightarrow 26$	$-15 \rightarrow h \rightarrow 14$ $-31 \rightarrow k \rightarrow 31$ $-11 \rightarrow l \rightarrow 14$ $-1 \rightarrow m \rightarrow 1$
Refinement		
Refinement on	F	F
R, wR, S (all reflections)	0.0357, 0.0388, 2.22	0.0501, 0.0487, 1.84
R, wR (main reflections)	–	0.0436 , 0.0442
R, wR (satellites)	–	0.0582, 0.0546
No. of reflections and parameters used in refinement	4803, 320	4247, 219
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/(\sigma^2F + 0.0001F^2)$	$w = 1/(\sigma^2F + 0.0001F^2)$
$(\Delta/\sigma)_{max}$	0.0021	0.0025
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.61, −1.77	2.35, −1.32
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)

Computer programs used: *SHELXS*97 (Sheldrick, 1990), *JANA*2000 (Petříček & Dušek, 2000).

$TeBr_6$ octahedron in the average structure (see Fig. 1), which can be coordinated by the Br_2Se_2 molecule at four different ligand positions *A*, *B*, *C* and *D*. These four positions are generated by the local site symmetry of the anion. The

Table 2
Bond lengths (in Å), bond angles and torsion angles (in °) in (I).

Te—Br1	2.6985 (5)	Se1—Br4	2.3873 (8)
Te—Br2	2.7388 (5)	Se1—Br2	3.2499 (8)
Te—Br3	2.6996 (5)	Se2—Br5	2.3708 (8)
Se1—Se2	2.2555 (8)	Se1···Br1	3.4556 (7)
		Se2···Br2^{ii}	3.3936 (8)
		Se2···Br3^{ii}	3.5610 (7)
Br1—Te—Br2	89.346 (15)	Se2—Se1—Br4	102.03 (2)
Br1—Te—Br2^{i}	90.654 (15)	Se1—Se2—Br5	102.06 (2)
Br1—Te—Br3	89.063 (16)	Se2—Se1—Br2	97.09 (2)
Br1—Te—Br3^{i}	90.937 (16)	Br4—Se1—Br2	157.77 (3)
Br2—Te—Br3	89.516 (15)	Te—Br2—Se1	102.712 (19)
Br2—Te—Br3^{i}	90.484 (15)	Se2—Se1···Br1	166.46 (3)
		Se1—Se2···Br2^{ii}	100.89 (2)
Br4—Se1—Se2—Br5	80.76 (3)	Br2—Se1—Se2—Br5	−87.84 (3)

Symmetry codes: (i) $2 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, -z$.

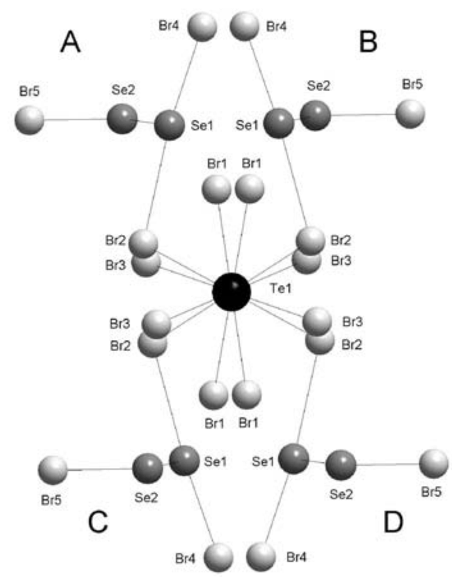

Figure 1
View of the $[TeBr_6(Se_2Br_2)_2]^{2-}$ ion in the average structure of (II). The four possible ligand positions for coordination by Se_2Br_2 are indicated by *A*, *B*, *C* and *D*.

simultaneous presence of *A* and *B* or *C* and *D* is impossible because of the short distances. This led us to hypothesize that the modulation has basically an occupational character and switches between two possible *trans* arrangements of the ligands (*A*–*C* and *B*–*D*) and/or between two possible *cis* arrangements (*A*–*D* and *B*–*C*).

The average model was used as a starting point for four-dimensional refinement. First we used the first harmonic for both the positional modulation of Te, Br and Se atoms and the occupational modulation of Br and Se atoms. The refined parameters confirmed that the occupational modulation function has a step-like character, which is obvious from the density sections through the Fourier density map (for atom Se2 see Fig. 2). This type of modulation can be described by the crenel functions that were introduced by Petříček *et al.* (1995). The refinement in which the crenel function was

Table 3
List of the orthogonalized functions used in the refinement of (II).

Atom	i	B_{i0}	A_{i1}	B_{i1}
Br1	0	1.0		
	1	0.287	1.471	
	2	2.049	0.799	3.123
Br2	0	1.0		
	1	1.648	2.726	
	2	−1.250	−1.512	1.686
Br3	0	1.0		
	1	1.478	2.524	
	2	−1.447	−1.695	1.821
Se1	0	1.0		
	1	1.123	2.126	
	2	−1.737	−1.835	2.161
Br4	0	1.0		
	1	1.184	2.191	
	2	−1.696	−1.833	2.097
Se2	0	1.0		
	1	−0.210	1.445	
	2	−2.058	0.598	3.180
Br5	0	1.0		
	1	0.047	1.416	
	2	−2.068	−0.136	3.246

applied for all occupationally modulated atoms showed that the Δ parameters were equal to within the standard deviations and that neighboring or symmetry-related Br_2Se_2 and $TeBr_6$ molecules are simultaneously either occupied or non-occupied. This allows us to state the following restrictions to occupationally modulated atoms:

$$x_4^0(A) = x_4^0(R) + \mathbf{q} \cdot [\mathbf{r}(A) - \mathbf{r}(R)],$$

where A stands for any atom of Br_2Se_2 or $TeBr_6$, R is the reference point, x_4^0 is the center of the crenel function and $\mathbf{r}$ is the three-dimensional coordinates of the atom. It can also be shown that the occupancies of Br_2Se_2 and $TeBr_6$ are related by a similar equation so that the same reference point can be used for all atoms of both molecules. Using the Se2 atom as a common reference point we could describe occupational modulation of both groups with only one parameter x_4^0(Se2).

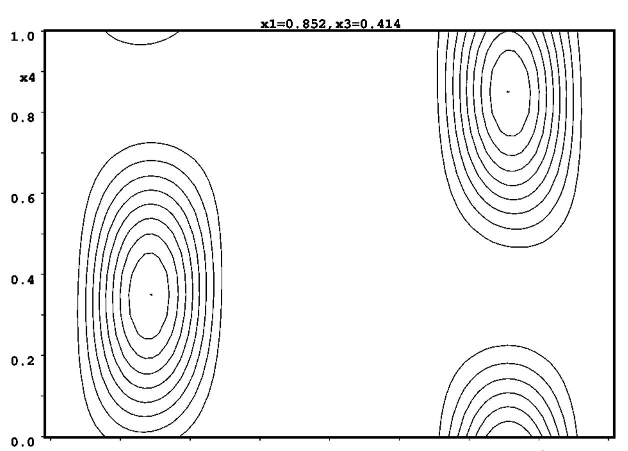

Figure 2
The $x_2 - x_4$ section through the Fourier map in the vicinity of the Se(2) atom in (II). The two peaks correspond to the basic and symmetry-related position (x_1, $1 - x_2$, x_3, $1/2 + x_4$) of the Se(2) atom.

The value of x_4^0(Se2) determines whether local disorder and unrealistic distances (as mentioned above for the basic structure) are present or avoided. The following condition guarantees the proper geometry:

$$x_4^0(\mathrm{Se2}) = \mathbf{q} \cdot [\mathbf{r}(\mathrm{Se2}') - \mathbf{r}(\mathrm{Se2})]/2,$$

where Se2′ stands for the atom related by the symmetry operator $1 - x$, y, $-z$. The original value of x_4^0(Se2), which is refined without this restriction, was consistent with the restricted value within the standard deviation. Therefore we included the restriction in the final refinement and the occupational parameters were fixed from geometrical and structural considerations. The number of parameters was greatly reduced without any significant impact on R values.

The occupational modulation leads to a complete separation of the *cis* and *trans* arrangements. The interval of $t \in (0, 1)$ is divided into four disjunctive intervals:

$(-1/4 + \alpha/2, 3/4 - \alpha/2)$, *cis A–C*
$(3/4 - \alpha/2, 1/4 + \alpha/2)$, *trans A–D*
$(1/4 + \alpha/2, 5/4 - \alpha/2)$, *cis B–D*
$(5/4 - \alpha/2, 3/4 + \alpha/2)$, *trans B–C*

where α stands for the first component of the modulation vector, 0.7363 (5). The sum of the lengths where the *trans* arrangement exists is equal to $2\alpha - 1$, and this arrangement yields a slightly lower occupation (47.26%) than the *cis* arrangement.

The use of the orthogonalization method as described by Petříček *et al.* (1995) was necessary to suppress the strong correlations between positional parameters that were induced by the crenel-like modulation function for the occupational parameters. In this method the regular harmonic functions used in ordinary modulated structures are replaced by orthogonalized sets of functions

$$\mathrm{Ortho}_i(x_4) = B_{i0} + \sum_{n=1}^{\lfloor (i+1)/2 \rfloor} A_{in} \sin(2\pi n x_4) + \sum_{n=1}^{\lfloor i/2 \rfloor} B_{in} \cos(2\pi n x_4),$$

where $\lfloor x \rfloor$ means an integer part of x. The coefficients are summarized in Table 3. The final refinement converged smoothly to $R = 0.05$. The refined atomic positional parameters and their modulations are given in Table 4.

The tetraphenylphosphonium cation is affected by the modulation as well. The central P atom was refined individually. The two independent phenyl groups were refined in a rigid-body approximation as two positions of the same molecule. Then the modulation function for each atom of the molecule is expressed as a combination of the translational and rotational modulation (Petříček *et al.*, 1985) of the molecule:

Table 4
Final values of coordinates and Fourier amplitudes of the displacive modulation functions of (II).

The waves are sorted by the term (s for sine, c for cosine, o for orthogonalized functions) and harmonic order.

Atom	Δ	x_4^0	Wave	x	y	z	$U_{\rm eq}/U_{\rm iso}$ (Å^2)
Te						0.0	0.0121 (3)
			s,1	0.0	0.00117 (4)	0.0	
			c,1	0.0	0.0	0.0	
Br1	1/2	0.54955		0.04905 (10)	0.01155 (9)	−0.23200(13)	0.0198 (5)
			o,1	−0.0021 (2)	0.01045 (10)	0.0017(3)	
			o,2	0.0023 (3)	−0.00657 (16)	0.0043(4)	
Br2	1/2	0.80077		0.1730 (2)	0.07696 (13)	0.0938(4)	0.0207 (5)
			o,1	−0.0003 (7)	0.002 2(3)	−0.0120 (6)	
			o,2	0.0037 (4)	0.0004 (2)	−0.0074 (4)	
Br3	1/2	0.81410		0.1738 (3)	−0.0770 1(13)	0.0556 (2)	0.0200 (7)
			o,1	0.0036 (4)	0.0026 (2)	0.0244 (3)	
			o,2	−0.0030 (4)	−0.00059 (18)	0.0037 (6)	
Se1	1/2	0.84432		0.35249 (11)	0.05142 (5)	−0.08605 (15)	0.0243 (4)
			o,1	0.0000 (2)	−0.0010 9(10)	−0.0037 (3)	
			o,2	−0.0004 (3)	−0.00001 (14)	−0.0017 (4)	
Br4	1/2	0.83877		0.45624 (12)	0.01994 (5)	−0.24449 (17)	0.0337 (4)
			o,1	0.0010 (3)	−0.00073 (15)	−0.0025 (3)	
			o,2	−0.0013 (4)	−0.00147 (18)	−0.0034 (4)	
Se2	1/2	0.03662		0.50538 (12)	0.09093 (5)	0.05825 (15)	0.0264 (4)
			o,1	0.00057 (13)	−0.00124 (6)	−0.00409 (16)	
			o,2	0.0008 (4)	−0.00015 (16)	−0.0016 (5)	
Br5	1/2	0.99178		0.52143 (13)	0.17905 (5)	−0.02883 (17)	0.0361 (5)
			o,1	0.00172 (15)	−0.00077 (5)	−0.00089 (18)	
			o,2	0.0026 (4)	−0.00013 (19)	0.0039 (6)	
P				0.5	0.1907 8(10)	0.5	0.0174 (9)
			s,1	0.0	−0.01044 (14)	0.0	
			c,1	−0.0177 (3)	0	0.0047 (4)	
Atoms of the phenyl group							
C1				0.374687	0.3747	0.1465	0.5149
C2				0.3195 (6)	0.3194 (6)	0.1502 (3)	0.6197 (7)
C3				0.2225 (7)	0.2223 (7)	0.1151 (3)	0.6245 (8)
C4				0.1835 (7)	0.1834 (7)	0.0775 (3)	0.5302 (9)
C5				0.2386 (7)	0.2385 (7)	0.0735 (3)	0.4293 (8)
C6				0.3348 (6)	0.3347 (7)	0.1079 (3)	0.4202 (7)
H2				0.353 (3)	0.349 (4)	0.1767 (14)	0.685 (3)
H3				0.193 (4)	0.191 (4)	0.1171 (18)	0.700 (3)
H4				0.120 (4)	0.118 (3)	0.0537 (14)	0.537 (5)
H5				0.213 (4)	0.208 (4)	0.0495 (16)	0.360 (3)
H6				0.377 (4)	0.375 (4)	0.1028 (18)	0.352 (3)

Table 5
Final values of molecular parameters for the phenyl molecule in (II).

The rotational parameters ψ, χ and φ are rotation angles around x, y and z, respectively. The waves are sorted by the term (s for sine, c for cosine) and harmonic order. The parameters U_{ij} are explained in equation (1).

Position	Wave	$\psi(^\circ)/U_{rx}$	$\chi(^\circ)/U_{ry}$	$\varphi(^\circ)/U_{rz}$	x/U_{tx}	y/U_{tx}	z/U_{tx}
1		0.0	0.0	0.0	0.0011 (5)	0.0005 (2)	0.0006 (6)
	s,1	0.0122 (5)	−0.0096 (2)	0.0075 (7)	−0.0057 (3)	0.00040 (16)	−0.0003 (3)
	c,1	−0.0146 (5)	−0.0042 (2)	0.0143 (6)	−0.0009 (4)	0.00362 (16)	−0.0013 (4)
2		−29.7 (4)	−56.1 (2)	151.5 (4)	0.0801 (5)	0.0877 (2)	−0.1524 (5)
	s,1	−0.0006 (5)	0.0052 (2)	−0.0157 (6)	0.0079 (3)	0.00007 (15)	0.0033 (3)
	c,1	0.0111 (5)	−0.0021 (2)	−0.0200 (6)	0.0056 (3)	−0.00063 (15)	0.0000 (3)

$$
\begin{aligned}
\mathbf{u}^{\mu}(x_4) = {} & \textstyle\sum_n \lfloor \mathbf{U}^{\mu}_{tsn} \sin(2\pi n x_4) \\
& + \mathbf{U}^{\mu}_{tcn} \cos(2\pi n x_4) \rfloor \\
& + \mathbf{g} \textstyle\sum_n \lfloor \mathbf{U}^{\mu}_{rsn} \sin(2\pi n x_4) \\
& + \mathbf{U}^{\mu}_{rcn} \cos(2\pi n x_4) \rfloor, \qquad (1)
\end{aligned}
$$

where $\mathbf{g}$ is the reference point of the molecule. The refined molecular parameters are given in Table 5. The distances and angles that are important for understanding the structure are summarized, together with bond-valence sums, in Table 6.

3. Results and discussion

3.1. Crystal chemistry

The anions $[TeBr_6(Se_2Br_2)_2]^{2-}$ of compounds (I) and (II) are shown in Figs. 3 and 4, respectively. They are composed of a nearly regular octahedral $TeBr_6$ and two Se_2Br_2 molecules. In compound (I) the Se_2Br_2 molecules are linked to *trans* Br atoms of the octahedron, whereas in the modulated structure (II) the Se_2Br_2 molecules are linked to *trans* or *cis* Br atoms of the octahedron. The alternation between two possible arrangements is the most pronounced feature of the modulation in (II). The anion in (I) is located, like $[SeBr_6(Se_2Br_2)_2]^{2-}$ (Hauge *et al.*, 1998), at the inversion center of the crystal structure. On the other hand, the anion in (II) is located at the local site with symmetry $2/m$ only in the basic structure approximation (see Fig. 1). In the modulated structure the individual positions have generally no local symmetry (see Fig. 4).

In Table 7 the selected distances and angles of the Se_2Br_2 units in (I) and (II) are compared with analogous values found in the anion of the pure selenium compound and in the α- and β-Se_2Br_2 modifications. The differences between the internal distances and angles of the Se_2Br_2 molecules in (I) and (II) are not significant. The Se_2Br_2 parts of the $[TeBr_6(Se_2Br_2)_2]^{2-}$ ion resemble those of the two solid Se_2Br_2 modifications published by Kniep *et al.* (1983) and the Se_2Br_2 units of the $[Se_4Br_6]^{2-}$ ion (Hauge *et al.*, 1998) and Se_2Br_2 parts of the $[SeBr_6(Se_2Br_2)_2]^{2-}$ ion. However, β-Se_2Br_2 and $[Se_4Br_6]^{2-}$ both form six-membered rings, whereas the Se_2Br_2 parts of the $[TeBr_6(Se_2Br_2)_2]^{2-}$ and $[SeBr_6(Se_2Br_2)_2]^{2-}$ ions have more open structures.

The Se_2Br_2 parts of (I) and (II) are acceptors in a donor–acceptor adduct. As expected, the bonds within the acceptor are weakly influenced by the contact. The bond lengths Br2(donor)—Se1(acceptor) of (I) and (II) in the *trans* arrangement are 3.2498 (8) and 3.25 (2) Å, respectively. These bonds are even longer than the 3.133 (2) Å bond length found in the $[SeBr_6(Se_2Br_2)_2]^{2-}$ ion. The analogous distance 3.09 (2) Å in the *cis* arrangement of

Table 6
Bond lengths (Å), bond angles and torsion angles (°) in (II).

	Average	Minimal	Maximal
$TeBr_6(Se_2Br_2)_2$ *cis* arrangement			
Te—Br1	2.721 (11)	2.663 (10)	2.771 (14)
Te—Br2	2.780 (17)	2.76 (2)	2.792 (15)
Te—Br3	2.685 (13)	2.661 (14)	2.757 (13)
Se1—Se2	2.270 (14)	2.251 (18)	2.304 (13)
Se1—Br4	2.412 (18)	2.377 (18)	2.428 (18)
Se1—Br2	3.09 (2)	3.05 (2)	3.18 (2)
Se2—Br5	2.380 (19)	2.36 (2)	2.422 (14)
$Se2\cdots Br4^{ii}$	3.359 (18)	3.36 (2)	3.361 (16)
$Br1—Te—Br1^{i}$	176.3 (3)	176.2 (3)	176.3 (3)
Br1—Te—Br2	90.0 (5)	89.1 (6)	91.7 (5)
$Br1—Te—Br2^{i}$	87.7 (5)	84.5 (6)	91.2 (5)
Br1—Te—Br3	89.9 (4)	89.2 (4)	91.2 (4)
$Br1—Te—Br3^{i}$	92.4 (4)	88.3 (4)	94.6 (4)
$Br2—Te—Br2^{i}$	90.9 (6)	90.1 (6)	91.3 (5)
Br2—Te—Br3	88.3 (5)	86.1 (4)	90.5 (6)
$Br2—Te—Br3^{i}$	176.4 (5)	173.7 (5)	178.3 (5)
$Br3—Te—Br3^{i}$	92.5 (4)	92.3 (4)	93.0 (4)
Se2—Se1—Br4	102.2 (5)	102.0 (5)	102.4 (5)
Se1—Se2—Br5	103.8 (6)	101.6 (5)	104.7 (7)
Se2—Se1—Br2	89.3 (5)	88.4 (5)	89.7 (6)
Br4—Se1—Br2	168.2 (6)	167.3 (6)	168.9 (6)
Te—Br2—Se1	99.1 (5)	97.1 (7)	100.1 (5)
Br4—Se1—Se2—Br5	82.9 (6)	80.3 (5)	84.0 (7)
Br2—Se1—Se2—Br5	−99.0 (6)	−101.4 (6)	−96.9 (5)
$TeBr_6(Se_2Br_2)_2$ *trans* arrangement			
Te—Br1	2.715 (13)	2.604 (10)	2.772 (15)
Te—Br2	2.73 (2)	2.700 (15)	2.76 (2)
Te—Br3	2.708 (15)	2.679 (16)	2.733 (13)
Br2—Se1	3.25 (2)	3.18 (2)	3.28 (2)
Se1—Se2	2.267 (16)	2.251 (18)	2.298 (13)
Se1—Br4	2.399 (18)	2.362 (18)	2.427 (18)
Se2—Br5	2.386 (19)	2.36 (2)	2.431 (14)
$Se2\cdots Br4^{iv}$	3.352 (19)	3.350 (16)	3.36 (2)
$Br1—Te—Br1^{ii}$	179.1 (3)	178.1 (2)	180 (2)
Br1—Te—Br2	89.4 (5)	89.1 (6)	90.0 (6)
$Br1—Te—Br2^{ii}$	90.6 (5)	89.8 (6)	91.1 (6)
Br1—Te—Br3	89.9 (5)	89.2 (5)	90.6 (5)
$Br1—Te—Br3^{ii}$	90.1 (5)	87.5 (5)	92.7 (5)
$Br2—Te—Br2^{ii}$	178.6 (7)	177.4 (6)	180 (2)
Br2—Te—Br3	90.1 (6)	88.0 (5)	90.8 (6)
$Br2—Te—Br3^{ii}$	89.9 (6)	87.1 (5)	94.3 (6)
$Br3—Te—Br3^{ii}$	176.9 (5)	174.1 (5)	180 (3)
Se2—Se1—Br4	102.4 (6)	102.1 (6)	102.7 (5)
Se1—Se2—Br5	102.6 (6)	99.9 (5)	104.6 (7)
Se2—Se1—Br2	88.8 (6)	87.7 (6)	89.6 (7)
Br4—Se1—Br2	168.1 (6)	167.2 (6)	169.5 (5)
Te—Br2—Se1	95.8 (6)	95.2 (5)	97.1 (7)
Br4—Se1—Se2—Br5	81.4 (6)	78.4 (5)	83.7 (7)
Br2—Se1—Se2—Br5	−102.6 (5)	−103.1 (5)	−101.4 (6)

Symmetry codes: (i) $-x, y, -z$; (ii) $-x, -y, -z$; (iii) $1-x, y, 1-z$; (iv) $1-x, -y, -z$.

(II) is significantly shorter. The Se1 atoms of the present compounds act as central atoms in asymmetric, nearly linear, 3*c*—4*e* Br2—Se1—Br4 systems. The weakness of the donor–acceptor bond is responsible for the large differences in the nearly linear angle Br4—Se1—Br2, which is significantly affected by molecular arrangements in (I) and (II).

The Se—Se bonds in the structure of $[SeBr_6(Se_2Br_2)_2]^{2-}$ were slightly but significantly longer (Hauge *et al.*, 1998) than those in the Se_2Br_2 modifications. This effect does not occur in (I) where the distances are in a good agreement with those in the α- and β-Se_2Br_2 modifications. The average Se—Se distances in (II) are closer to those from the structure of $[SeBr_6(Se_2Br_2)_2]^{2-}$, but unfortunately s.u. values from the modulated structure refinement are too high to draw an unambiguous conclusion.

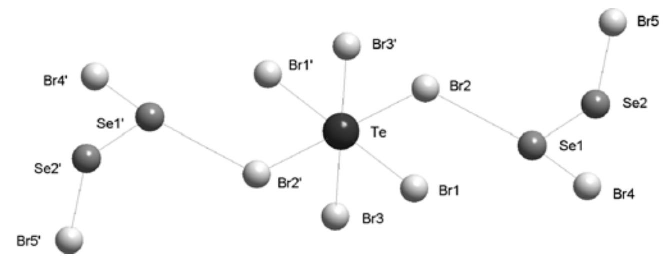

Figure 3
View of the $[TeBr_6(Se_2Br_2)_2]^{2-}$ ion, point group −1, as found in the structure of (I).

The central $TeBr_6$ octahedron in (I) has nearly ideal octahedral symmetry with the largest deviation from the average value being 0.937° for angles and 0.0403 Å for bond lengths. The analogous values 1.28° and 0.0125 Å have been found in the structure of the hexabromotellurate(IV) of the phenyltrimethylammonium cation (Hauge & Marøy, 1998), where, like in (I), the Te atom is situated on the center of symmetry. The deviations from ideal symmetry are in accordance with those determined by Krebs & Ahlers (1990). On the other hand, the $TeBr_6$ octahedron in (II) is less regular because of the lack of local symmetry.

Variation of the bond lengths seems to be common for 3*c*—4*e* systems. Lengths vary in the ranges 2.671 (4)–2.716 (4) Å and 2.671 (4)–2.716 (4) Å for $[H_9O_4]_2[TeBr_6]$ (Krebs *et al.*, 1991) and $[C_6H_5(CH_3)_3N]_2[TeBr_6]$ (Hauge & Marøy, 1998), respectively, and these values are in agreement with the present investigation. The Te—Br distances are different for Br atoms that are linked and not linked to Se_2Br_2; the former distances are slightly but significantly shorter (see Table 6). Thus the coordination of the two Se_2Br_2 molecules has only a slight influence on the length of the complex Te—Br bond.

Hauge *et al.* (1998) noted that in adducts with a bromine molecule as acceptor coordinated to Se as donor the acceptor has to be co-linear with the Br—Se—Br sequence to have a stronger influence on the length of the complex Se—Br bond. In the crystal structure of $[C_6H_5(CH_3)_3N]_2[SeBr_6(Se_2Br_2)_2]$, the angle Se—Br2—Se1 is 135.46 (6)° and no strong influence on the complex bond was observed. In the structures (I), (II) *cis* and (II) *trans* the angles Te—Br—Se1 are even smaller: 102.712 (19)°, 99.1 (5)° and 95.8 (6)°, respectively, which are in accordance with the values mentioned above.

The arrangement of intermolecular contacts between anions is quite different for (I) and (II) (see Fig. 5). In (I) the contacts of Se1 to the adjacent octahedron, $Se1\cdots Br1$ and $Se2\cdots Br3$, are nearly parallel to the Se1—Se2 bond. The additional weak contacts $Se2\cdots Br2$ have a similar orientation to the Se1—Br2 bonds with respect to Se1—Se2. In fact, Se1 and Se2 bond in a similar manner, and the only difference is that the relevant contacts of Se1 are shorter. On the other

Table 7
Distances (Å) and angles (°) in Se_2Br_2 molecules and Se_2Br_2 units of $[SeBr_6(Se_2Br_2)_2]^{2-}$ and $[TeBr_6(Se_2Br_2)_2]^{2-}$ ions.

	α-Se_2Br_2	β-Se_2Br_2	$[SeBr_6(Se_2Br_2)_2]^{2-}$	$[TeBr_6(Se_2Br_2)_2]^{2-}$	$[TeBr_6(Se_2Br_2)_2]^{2-}$	$[TeBr_6(Se_2Br_2)_2]^{2-}$
Se1—Se2	2.258 (2)	2.241 (1)	2.272 (2)	2.2555 (8)	2.270 (14)	2.267 (16)
Se1—Br4	2.357 (2)	2.366 (1)	2.347 (2)	2.3873 (8)	2.412 (18)	2.399 (18)
Se2—Br5		2.369 (1)	2.360 (2)	2.3708 (8)	2.380 (19)	2.386 (19)
Se2—Se1—Br4	107.23 (8)	103.86 (5)	102.40 (8)	102.03 (2)	102.2 (5)	102.4 (6)
Se1—Se2—Br5		104.51 (5)	104.22 (7)	102.06 (2)	103.8 (6)	102.6 (6)
Br4—Se1—Br2		162.3 (6)	166.24 (7)	157.77 (3)	168.2 (6)	168.1 (6)
Br4—Se1—Se2—Br5	85.0 (1)	86.41 (8)	97.49 (8)	80.76 (3)	82.9 (6)	81.4 (6)
Reference	Kniep *et al.* (1983)	Kniep *et al.* (1983)	Hauge *et al.* (1998)	This work (I)	This work (II) *cis*	This work (II) *trans*

hand, in (II) there are no contacts between atoms of Br_2Se_2 and the octahedron except the Se1—Br2 bond. Thus the octahedron in (II) is much less fixed and this is obviously the main reason why the structure of this compound is modulated. Conversely, the weak contacts Se2···Br4 (see Table 6) are virtually unaffected by the modulation.

3.2. Origin of modulations in compound (II)

A comparison of the anions in (I) and (II) suggests two basic questions: firstly, why is the packing of the two neighboring Se_2Br_2 molecules different (Fig. 5); secondly, why do the *cis* and *trans* arrangements alternate in (II) (Fig. 4)?

In (II), atoms Br(5) point out of the Se_2Br_2—$TeBr_6$ chain and fit into the holes in the surrounding cation (see Fig. 6). The frequency of these holes is determined by the P—P distance, which is on average 11.27 Å along the chain. In this way the space requirements of the cation determine the distance between two Se_2Br_2 molecules. The same conclusions can be used in (I) where the atoms pointing out of the chain are Br(4) and Br(5) (Fig. 5*b*) and the P—P distance is 10.36 Å. The $TeBr_6$ octahedron is positioned between Se_2Br_2 molecules, which means that the Te—Te distance is also constrained: it is 10.36 and 11.26 Å in (I) and (II), respectively. The difference in packing of Se_2Br_2 molecules can be understood from the way in which the given spacing is achieved in the chain. The arrangement in the ring (see Fig. 5*a*) is closer and yields

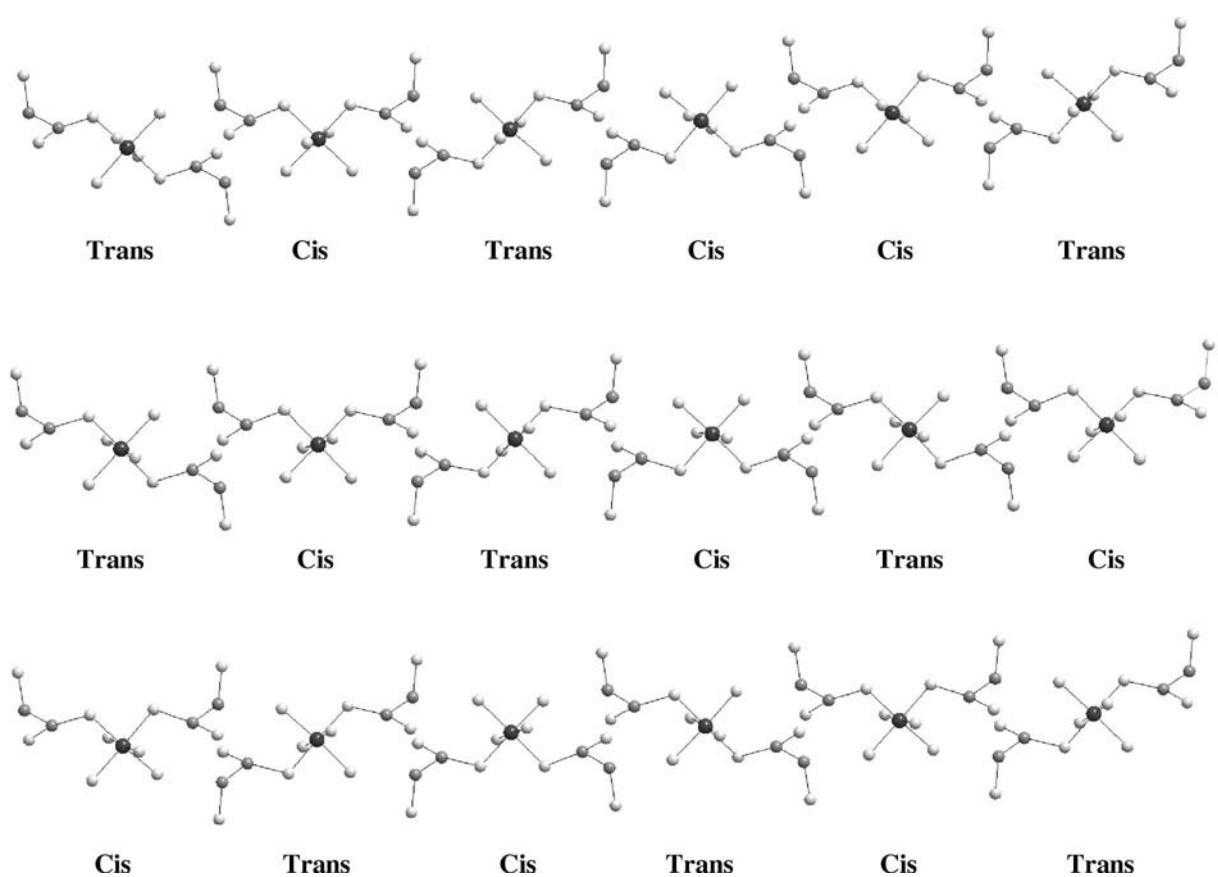

Figure 4
Packing of the $[TeBr_6(Se_2Br_2)_2]^{2-}$ ion, point group $2/m$, in the structure of (II).

shorter Te—Te distance in (I). The rather looser arrangement shown in Fig. 5(*b*) enables the Te—Te distance in (II) to be longer by almost 1 Å.

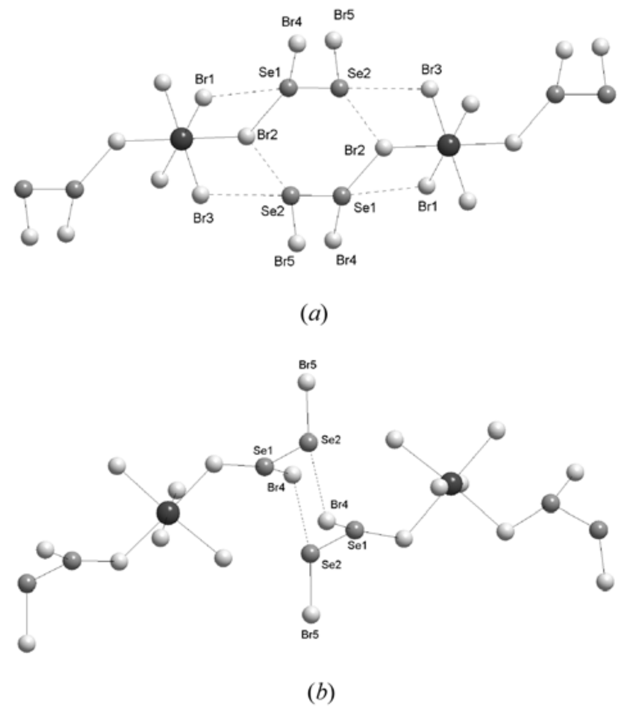

Figure 5
Intermolecular contacts of anions in (*a*) $[(C_2H_5)(C_6H_5)_3P]_2$ $[TeBr_6(Se_2Br_2)_2]$, (*b*) $[(C_6H_5)_4P]_2$ $[TeBr_6(Se_2Br_2)_2]$.

The relative positions of Se_2Br_2 and $TeBr_6$ in (I) are given by the Se—Br intermolecular bonds (see Fig. 5*b*). This geometry enables unambiguous connection of these units along the *a* axis. On the other hand, in (II), the chain can be formed in several ways (see Fig. 4): by Se_2Br_2 molecules in the *trans*- arrangement, in the *cis*- arrangement or in a combination of these arrangements. This ambiguity allows very weak interactions to play a role.

Table 8 shows that the Br—H distances are often significantly below the sum of the van der Waals radii (3.05 Å). In Fig. 6 only the Br—H distances shorter than 2.9 Å are plotted. Fig. 6 illustrates the fact that most of the interactions occur in the *cis* arrangement and only on one side of the chain. Although simple geometric considerations cannot quantify the strength of C—H···Br interactions, this arrangement probably introduces an instability that can be understood to be the source of the modulation. The creation of weak interactions at the opposite side implies that the existing weak interactions are destroyed and the $TeBr_6$ octahedron is turned upside down. The *trans* configuration without weak interactions represents an equilibrium stage.

Based on the above considerations the modulations in (II) are governed by the space requirements of the cation, which influence the packing of the Se_2Br_2 molecules. This packing leads to ambiguous arrangements in the Se_2Br_2—$TeBr_6$ chain, which is therefore affected by weak C—H···Br interactions. The modulation of the surrounding cation can be understood to be a response to the discontinuous modulations in the chain.

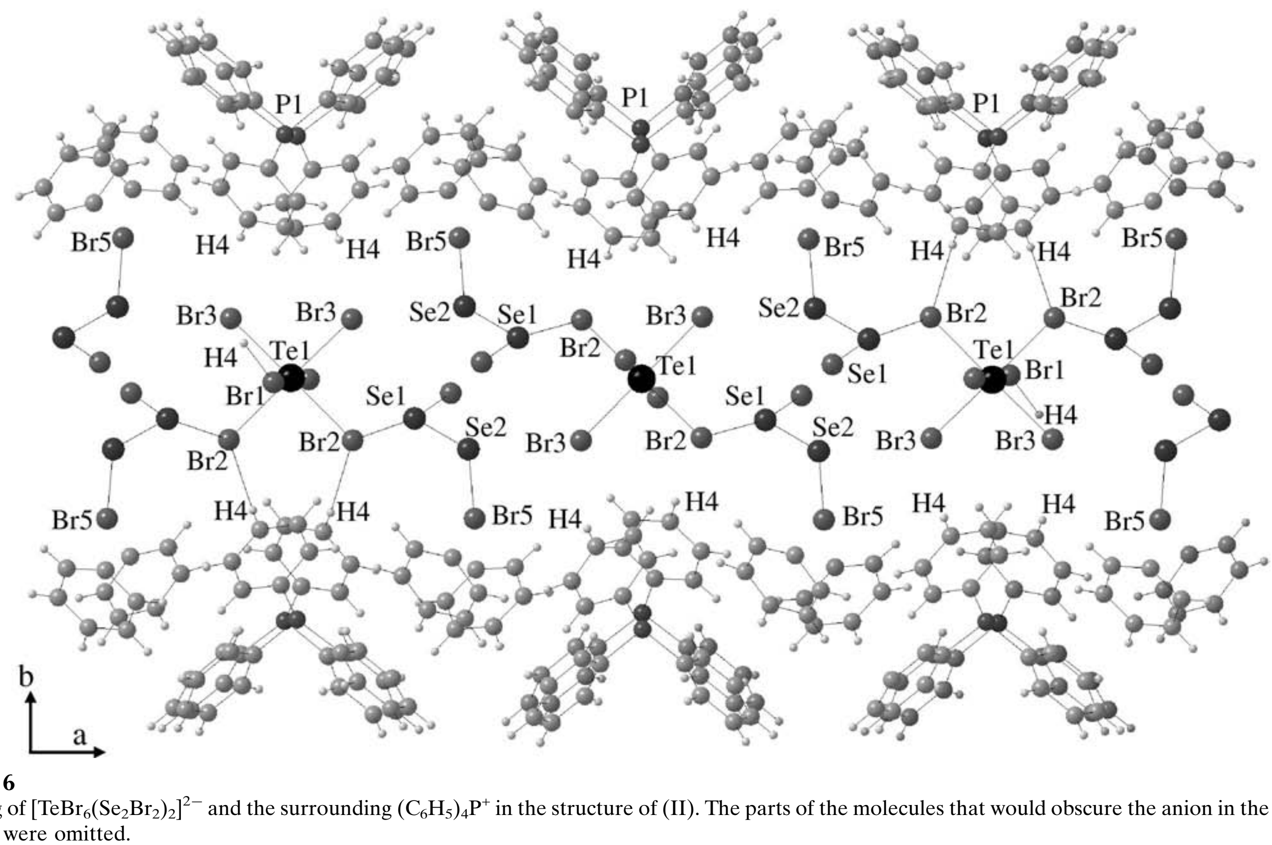

Figure 6
Packing of $[TeBr_6(Se_2Br_2)_2]^{2-}$ and the surrounding $(C_6H_5)_4P^+$ in the structure of (II). The parts of the molecules that would obscure the anion in the view along **c** were omitted.

Table 8
Distances (Å) between bromine and hydrogen in (II).

	Average	Minimal	Maximal
Br1—H4a^{i}	2.94 (5)	2.79 (5)	3.21 (5)
Br2—H3b^{ii}	3.08 (5)	2.89 (5)	3.24 (5)
Br2—H4b^{iii}	2.89 (5)	2.86 (5)	2.92 (5)
Br3—H5a^{iv}	3.06 (4)	2.91 (4)	3.13 (4)
Br3—H6a^{iv}	3.52 (4)	2.97 (4)	3.78 (4)
Br3—H4b^{v}	2.99 (5)	2.93 (5)	3.15 (5)
Br4—H6a^{vi}	3.28 (5)	2.87 (5)	3.49 (5)

Symmetry codes: (i) $-x, y, -1-z$; (ii) $-\frac{1}{2}-x, \frac{1}{2}+y, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iv) $-x, y, -z$; (v) $-x, -1+y, -z$; (vi) $\frac{3}{2}-x, \frac{1}{2}+y, -z$.

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