

Fig. 1. Stereoscopic drawing of the structure. Atoms are represented by their thermal ellipsoids of 50% probability.

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s

Te(2 ⁱ)-Am-Te(2 ⁱⁱ) Te(2 ⁱⁱ)-Am-Te(2 ⁱⁱⁱ) Te(2 ⁱ)-Am-Te(1 ⁱⁱ) Te(2 ⁱ)-Am-Te(1 ⁱⁱⁱ)	73.83 (4) 85.55 (2) 147.66 (7) 75.81 (3) 131.32 (3) 56.23 (2)
	56.23(2) 83.59(4)
	$Te(2^{ii})-Am-Te(2^{iii})$ $Te(2^{i})-Am-Te(1^{ii})$

Symmetry code: (i) 1 - x, 1 - y, 1 - z; (ii) 1 - x, -y, 1 - z; (iii) -x, -y, 1 - z; (iii) -x, 1 - y, 1 - z; (iv) x, y, 1 + z; (v) -x, 1 - y, -z.

perature of its preparation. From examination of the structure it seems reasonable that changes in stoichiometry limited to Te layers should affect the c/a ratio in this manner; namely that a decreases with increasing Te vacancies while c is little affected. In Table 3 can be seen some instances of the effect on c/a and on bond lengths of changing both the stoichiometry and the radius of the metallic element, M, in MTe_{2-x} .

Interatomic distances between Te(1) atoms are considerably less than van der Waals (4.4 Å) or Te^{2–} interionic distances (4.4 Å) and nearer to the Te–Te covalent bond length (2.8 Å); thus, there is probably some covalent bonding within the pure Te layer. The

Table 3. Comparison of distances (Å) in three tellurides, MTe,

	LaTe _{2.0}	NdTe ₁₋₈₀	AmTe ₁₋₇₃
M-Te(1)	3·38	3·29	3·27
M-Te(2)	3·29	3·27	3·26
M-Te(3)	3·26	3·22	3·21
Te(1)-Te(1)	$3 \cdot 19$	3·10	3.08
Te(1) - Te(2)	$4 \cdot 04$	3·99	3.98
Te(2)- Te(2)	$4 \cdot 01$	3·91	3.88
c/a	2.03	2.07	2.07

Te(2)-Te(2) distances are much longer than the Te(1)-Te(1) distances, and therefore can have much less, if any, electron interchange. The Am-Te(1) and Am-Te(2) bond lengths are not very different from each other in spite of the different structural role played by Te(1) and Te(2). These bonds are likely to have both ionic and covalent character.

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final R was 0.093 for 743 photographic data. The

distortion from the ideal structure is described in terms

of a rotation of the regular $SnBr_6^{2-}$ octahedron and a

shift of the K^+ ion mostly in the *b* direction. The

transition point at 399.8 (4) K was confirmed by

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Structure of Potassium Hexabromostannate(IV) at Room Temperature

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Abstract. K₂SnBr₆ at room temperature, monoclinic, $P2_1/n$, a = 10.621 (2), b = 7.427 (2), c = 7.442 (2) Å, $\beta = 90.18$ (2)°, $D_x = 3.825$ Mg m⁻³ for Z = 2. The crystal structure is a distorted K₂PtCl₆ structure. The

thermal measurement.

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Introduction. Two crystallographic studies on K_2SnBr_6 have previously been published: Ketelaar, Rietdijk & van Staveren (1937) concluded from powder data that the structure was the K_2PtCl_6 type with cubic *Fm3m* symmetry, while Markstein & Nowotny (1939) reported a distorted structure with tetragonal $P42_12$ symmetry. On the other hand, a pure quadrupole resonance study of this compound showed the presence of three kinds of non-equivalent Br atoms in the crystal, suggesting that the crystal symmetry is lower than tetragonal (Nakamura, Ito & Kubo, 1962). The present work was undertaken to establish the structure of K_2SnBr_6 and solve the inconsistency.

Single yellow crystals were grown by slow evaporation of an aqueous solution prepared by the procedure of Ketelaar et al. (1937), keeping the temperature at 343 K to prevent twinning. The crystals were easily twinned by slight stress and required cautious handling. The intensity distribution on precession photographs showed distinct 2/m point symmetry, though apparently pseudo-cubic or pseudotetragonal. Lattice parameters were measured from Weissenberg photographs calibrated with NaCl powder lines. The systematic absences, h0l with h + l = 2n + 1, 0k0 with k = 2n + 1, indicated the space group $P2_1/n$. Visually estimated intensities recorded on the precession photographs taken with Zr-filtered Mo Ka radiation were reduced to 743 observed F data by application of the usual corrections. An absorption correction was not applied. All atoms except the Sn atom at the special position (1) were located by Patterson and successive Fourier syntheses. Several cycles of fullmatrix least-squares refinement with the ansiotropic thermal parameters gave the final R of 0.093.*Anomalous dispersion was accounted for in the structure factor calculation. Atomic scattering factors for K⁺, Sn⁴⁺, and Br⁻ were taken from *International* Tables for X-ray Crystallography (1974). The final atomic parameters are given in Table 1. Interatomic distances and angles are listed in Table 2.

Discussion. K_2SnBr_6 has a distorted K_2PtCl_6 type structure at room temperature. The symmetry is not

Table 1. Final positional parameters

	x	У	Ζ
Sn	0	0	0
К	0.2514 (10)	0-4682 (14)	-0.0055 (14)
Br(1)	0.0249 (4)	0.2088 (5)	<i>−</i> 0·2765 (5)
Br(2)	0.0199 (4)	<i>−</i> 0·2782 (5)	-0.2078 (5)
Br(3)	0.2426 (3)	0.0005 (7)	0.0450 (5)

tetragonal (Markstein & Nowotny, 1939) but monoclinic $P2_1/n$, though the shape of the unit cell is close to that of a tetragonal lattice. There are three crystallographically non-equivalent Br atoms, which are consistent with the triplet resonance spectra (Nakamura et al., 1962). The $SnBr_{6}^{2-}$ anion forms a regular octahedron within experimental error (Fig. 1, Table 2) with an averaged Sn-Br length of 2.593 (2) Å, in good agreement with the sum of the Br covalent radius (1.14 Å) and the Sn^{1V} octahedral radius (1.45 Å). The corrected Sn-Br distance was 2.600 Å, assuming the libration of the rigid $SnBr_6^{2-}$ ion (Cruickshank, 1956). The distortion from the ideal K_2PtCl_6 structure (Fig. 2) is described by the rotation of the SnBr₆ octahedron about the a and b axes by $8 \cdot 10$ and $7 \cdot 48^{\circ}$ respectively, resulting in the change of the Br arrangement around the K⁺ cation. In the K_2 PtCl₆ structure the K⁺ ion has twelve equally separated Cl neighbours, three from each of four PtCl²⁻ ions, while in the present structure the K⁺ ion, of which the position is shifted by 0.239 Å from $(\frac{1}{4},\frac{1}{2},0)$ mainly in the b direction, has four Br neighbours, each from four different SnBr₆²⁻ ions, roughly in the form of a tetrahedron, and the other Br atoms are situated at rather larger distances. A stereoscopic view of the structure is shown in Fig. 3.

In A_2BX_6 compounds of this type, K_2TeBr_6 (Brown, 1964) and K_2TeI_6 (Syoyama, Osaki & Kusanagi, 1972) have been reported to show similar distortions from the cubic K_2PtCI_6 structure. The symmetry of both

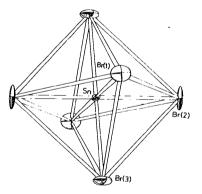


Fig. 1. The structure of the $SnBr_6^{2-}$ anion.

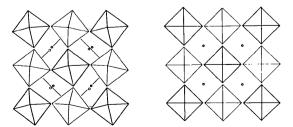


Fig. 2. The crystal structures of K₂SnBr₆ (left) and K₂PtCl₆(right). Full and dotted lines in the left figure represent monoclinic and pseudo-cubic unit cells respectively.

^{*} Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33933 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

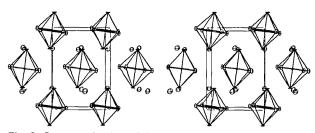


Fig. 3. Stereoscopic view of the crystal structure projected along the *b* axis.

Table 2. Interatomic distances (Å) and angles (°)

Standard deviations are Sn-Br = 0.003 Å, $Br-Sn-Br = 0.2^{\circ}$, K-Br = 0.01 Å, Br-Br = 0.005 Å.

Sn-Br(1)	2.591	$\begin{array}{l} Br(1)-Sn-Br(2)\\ Br(2)-Sn-Br(3)\\ Br(3)-Sn-Br(1)\\ Br(1)-Br(2^{i})\\ Br(2)-Br(3^{i})\\ Br(3)-Br(1^{i}) \end{array}$	89.7
Sn-Br(2)	2.590		89.7
Sn-Br(3)	2.597		89.9
Br(1)-Br(2)	3.654		3.673
Br(2)-Br(3)	3.659		3.676
Br(3)-Br(1)	3.664		3.673
$\begin{array}{l} K - Br(1^{iii} - c) \\ K - Br(3^{iii}) \\ K - Br(2 + b) \\ K - Br(3) \\ K - Br(2^{i}) \\ K - Br(1^{ii}) \end{array}$	3.39 3.44 3.44 3.49 3.58 3.61		3.68 3.72 3.97 4.02 4.28 4.34
$Br(3)-Br(2^{ii}-b)$	3·841	$Br(1)-Br(2^{ii}-c)$	3.900
Br(1)-Br(2+b)	3·845	$Br(3)-Br(1^{ii})$	3.924
$Br(1)-Br(3^{iii}-c)$	3·849	$Br(3)-Br(2^{iii}-c)$	3.925

Symmetry code: (i) -x,-y,-z; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. The other symbols represent cell translations.

compounds is monoclinic $P2_1/n$ and the regular BX_6 octahedron is rotated from the ideal position about the a and b axes by 12 and 9° in K_2 TeBr₆, and by 11.0 and 11.5° in K₂TeI₆, respectively. In particular, the mean distance from the K⁺ ion to the tetrahedral Br atoms, 3.44 Å in K₂SnBr₆, is in good agreement with that in K_2 TeBr₆ (3.43 Å) which has a similar tetrahedral Br environment around the K⁺ ion, and the average Br-Br contact between different octahedra is 3.88 Å in both compounds. This suggests that the distortion from the K_2 PtCl₆ structure in the A_2BX_6 compounds of this type, as pointed out by Brown (1964), arises from a cooperative rotation of BX_6 octahedra so as to fix the small A cation, which is too small to lie settled in the larger cavity offered by a cubic lattice. This explanation is consistent with the fact that the rotation is smaller for a small $SnBr_{6}$ octahedron (Sn-Br = 2.593 Å) than for larger TeBr₆ (Te-Br = 2.706 Å) and TeI₆ (Te-I = 2.93 Å) octahedra. Also, the thermal motion of the K⁺ ion having a larger component in a more open direction in the tetrahedral cage seems to support this view. The ease of twinning, which is common in these compounds, is probably related to the easiness of the rotational motion of the BX_6 octahedron, represented by the anisotropic thermal motion of the Br atoms (average r.m.s. amplitude 0.07 Å along the Sn-Br bond, 0.27 Å perpendicular to it).

 K_2 SnBr₆ has been shown by powder diffractometry to undergo a phase transition at 399.5 K (Galloni, de Benyacar & de Abeledo, 1962) and our thermal measurement by differential scanning calorimetry (DSC) confirmed its occurrence, at 399.8 (4) K. The present structure analysis at room temperature, therefore, is that of the low-temperature form. A similar transition was found in K₂SnCl₆ at 262.0 K (Morfee, Staveley, Walters & Wigley, 1960), where the hightemperature form was recently determined to be the K₂PtCl₆ type (Lerbscher & Trotter, 1976). The similarity of both compounds suggests that the hightemperature form of K₂SnBr₆ has the K₂PtCl₆ structure as assumed by Galloni, de Benyacar & de Abeledo (1962) and the low-temperature form of K₂SnCl₆ is probably isomorphous with the present structure.* The difference in the transition temperature of both compounds can be explained by the difference in size of SnBr_{6} and SnCl_{6} octahedra (Sn-Cl = 2.409 Å).

The authors wish to thank the Shimadzu Co. Ltd for the DSC measurement. The computation was performed at the Data Processing Center, Kyoto University.

* After completion of this manuscript, a neutron powder diffraction study of K_2SnCl_6 came to our notice (Boysen & Hewat, 1978), where the low-temperature structure was concluded to be the same as that of K_2SnBr_6 at room temperature.

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