

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 $Fm\bar{3}m$ symmetry, while Markstein & Nowotny (1939) reported a distorted structure with tetragonal $P4_2,2$ 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 pseudo-tetragonal. 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 $K\alpha$ 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 full-matrix least-squares refinement with the anisotropic thermal parameters gave the final R of 0.093.* Anomalous dispersion was accounted for in the structure factor calculation. Atomic scattering factors for K^+ , Sn^{4+} , 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

* 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.

Table 1. *Final positional parameters*

	<i>x</i>	<i>y</i>	<i>z</i>
Sn	0	0	0
K	0.2514 (10)	0.4682 (14)	-0.0055 (14)
Br(1)	0.0249 (4)	0.2088 (5)	-0.2765 (5)
Br(2)	0.0199 (4)	-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^{IV} 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 $SnBr_6$ octahedron about the *a* and *b* axes by 8.10 and 7.48° respectively, resulting in the change of the Br arrangement around the K^+ cation. In the K_2PtCl_6 structure the K^+ ion has twelve equally separated Cl neighbours, three from each of four $PtCl_6^{2-}$ 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 $SnBr_6^{2-}$ 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_2PtCl_6 structure. The symmetry of both

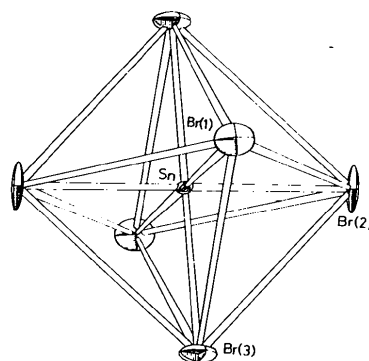


Fig. 1. The structure of the $SnBr_6^{2-}$ anion.

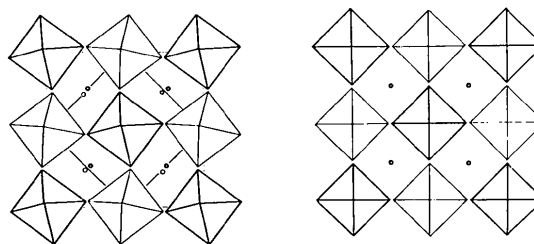


Fig. 2. The crystal structures of K_2SnBr_6 (left) and K_2PtCl_6 (right). Full and dotted lines in the left figure represent monoclinic and pseudo-cubic unit cells respectively.

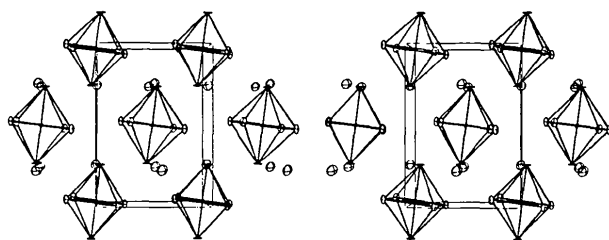


Fig. 3. Stereoscopic view of the crystal structure projected along the b axis.

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

Standard deviations are Sn—Br = 0.003 Å, Br—Sn—Br = 0.2°, K—Br = 0.01 Å, Br—Br = 0.005 Å.

Sn—Br(1)	2.591	Br(1)—Sn—Br(2)	89.7
Sn—Br(2)	2.590	Br(2)—Sn—Br(3)	89.7
Sn—Br(3)	2.597	Br(3)—Sn—Br(1)	89.9
Br(1)—Br(2)	3.654	Br(1)—Br(2 ⁱ)	3.673
Br(2)—Br(3)	3.659	Br(2)—Br(3 ⁱ)	3.676
Br(3)—Br(1)	3.664	Br(3)—Br(1 ⁱ)	3.673
K—Br(1 ⁱⁱⁱ - c)	3.39	K—Br(1)	3.68
K—Br(3 ⁱⁱⁱ)	3.44	K—Br(2 ⁱⁱⁱ - c)	3.72
K—Br(2 + b)	3.44	K—Br(3 + b)	3.97
K—Br(3)	3.49	K—Br(3 ⁱⁱⁱ - c)	4.02
K—Br(2 ⁱ)	3.58	K—Br(2 ⁱⁱ)	4.28
K—Br(1 ⁱⁱ)	3.61	K—Br(1 ⁱ + b)	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_2TeBr_6 , and by 11.0 and 11.5° in K_2TeI_6 , respectively. In particular, the mean distance from the K^+ ion to the tetrahedral Br atoms, 3.44 Å in K_2SnBr_6 , is in good agreement with that in K_2TeBr_6 (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_2PtCl_6 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 $TeBr_6$ (Te—Br = 2.706 Å) and TeI_6 (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 com-

pounds, 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_2SnBr_6 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 K_2SnCl_6 at 262.0 K (Morfee, Staveley, Walters & Wigley, 1960), where the high-temperature form was recently determined to be the K_2PtCl_6 type (Lerbscher & Trotter, 1976). The similarity of both compounds suggests that the high-temperature form of K_2SnBr_6 has the K_2PtCl_6 structure as assumed by Galloni, de Benyacar & de Abeledo (1962) and the low-temperature form of K_2SnCl_6 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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