

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

Table 2. Bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ with e.s.d.'s

| Am-Te(1) | 3.269 (1) | $\mathrm{Te}(2)-\mathrm{Am}-\mathrm{Te}\left(2^{\text {i }}\right.$ ) | $73 \cdot 83$ (4) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Am}-\mathrm{Te}(2)$ | $3 \cdot 258$ (2) | $\mathrm{Te}\left(2^{\mathrm{i}}\right)-\mathrm{Am}-\mathrm{Te}\left(2^{\text {ii }}\right)$ | 85.55 (2) |
| $\mathrm{Am}-\mathrm{Te}\left(2^{\mathrm{i}}\right)$ | $3 \cdot 208$ (1) | $\mathrm{Te}\left(2^{\text {ii }}\right)-\mathrm{Am}-\mathrm{Te}\left(2^{\text {iii }}\right)$ | 147.66 (7) |
| $\mathrm{Te}(1)-\mathrm{Te}\left(\mathrm{I}^{\text {V }}\right.$ ) | 3.081 (1) | $\mathrm{Te}\left(2^{\mathrm{i}}\right)-\mathrm{Am}-\mathrm{Te}\left(1^{\text {iii }}\right)$ | 75.81 (3) |
| $\mathrm{Te}(1)-\mathrm{Te}(2)$ | 3.980 (2) | $\mathrm{Te}\left(2^{\mathrm{i}}\right)-\mathrm{Am}-\mathrm{Te}\left(1^{\text {iii }}\right)$ | 131.32 (3) |
| $\mathrm{Te}(2)-\mathrm{Te}\left(2^{\text {i }}\right.$ ) | $3 \cdot 884$ (2) | $\mathrm{Te}\left(1^{\mathrm{i}}\right)-\mathrm{Am}-\mathrm{Te}\left(1^{\text {iv }}\right)$ | $56 \cdot 23$ (2) |
|  |  | $\mathrm{Te}\left(1^{\text {i }}\right.$ )-Am-Te( ${ }^{\text {iiii }}$ ) | $83 \cdot 59$ (4) |

Symmetry code: (i) $1-x, 1-y, 1-z$; (ii) $1-x,-y, 1-z$; (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 $M \mathrm{Te}_{2-x}$.

Interatomic distances between $\mathrm{Te}(1)$ atoms are considerably less than van der Waals ( $4 \cdot 4 \AA$ ) or $\mathrm{Te}^{2-}$ interionic distances $(4.4 \AA)$ and nearer to the $\mathrm{Te}-\mathrm{Te}$ covalent bond length ( $2.8 \AA$ ); thus, there is probably some covalent bonding within the pure Te layer. The

Table
3. Comparison of distances
( $\AA$ ) in three tellurides, $M \mathrm{Te}_{2}$,

|  | $\mathrm{LaTe}_{2.11}$ | $\mathrm{NdTe}_{1.811}$ | $\mathrm{AmTe}_{1.77}$ |
| :--- | :---: | :---: | :---: |
| $M-\mathrm{Te}(1)$ | 3.38 | 3.29 | 3.27 |
| $M-\mathrm{Te}(2)$ | 3.29 | 3.27 | 3.26 |
| $M-\mathrm{Te}(3)$ | 3.26 | 3.22 | 3.21 |
| $\mathrm{Te}(1)-\mathrm{Te}(1)$ | 3.19 | 3.10 | 3.08 |
| $\mathrm{Te}(1)-\mathrm{Te}(2)$ | 4.04 | 3.99 | 3.98 |
| $\mathrm{Te}(2)-\mathrm{Te}(2)$ | 4.01 | 3.91 | 3.88 |
| $\boldsymbol{c} a$ | 2.03 | 2.07 | 2.07 |

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

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# Structure of Potassium Hexabromostannate(IV) at Room Temperature 

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#### Abstract

K}_{2} \mathrm{SnBr}_{6}\) at room temperature, monoclinic, $P 21_{1} / n, a=10.621$ (2), $b=7.427$ (2), $c=7.442$ (2) $\AA$ A, $\beta=90.18(2)^{\circ}, D_{x}=3.825 \mathrm{Mg} \mathrm{m}^{-3}$ for $Z=2$. The crystal structure is a distorted $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ structure. The


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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 $\mathrm{SnBr}_{6}^{2-}$ octahedron and a shift of the $\mathrm{K}^{+}$ion mostly in the $b$ direction. The transition point at 399.8 (4) K was confirmed by thermal measurement.

Introduction. Two crystallographic studies on $\mathrm{K}_{2} \mathrm{SnBr}_{6}$ have previously been published: Ketelaar, Rietdijk \& van Staveren (1937) concluded from powder data that the structure was the $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ type with cubic Fm 3 m symmetry, while Markstein \& Nowotny (1939) reported a distorted structure with tetragonal $P 42,2$ 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 $\mathrm{K}_{2} \mathrm{SnBr}_{6}$ 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 $2 / \mathrm{m}$ point symmetry, though apparently pseudo-cubic or pseudotetragonal. Lattice parameters were measured from Weissenberg photographs calibrated with NaCl powder lines. The systematic absences, $h 0 l$ with $h+l=2 n+1$, $0 k 0$ with $k=2 n+1$, indicated the space group $P 2_{1} / n$. Visually estimated intensities recorded on the precession photographs taken with Zr -filtered Mo Kr 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 (i) 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 $\mathrm{K}^{+}, \mathrm{Sn}^{4+}$, and $\mathrm{Br}^{-}$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. $\mathrm{K}_{2} \mathrm{SnBr}_{6}$ has a distorted $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ type structure at room temperature. The symmetry is not

[^1]Table 1. Final positional parameters

|  | $x$ | $y$ | $z$ |
| :--- | :--- | :--- | :--- |
|  | 0 | 0 | 0 |
| Sn | 0 | $0.4682(14)$ | $-0.0055(14)$ |
| K | $0.2514(10)$ | $x$ |  |
| $\operatorname{Br}(1)$ | $0.0249(4)$ | $0.2088(5)$ | $-0.2765(5)$ |
| $\operatorname{Br}(2)$ | $0.0199(4)$ | $-0.2782(5)$ | $-0.2078(5)$ |
| $\operatorname{Br}(3)$ | $0.2426(3)$ | $0.0005(7)$ | $0.0450(5)$ |

tetragonal (Markstein \& Nowotny, 1939) but monoclinic $P 2_{1} / n$, 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 $\mathrm{SnBr}_{6}^{2-}$ anion forms a regular octahedron within experimental error (Fig. 1, Table 2) with an averaged $\mathrm{Sn}-\mathrm{Br}$ length of 2.593 (2) $\AA$, in good agreement with the sum of the Br covalent radius ( 1.14 $\AA$ ) and the $\mathrm{Sn}^{\mathrm{IV}}$ octahedral radius $(1.45 \AA)$. The corrected $\mathrm{Sn}-\mathrm{Br}$ distance was $2 \cdot 600 \AA$, assuming the libration of the rigid $\mathrm{SnBr}_{6}^{2-}$ ion (Cruickshank, 1956). The distortion from the ideal $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ structure (Fig. 2) is described by the rotation of the $\mathrm{SnBr}_{6}$ octahedron about the $a$ and $b$ axes by $8 \cdot 10$ and $7.48^{\circ}$ respectively, resulting in the change of the Br arrangement around the $\mathrm{K}^{+}$cation. In the $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ structure the $\mathrm{K}^{+}$ion has twelve equally separated Cl neighbours, three from each of four $\mathrm{PtCl}_{6}^{2-}$ ions, while in the present structure the $\mathrm{K}^{+}$ion, of which the position is shifted by $0.239 \AA$ from ( $\frac{1}{4}, \frac{1}{2}, 0$ ) mainly in the $b$ direction, has four Br neighbours, each from four different $\mathrm{SnBr}_{6}^{2-}$ 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 $A_{2} B X_{6}$ compounds of this type, $\mathrm{K}_{2} \mathrm{TeBr}_{6}$ (Brown, 1964) and $\mathrm{K}_{2} \mathrm{TeI}_{6}$ (Syoyama, Osaki \& Kusanagi, 1972) have been reported to show similar distortions from the cubic $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ structure. The symmetry of both


Fig. 1. The structure of the $\mathrm{SnBr}_{6}^{2-}$ anion.


Fig. 2. The crystal structures of $\mathrm{K}_{2} \mathrm{SnBr}_{6}$ (left) and $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ (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 $(\AA)$ and angles $\left({ }^{\circ}\right)$
Standard deviations are $\mathrm{Sn}-\mathrm{Br}=0.003 \dot{\mathrm{~A}}, \mathrm{Br}-\mathrm{Sn}-\mathrm{Br}=0.2^{\circ}$. $\mathrm{K}-\mathrm{Br}=0.01 \AA, \mathrm{Br}-\mathrm{Br}=0.005 \AA$.

| $\mathrm{Sn}-\mathrm{Br}(1)$ | 2.591 | $\mathrm{Br}(1)-\mathrm{Sn}-\mathrm{Br}(2)$ | 89.7 |
| :---: | :---: | :---: | :---: |
| $\mathrm{Sn}-\mathrm{Br}(2)$ | 2.590 | $\mathrm{Br}(2)-\mathrm{Sn}-\mathrm{Br}(3)$ | 89.7 |
| $\mathrm{Sn}-\mathrm{Br}(3)$ | 2.597 | $\mathrm{Br}(3)-\mathrm{Sn}-\mathrm{Br}(1)$ | 89.9 |
| $\operatorname{Br}(1)-\operatorname{Br}(2)$ | 3.654 | $\operatorname{Br}(1)-\operatorname{Br}\left(2^{\text {i }}\right.$ ) | 3.673 |
| $\mathrm{Br}(2)-\mathrm{Br}(3)$ | $3 \cdot 659$ | $\operatorname{Br}(2)-\operatorname{Br}\left(3^{\text {i }}\right.$ ) | 3.676 |
| $\operatorname{Br}(3)-\operatorname{Br}(1)$ | 3.664 | $\operatorname{Br}(3)-\operatorname{Br}\left(\mathrm{I}^{\text {i }}\right.$ ) | 3.673 |
| $\mathrm{K} \cdot-\operatorname{Br}\left(\mathrm{I}^{\mathrm{iii}}-c\right)$ | $3 \cdot 39$ | $\mathrm{K}-\operatorname{Br}(1)$ | 3.68 |
| $\mathrm{K}-\mathrm{Br}\left(3^{\text {iii) }}\right.$ ) | 3.44 | $\mathrm{K}-\operatorname{Br}\left(2^{\text {iii }}-c\right)$ | 3.72 |
| $\mathrm{K}-\mathrm{Br}(2+b)$ | 3.44 | $\mathrm{K}-\mathrm{Br}(3+b)$ | 3.97 |
| $\mathrm{K}-\mathrm{Br}(3)$ | 3.49 | $\mathrm{K}-\mathrm{Br}\left(3^{\text {iii }}-c\right)$ | 4.02 |
| $\mathrm{K}-\mathrm{Br}\left(2^{\text {i }}\right.$ ) | 3.58 | $\mathrm{K}-\operatorname{Br}\left(2^{\text {ii }}\right.$ ) | 4.28 |
| $\mathrm{K}-\mathrm{Br}\left(\mathrm{I}^{\text {ii }}\right.$ ) | 3.61 | $\mathrm{K}-\mathrm{Br}\left(\mathrm{l}^{\mathbf{i}}+\mathrm{b}\right)$ | 4.34 |
| $\operatorname{Br}(3)-\operatorname{Br}\left(2^{\text {ii }}+\right.$ b $)$ | 3.841 | $\operatorname{Br}(1)-\operatorname{Br}\left(2^{\mathrm{ii}}-\boldsymbol{c}\right)$ | 3.900 |
| $\operatorname{Br}(1)-\operatorname{Br}(2+b)$ | 3.845 | $\operatorname{Br}(3)-\operatorname{Br}\left(1^{\text {ii }}\right)$ | 3.924 |
| $\operatorname{Br}(1)-\operatorname{Br}\left(3^{\text {iii }}-c\right)$ | 3.849 | $\operatorname{Br}(3)-\operatorname{Br}\left(2^{\text {iii }}-c\right)$ | 3.925 |

Symmetry code: (i) $-x,-y,-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x$. $\frac{1}{2}+1 ; \frac{1}{2}-z$. The other symbols represent cell translations.
compounds is monoclinic $P 2_{1} / n$ and the regular $B X_{6}$ octahedron is rotated from the ideal position about the $a$ and $b$ axes by 12 and $9^{\circ}$ in $\mathrm{K}_{2} \mathrm{TeBr}_{6}$, and by 11.0 and $11.5^{\circ}$ in $\mathrm{K}_{2} \mathrm{TeI}_{6}$, respectively. In particular, the mean distance from the $\mathrm{K}^{+}$ion to the tetrahedral Br atoms, $3.44 \AA$ in $\mathrm{K}_{2} \mathrm{SnBr}_{6}$, is in good agreement with that in $\mathrm{K}_{2} \mathrm{TeBr}_{6}(3.43 \AA)$ which has a similar tetrahedral Br environment around the $\mathrm{K}^{+}$ion, and the average $\mathrm{Br}-\mathrm{Br}$ contact between different octahedra is $3.88 \AA$ in both compounds. This suggests that the distortion from the $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ structure in the $A_{2} B X_{6}$ compounds of this type, as pointed out by Brown (1964), arises from a cooperative rotation of $B X_{6}$ 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 $\mathrm{SnBr}_{6}$ octahedron ( $\mathrm{Sn}-\mathrm{Br}=2.593 \AA$ ) than for larger $\mathrm{TeBr}_{6}(\mathrm{Te}-\mathrm{Br}=2.706 \AA)$ and $\mathrm{TeI}_{6}(\mathrm{Te}-\mathrm{I}=$ $2.93 \AA$ ) octahedra. Also, the thermal motion of the $\mathrm{K}^{+}$ 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 $B X_{6}$ octahedron, represented by the anisotropic thermal motion of the Br atoms (average r.m.s. amplitude $0.07 \AA$ along the $\mathrm{Sn}-\mathrm{Br}$ bond, $0.27 \AA$ perpendicular to it).
$\mathrm{K}_{2} \mathrm{SnBr}_{6}$ 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 $\mathrm{K}_{2} \mathrm{SnCl}_{6}$ at 262.0 K (Morfee, Staveley, Walters \& Wigley, 1960), where the hightemperature form was recently determined to be the $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ type (Lerbscher \& Trotter, 1976). The similarity of both compounds suggests that the hightemperature form of $\mathrm{K}_{2} \mathrm{SnBr}_{6}$ has the $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ structure as assumed by Galloni, de Benyacar \& de Abeledo (1962) and the low-temperature form of $\mathrm{K}_{2} \mathrm{SnCl}_{6}$ 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 $\mathrm{SnBr}_{6}$ and $\mathrm{SnCl}_{6}$ octahedra $(\mathrm{Sn}-\mathrm{Cl}=2.409 \AA$ ).

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* After completion of this manuscript, a neutron powder diffraction study of $\mathrm{K}_{2} \mathrm{SnCl}_{6}$ came to our notice (Boysen \& Hewat, 1978), where the low-temperature structure was concluded to be the same as that of $\mathrm{K}_{2} \mathrm{SnBr}_{6}$ at room temperature.


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[^1]:    * 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 CH 1 2HU, England.

