GRENTHE, I. & NORDIN, E. (1978). To be published.

HANSSON, M. & BÖRTIN, O. (1968). Acta Chem. Scand. 22, 1689.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KAY, M. I. & FRAZER, B. C. (1961). Acta Cryst. 14, 56–57.

KLANDERMAN, K. A., HAMILTON, W. C. & BERNAL, I. (1977). Inorg. Chim. Acta, 23, 117–129.

LINHARD, M., SIEBERT, H. & WEIGEL, M. (1955). Z. Anorg. Allg. Chem. 278, 287–299.

MORI, M. (1957). Inorg. Synth. 5, 131–135.

NAKAMOTO, K., FUJITA, J. & MURATA, H. (1958). J. Am. Chem. Soc. 80, 4817–4823.

RAYMOND, K. N., MEEK, D. W. & IBERS, J. A. (1968). Inorg. Chem. 7, 1111–1117.

STEPHENS, F. S. (1969). J. Chem. Soc. A, pp. 2081–2087.

SVENSSON, C. (1975). Acta Cryst. B31, 2016–2018.

# Rubidium Hexabromobismuthate(III)

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**Abstract.** $Rb_3BiBr_6$, orthorhombic, Pnma, $a = 13.311$ (8), $b = 26.63$ (1), $c = 8.603$ (4) Å; $D_o = 4.10$ (1) g cm$^{-3}$, $Z = 8$, $D_c = 4.115$ g cm$^{-3}$; $R = 0.079$ for 1240 reflexions [$I > 4\sigma(I)$]. The structure consists of isolated octahedral $BiBr_6^{3-}$ anions and of $Rb^+$ cations with thoroughly irregular coordination polyhedra.

**Introduction.** This work is a new part of the systematic investigation of the stereochemical behaviour of the hexahalobismuthate(III) groups in the presence of various cations (Lazarini, 1977a,b,c,d). There are few known $A_3BX_6$ structures (Wells, 1975). Almost all of them can be derived from the cryolite structural type. $Rb_3BiBr_6$ seems to be unrelated to this structural family.

Yellow crystals of $Rb_3BiBr_6$ were grown by slow evaporation from an aqueous solution obtained by dissolving $Bi(OH)_3$ and $Rb_2CO_3$ (molar 2:3 ratio) in a dilute HBr solution. The formula was determined by standard chemical analytical methods (calculated: 22.12% Bi, 50.74% Br; found: 22.0% Bi, 51.2% Br). A well developed crystal, selected for the intensity measurements, was characterized by the following planes (in parentheses are the distances from the crystal faces to an arbitrary origin inside the crystal): (010) (0.316 mm), (0$\bar{1}$0) (0.012 mm), $\pm$(011) (0.178 mm), $\pm$(0$\bar{1}$1) (0.178 mm), (111) (0.234 mm), ($\bar{1}$1$\bar{1}$) (0.222 mm), (11$\bar{1}$) (0.225 mm), ($\bar{1}$1$\bar{1}$) (0.197 mm), ($\bar{1}$11) (0.233 mm), (11$\bar{1}$) (0.190 mm) and ($\bar{1}$11) (0.240 mm).

The intensity data were collected at 20 (1)°C with an Enraf–Nonius CAD-4 diffractometer. Experi-

mental conditions were: graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), $\omega$–$2\theta$ scan, $\theta_{min} = 1$, $\theta_{max} = 25°$, $2\theta$ scan width (°) $= 0.9 + 0.2 \tan \theta$, aperture (mm) $= 2.5 + 0.9 \tan \theta$, maximum scan time $= 30$ s, background: $\frac{1}{4}$ of the scan time at each of the scan limits. A set of 2722 independent reflexions were recorded. During the refinement procedure, it became apparent that the weaker reflexions were poorly measured. Therefore all reflexions with $I < 4\sigma(I)$ (calculations based on counting statistics) were rejected and only 1240 reflexions used in the refinement. Corrections were applied for Lorentz and polarization effects and for absorption [$\mu$(Mo $K\alpha$) $= 376.4$ cm$^{-1}$]. The absorption corrections $A^*$, calculated with the measured crystal dimensions (Gaussian-grid method), range from 34.9 to 206.3. The unit-cell parameters were obtained from a least-squares fit of the $\theta$ values of 15 reflexions measured on the diffractometer. The systematic absences ($0kl$: $k + l = 2n + 1$; $hk0$: $h = 2n + 1$) and the clearly centrosymmetric distribution of the normalized structure factors indicated the space group Pnma, which was subsequently confirmed by successful refinement.†

The positions of two Bi atoms of the asymmetrical set [on special 4(b) and 4(c) positions] were determined from the three-dimensional Patterson map, while the Br and Rb atoms were located from two successive

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33486 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fourier summations. The structure was then refined by full-matrix least-squares techniques with anisotropic thermal parameters and anomalous-dispersion correction for all atoms. The function minimized in the least-squares procedure was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was as follows: when $|F_o| \leq 100$: $w_F = (|F_o|/100)^{2\cdot5}$, when $100 < |F_o| \leq 220$: $w_F = 1\cdot0$, when $|F_o| > 220$: $w_F = (220/|F_o|)^{1\cdot5}$, when $\sin\theta \leq 0\cdot20$: $w_S = (\sin\theta/0\cdot20)^{1\cdot5}$, when $0\cdot20 < \sin\theta \leq 0\cdot38$: $w_S = 1\cdot0$, when $\sin\theta > 0\cdot38$: $w_S = (0\cdot38/\sin\theta)^{2\cdot0}$, $w = 0\cdot1 w_F w_S$. An isotropic extinction parameter (Zachariasen, 1963; Larson, 1967) was also included in the final stage of the refinement [$g = 2\cdot6$ (4) $\times 10^{-3}$]. Final $R$ values are: $R = \sum||F_o| - |F_c||/\sum|F_o| = 0\cdot079$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0\cdot098$ for 1240 reflexions and 98 parameters. The average parameter shift to error ratio was 0·03 in the final cycle.

All calculations were performed on the CDC Cyber computer of RRC Ljubljana with the XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) adapted by Professor L. Golič. Atomic scattering factors for neutral atoms tabulated by Cromer & Mann (1968) and the values of $f'$ and $f''$ for the anomalous-dispersion correction tabulated by Cromer & Liberman (1970) were applied.

The positional parameters are listed in Table 1. A stereoscopic drawing (Johnson, 1965) of the structure and the atom-numbering system used are shown in Fig. 1. Some important interatomic distances and angles are given in Table 2.

**Discussion.** The structure of $Rb_3BiBr_6$ consists of isolated octahedral $BiBr_6^{3-}$ anions and $Rb^+$ cations. The coordination polyhedra of Br atoms around $Rb^+$ cations are thoroughly irregular. The two $BiBr_6^{3-}$ octahedra of the asymmetrical set [Bi(1) is on a mirror plane, Bi(2) on a symmetry centre] are similar, as regards bond distances and angles, but both are slightly distorted. The deviations from the regular octahedral geometry are not very significant and are probably due to crystal-packing forces.

The Bi—Br bond lengths range from 2·824 to 2·884 Å. It is interesting to compare these bond lengths with the Bi—Br(terminal) and Bi—Br(bridging) distances in

Table 1. *Final positional parameters* $(\times10^4)$ *with standard deviations in parentheses*

|  | x | y | z |
|---|---|---|---|
| Bi(1) | 1702 (2) | 2500 | −38 (5) |
| Bi(2) | 5000 | 0 | 0 |
| Br(1) | 3634 (5) | 2500 | −1456 (11) |
| Br(2) | −245 (5) | 2500 | 1384 (10) |
| Br(3) | 2313 (4) | 1713 (2) | 2039 (8) |
| Br(4) | 1075 (5) | 1704 (3) | −1986 (10) |
| Br(5) | 6712 (4) | 626 (2) | 10 (11) |
| Br(6) | 4336 (4) | 490 (2) | 2807 (8) |
| Br(7) | 3850 (5) | 691 (2) | −1748 (9) |
| Rb(1) | 4947 (5) | 1606 (2) | 708 (8) |
| Rb(2) | 3451 (5) | 1580 (2) | 5632 (8) |
| Rb(3) | 1766 (5) | 458 (3) | 589 (11) |

Table 2. *Interatomic distances* (Å) *and angles* (°) *with standard deviations in parentheses*

| | | | |
|---|---|---|---|
| Bi(1)–Br(1) | 2·847 (8) | Rb(1)–Br(5) | 3·563 (8) |
| Bi(1)–Br(2) | 2·865 (8) | Rb(1)–Br(6) | 3·573 (9) |
| Bi(1)–Br(3),Br(3$^i$) | 2·872 (7) | Rb(1)–Br(7) | 3·540 (9) |
| Bi(1)–Br(4),Br(4$^i$) | 2·828 (8) | Rb(2)–Br(1$^v$) | 3·511 (9) |
| Bi(2)–Br(5),Br(5$^{ii}$) | 2·824 (5) | Rb(2)–Br(2$^{iii}$) | 3·467 (8) |
| Bi(2)–Br(6),Br(6$^{ii}$) | 2·884 (7) | Rb(2)–Br(3) | 3·461 (9) |
| Bi(2)–Br(7),Br(7$^{ii}$) | 2·827 (7) | Rb(2)–Br(4$^{vi}$) | 3·696 (9) |
| | | Rb(2)–Br(5$^{vii}$) | 3·482 (8) |
| Rb(1)–Br(1) | 3·492 (8) | Rb(2)–Br(7$^v$) | 3·312 (9) |
| Rb(1)–Br(2$^{iii}$) | 3·642 (9) | Rb(3)–Br(3) | 3·64 (1) |
| Rb(1)–Br(3) | 3·700 (9) | Rb(3)–Br(5$^{ii}$) | 3·563 (9) |
| Rb(1)–Br(4$^{iv}$) | 3·55 (1) | Rb(3)–Br(6$^{vii}$) | 3·518 (9) |
| | | Rb(3)–Br(7) | 3·48 (1) |
| Br(1)–Bi(1)–Br(2) | 179·9 (1) | Br(5)–Bi(2)–Br(6) | 88·7 (2) |
| Br(1)–Bi(1)–Br(3) | 90·6 (2) | Br(5$^{ii}$)–Bi(2)–Br(6$^{ii}$) | 88·7 (2) |
| Br(1)–Bi(1)–Br(3$^i$) | 90·6 (2) | Br(5)–Bi(2)–Br(7) | 93·1 (2) |
| Br(1)–Bi(1)–Br(4) | 90·7 (2) | Br(5$^{ii}$)–Bi(2)–Br(7$^{ii}$) | 93·1 (2) |
| Br(1)–Bi(1)–Br(4$^i$) | 90·7 (2) | Br(5)–Bi(2)–Br(6$^{ii}$) | 91·3 (2) |
| Br(2)–Bi(1)–Br(3) | 89·5 (2) | Br(6)–Bi(2)–Br(5$^{ii}$) | 91·3 (2) |
| Br(2)–Bi(1)–Br(3$^i$) | 89·5 (2) | Br(5)–Bi(2)–Br(7$^{ii}$) | 86·9 (2) |
| Br(2)–Bi(1)–Br(4) | 89·2 (2) | Br(7)–Bi(2)–Br(5$^{ii}$) | 86·9 (2) |
| Br(2)–Bi(1)–Br(4$^i$) | 89·2 (2) | Br(6)–Bi(2)–Br(7) | 89·1 (2) |
| Br(3)–Bi(1)–Br(4) | 84·6 (2) | Br(6$^{ii}$)–Bi(2)–Br(7$^{ii}$) | 89·1 (2) |
| Br(3$^i$)–Bi(1)–Br(4$^i$) | 84·6 (2) | Br(6)–Bi(2)–Br(7$^{ii}$) | 90·9 (2) |
| Br(3)–Bi(1)–Br(3$^i$) | 93·8 (2) | Br(7)–Bi(2)–Br(6$^{ii}$) | 90·9 (2) |
| Br(3)–Bi(1)–Br(4$^i$) | 177·9 (2) | Br(5)–Bi(2)–Br(5$^{ii}$) | 180·0 |
| Br(4)–Bi(1)–Br(3$^i$) | 177·9 (2) | Br(6)–Bi(2)–Br(6$^{ii}$) | 180·0 |
| Br(4)–Bi(1)–Br(4$^i$) | 97·0 (3) | Br(7)–Bi(2)–Br(7$^{ii}$) | 180·0 |

Symmetry code

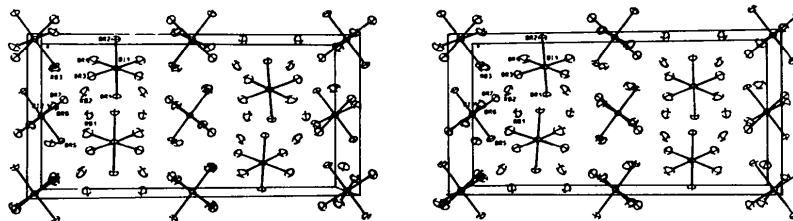| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (i) | $x,$ | $\frac{1}{2}-y,$ | $z;$ | (v) | $x,$ | $y,$ | $1+z;$ |
| (ii) | $1-x,$ | $-y,$ | $-z;$ | (vi) | $\frac{1}{2}+x,$ | $y,$ | $\frac{1}{2}-z;$ |
| (iii) | $\frac{1}{2}+x,$ | $\frac{1}{2}-y,$ | $\frac{1}{2}-z;$ | (vii) | $-\frac{1}{2}+x,$ | $y,$ | $\frac{1}{2}-z.$ |
| (iv) | $\frac{1}{2}+x,$ | $y,$ | $-\frac{1}{2}-z;$ | | | | |



Fig. 1. Stereoscopic drawing of the unit cell viewed along [001]. The atoms are represented by thermal ellipsoids drawn at the 70% probability level.

other bromobismuthates(III) with BiBr$_6^{3-}$ groups linked to polyanions. For example, in potassium decabromo-dibismuthate(III) tetrahydrate (Lazarini, 1977a) with binuclear Bi$_2$Br$_{10}^{4-}$ anions, the Bi—Br(terminal) distances range from 2·749 to 2·878 Å, the Bi—Br(bridging) distances are 2·979 and 3·006 Å; in tetraphenyl-phosphonium enneabromodibismuthate(III) (Lazarini, 1977c) with binuclear Bi$_2$Br$_9^{3-}$ anions, the Bi—Br(terminal) distances range from 2·704 to 2·766 Å and the Bi—Br(bridging) distances from 2·987 to 3·109 Å; while in caesium enneabromodibismuthate(III) (Lazarini, 1977d), with BiBr$_6^{3-}$ octahedra sharing three cis-vertices with three other octahedra forming cor-rugated layers, the Bi—Br(terminal) distances are 2·713 and the Bi—Br(bridging) distances 2·979 Å. It is obvious that the Bi—Br distances in isolated BiBr$_6^{3-}$ anions are slightly longer than the Bi—Br(terminal) distances and considerably shorter than the Bi—Br(bridging) distances, in structures with BiBr$_6^{3-}$ groups linked to polynuclear anions.

The Rb—Br contacts are in agreement with expected values (ionic radii: Rb$^+$ 1·49, Br$^-$ 1·95 Å; Wells, 1975). Contacts between Br atoms of different anions shorter than 3·90 Å are not present.

### References

CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.
JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
LARSON, A. C. (1967). Acta Cryst. 23, 664–665.
LAZARINI, F. (1977a). Acta Cryst. B33, 1954–1956.
LAZARINI, F. (1977b). Acta Cryst. B33, 1957–1959.
LAZARINI, F. (1977c). Acta Cryst. B33, 2686–2689.
LAZARINI, F. (1977d). Acta Cryst. B33, 2961–2964.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
WELLS, A. F. (1975). Structural Inorganic Chemistry, 4th ed. Oxford: Clarendon Press.
ZACHARIASEN, W. H. (1963). Acta Cryst. 16, 1139–1144.

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# Barium Chloride Dihydrate by Neutron Diffraction*

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**Abstract.** BaCl$_2$.2H$_2$O, monoclinic, $P2_1/n$, $Z = 4$, $a = 6\cdot7215$ (2), $b = 10\cdot9080$ (3), $c = 7\cdot1316$ (2) Å, $\beta = 91\cdot104$ (3)° from room-temperature X-ray measure-ments, $\lambda$(Cu $K\alpha_1$) $= 1\cdot54051$ Å. Ferroelastic species: $mmmF2/m$. Each Ba$^{2+}$ ion is linked to four others in a flat square pyramidal arrangement forming puckered layers parallel to (010). Each link consists of one bridging Cl$^-$ ion and one bridging water molecule. The latter is oriented so that two Ba$^{2+}$ neighbors and two H atoms are arranged approximately tetrahedrally about the O atom.

**Introduction.** The neutron-diffraction data collection and preliminary results have been described previously (Padmanabhan, Busing & Levy, 1963). We have recently made a final least-squares refinement assuming anisotropic extinction of type 1 (Coppens & Hamilton, 1970). Intense reflections omitted in the earlier work are now included. Ten reflections judged to be affected

Table 1. Fractional coordinates ($\times 10^4$) for BaCl$_2$.2H$_2$O

Standard errors are given in parentheses. The equipoints for $P2_1/n$ are $\pm (x,y,z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$.

|       | $x$       | $y$      | $z$       |
|-------|-----------|----------|-----------|
| Ba    | 5410 (2)  | 2831 (1) | 6461 (2)  |
| Cl(1) | 8625 (1)  | 811 (1)  | 7946 (1)  |
| Cl(2) | 6419 (1)  | 1049 (1) | 3020 (1)  |
| O(1)  | 3777 (2)  | 1404 (1) | 9409 (2)  |
| O(2)  | 2007 (2)  | 1474 (1) | 5060 (2)  |
| H(11) | 3534 (5)  | 621 (2)  | 8837 (4)  |
| H(12) | 4755 (5)  | 1252 (3) | 10405 (4) |
| H(21) | 984 (5)   | 1374 (3) | 5969 (4)  |
| H(22) | 2471 (5)  | 656 (3)  | 4891 (5)  |