only regular polyhedron is the central icosahedron, and that the least regular is the equatorial one. The figure also shows that the bonding distances between the polyhedra are shorter than those within the polyhedra. It should be noted that the coordination is sixfold for most atoms (Table 2) and that a higher coordination in all cases except one involves B(13) and B(16), which are only partially present.

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Potassium and Ammonium Decabromodibismuthate(III) Tetrahydrate

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Abstract. $K_4[Bi_2Br_{10}].4H_2O$: orthorhombic, *Pnma*, $a = 8.794$ (1), $b = 22.737$ (3), $c = 12.860$ (2) Å; $D_o = 3.70$ (1), $Z = 4$, $D_c = 3.733$ g cm^{-3}. $(NH_4)_4[Bi_2Br_{10}].4H_2O$: orthorhombic, *Pnma*, $a = 8.945$ (3), $b = 22.887$ (9), $c = 13.083$ (1) Å; $Z = 4$, $D_c = 3.375$ g cm^{-3}. The title compounds are isomorphous. The structural analysis was carried out for the K compound; $R = 0.079$ for 1836 reflexions $[I > 3.5\sigma(I)]$. The structure contains binuclear decabromodibismuthate(III) anions with two $BiBr_6$ octahedra sharing an edge.

Introduction. Only a few structures of bromo- and iodobismuthates(III) are known: bis(piperidinium) pentabromobismuthate(III) (McPherson & Meyers, 1968), with chain-anions built of octahedra sharing *cis* vertices; 2-picolinium tetrabromo- and tetraiodobismuthate(III) (Robertson, McPherson & Meyers, 1967), with chain-anions built of octahedra sharing edges; and Cs enneaiododibismuthate(III) (Lindqvist, 1968), with anions built of two octahedra sharing a face. The present investigation is the first part of a systematic study of bromo- and iodobismuthates(III). A number of alkali bromo- and iodobismuthates(III)

were synthesized (the methods of preparation will be published elsewhere) in order to study their structures and the conditions for linking the hexahalobismuthate(III) groups into such a variety of polynuclear species. Some of these compounds (*e.g.* the title compounds) were mentioned in the literature towards the end of the nineteenth century (Pascal, 1958).

Pale-yellow crystals were grown by slow evaporation from an aqueous solution obtained by dissolving $Bi(OH)_3$ and K_2CO_3 [or $(NH_4)_2CO_3$] in 1:1 molar ratio in a dilute HBr solution. A well developed crystal of $K_4[Bi_2Br_{10}].4H_2O$, selected for the intensity measurements, was characterized by the planes $\pm\{010\}$, $\pm\{101\}$ and $\pm\{10\bar{1}\}$; its dimensions along [100], [010] and [001] were 0.48, 0.16 and 0.34 mm respectively.

The intensity data were collected at 20 (1)°C with an Enraf–Nonius CAD-4 diffractometer. Experimental conditions were: Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å); ω–2θ scan; $\theta_{min} = 1.5°$, $\theta_{max} = 75.0°$; 2θ scan width (°): $0.8 + 0.2 \tan \theta$; aperture (mm): $2.5 + 0.9 \tan \theta$; maximum scan time 40 s; background: a quarter of the scan time at each of the scan limits. 2618 independent reflexions were recorded and, of these,

1836 with $I > 3\cdot5\sigma(I)$ (calculations based on counting statistics) were used in the structure analysis. Corrections were applied for Lorentz and polarization effects and for absorption $[\mu(Cu\ K\alpha) = 525\cdot4\ cm^{-1}]$. The absorption corrections A^*, calculated with the measured crystal dimensions (Gaussian-grid method), range from $9\cdot57$ to $167\cdot38$.

The unit-cell parameters for the K and NH_4 compounds were calculated by a least-squares method from the θ values for 15 reflexions measured on the four-circle diffractometer. The following systematic absences (checked by Weissenberg and precession photographs) were observed: $hk0$ for $h = 2n + 1$; $0kl$ for $k = 2n + 1$ and $l = 2n + 1$. The distribution of the normalized structure factors was clearly centrosymmetric. Taking into account an additional false glide plane, caused by the position of the heavy atom ($z = 0$), the

possible centrosymmetric space groups were: $Pcma$ (alternative setting for $Pbam$, No. 55), $Pbma$ (alternative setting for $Pbcm$, No. 57) and $Pnma$ (No. 62). However, only $Pbma$ and $Pnma$ had been implied by the Patterson function. $Pnma$ was subsequently confirmed by successful refinement.

The positions of Bi and Br atoms were determined from the three-dimensional Patterson function. K atoms and O atoms of the water molecules were located from a Fourier summation. The structure was then refined by least squares with anisotropic thermal parameters for Bi, Br and K atoms, isotropic for O, and with anomalous-dispersion corrections for Bi, Br and K. The function minimized in the least-squares procedure was $\Sigma\ w(|F_o| - |F_c|)^2$. The weighting scheme applied was: $|F_o| < 50$: $w_F = (|F_o|/50)^{0\cdot7}$; $\sin\ \theta < 0\cdot70$: $w_S = (\sin\ \theta/0\cdot70)^{1\cdot8}$; $50 < |F_o| \le 150$: $w_F = 1\cdot0$; $0\cdot70 < \sin\ \theta \le 0\cdot85$: $w_S = 1\cdot0$; $|F_o| \ge 150$: $w_F = (150/|F_o|)^{2\cdot1}$; $\sin\ \theta \ge 0\cdot85$: $w_S = (0\cdot85/\sin\ \theta)^{0\cdot5}$; $w = 0\cdot1w_Fw_S$.

No attempts have been made to locate H atoms. An isotropic extinction parameter (Zachariasen, 1963; Larson, 1967) was also included in the final stage of refinement ($g = 5\cdot2 \times 10^{-3}$). Final R values are $R = \Sigma\ ||F_o| - |F_c||/\Sigma\ |F_o| = 0\cdot079$ and $R_w = [\Sigma\ w(F_o - F_c)^2/\Sigma\ wF_o^2]^{1/2} = 0\cdot092$ for 1836 reflexions and 88 parameters. The average parameter shift-to-error ratio was $0\cdot02$ in the final cycle.

All calculations were performed on the CDC Cyber 72 computer of RRC Ljubljana with the XRAY 72 system (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 $\Delta f'$ and $\Delta f''$ for anomalous-

Table 1. *Final positional parameters* $(\times 10^5)$ *with standard deviations in parentheses*

	x	y	z
Bi	36912 (9)	15000 (3)	50287 (7)
Br(1)	14941 (34)	6501 (12)	54442 (23)
Br(2)	58720 (33)	7002 (12)	44401 (22)
Br(3)	24438 (31)	15406 (12)	29599 (20)
Br(4)	49343 (35)	14776 (14)	70401 (23)
Br(5)	17145 (41)	25000	57429 (29)
Br(6)	56489 (38)	25000	43595 (33)
K(1)	45036 (101)	25000	15338 (67)
K(2)	28766 (108)	25000	83662 (72)
K(3)	47831 (101)	4471 (45)	19813 (73)
O(1)	37269 (254)	16777 (103)	−670 (195)
O(2)	24703 (332)	1800 (129)	80803 (247)

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

Bi—Br(1)	2·784 (3)	K(2)—O(1^{vii}), O(1^{viii})	2·85 (3)	Br(1)—Bi—Br(2)	94·46 (9)
Bi—Br(2)	2·749 (3)	K(2)—Br(5)	3·52 (1)	Br(1)—Bi—Br(3)	86·28 (9)
Bi—Br(3)	2·879 (3)	K(2)—Br(6^v)	3·52 (1)	Br(1)—Bi—Br(4)	94·63 (9)
Bi—Br(4)	2·809 (3)	K(2)—Br(5^{ix})	3·56 (1)	Br(1)—Bi—Br(5)	93·73 (8)
Bi—Br(5)	3·006 (2)	K(3)—Br(2)	3·35 (1)	Br(1)—Bi—Br(6)	170·4 (1)
Bi—Br(6)	2·979 (2)	K(3)—Br(3)	3·46 (1)	Br(2)—Bi—Br(3)	91·87 (9)
K(1)—Br(3), Br(3^i)	3·377 (7)	K(3)—Br(3^{ii})	2·41 (1)	Br(2)—Bi—Br(4)	88·27 (9)
K(1)—Br(3^{ii}), Br(3^{iii})	3·445 (7)	K(3)—Br(1^{ii})	3·49 (1)	Br(2)—Bi—Br(5)	171·09 (9)
K(1)—O(1), O(1^i)	2·86 (3)	K(3)—Br(1^x)	3·38 (1)	Br(2)—Bi—Br(6)	91·27 (8)
K(1)—Br(6)	3·77 (1)	K(3)—O(2^{xi})	2·81 (3)	Br(3)—Bi—Br(4)	179·06 (9)
K(1)—Br(5^{ii})	3·515 (9)	K(3)—O(2^x)	2·82 (3)	Br(3)—Bi—Br(5)	92·16 (9)
K(1)—Br(6^{iv})	3·579 (9)	Br(2)—Br(2^{xi})	3·816 (4)	Br(3)—Bi—Br(6)	85·9 (1)
K(2)—Br(4), Br(4^i)	3·404 (8)	Br(2)—Br(1^{xi})	3·849 (4)	Br(4)—Bi—Br(5)	87·5 (1)
K(2)—Br(4^v), Br(4^{vi})	3·517 (8)	Br(2)—Br(3^{ii})	3·884 (4)	Br(4)—Bi—Br(6)	93·2 (1)
				Br(5)—Bi—Br(6)	81·09 (8)
				Bi—Br(5)—Bi^i	98·3 (1)
				Bi—Br(6)—Bi^i	99·5 (1)

Symmetry code

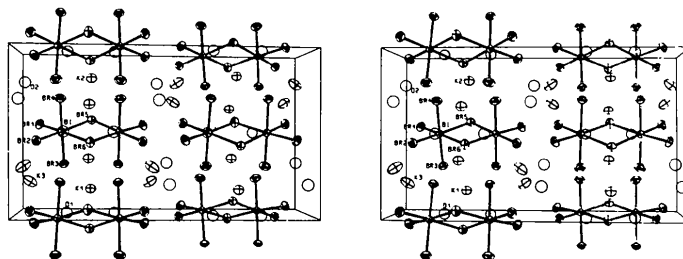|												
(i)		x,	$\frac{1}{2} - y$,	z	(v)	$-\frac{1}{2} + x$,	y,	$\frac{3}{2} - z$	(ix)	$\frac{1}{2} + x$,	y,	$\frac{3}{2} - z$
(ii)		$\frac{1}{2} + x$,	y,	$\frac{1}{2} - z$	(vi)	$-\frac{1}{2} + x$,	$\frac{1}{2} - y$,	$\frac{3}{2} - z$	(x)	$\frac{1}{2} - x$,	$-y$,	$-\frac{1}{2} + z$
(iii)		$\frac{1}{2} + x$,	$\frac{1}{2} - y$,	$\frac{1}{2} - z$	(vii)	x,	y,	$1 + z$	(xi)	$1 - x$,	$-y$,	$1 - z$
(iv)		$-\frac{1}{2} + x$,	y,	$\frac{1}{2} - z$	(viii)	x,	$\frac{1}{2} - y$,	$1 + z$				

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

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 $K_4[Bi_2Br_{10}].4H_2O$ consists of K^+ cations, binuclear $[Bi_2Br_{10}]^{4-}$ anions and water molecules, coordinated to the cations. The anion is composed of two slightly distorted octahedra sharing an edge. The bridging Br atoms are on a mirror plane. The Bi—Br(terminal) distances (from 2·749 to 2·879 Å) are somewhat longer than the corresponding distances (2·64 Å) in 2-picolinium tetrabromo-bismuthate(III) (Robertson, McPherson & Meyers, 1967), probably because of the relatively strong interaction between the Br atoms and the cations. There are two types of coordination polyhedra around the

cations (Fig. 2). K(1) and K(2) (on a mirror plane) are coordinated by four Br atoms and two water molecules (in cis position) in a trigonal prism, with three more Br atoms at longer distances perpendicular to the rectangular faces. The polyhedron around K(3) – five Br atoms and two water molecules – is thoroughly irregular. All polyhedra are linked by sharing edges into a three-dimensional network. Some close contacts (in the range 3·816 to 3·884 Å) between Br atoms of different anions were observed.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32450 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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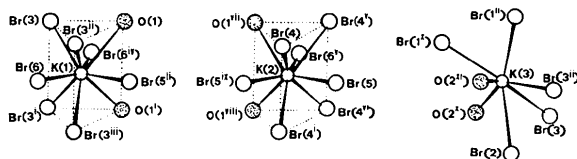
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Fig. 2. The coordination sphere around the K^+ cations.