

## Sodium Hexabromobismuthate(III) Decabromodibismuthate(III) 18-Hydrate

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**Abstract.**  $\text{Na}_7[\text{BiBr}_6][\text{Bi}_2\text{Br}_{10}]\cdot 18\text{H}_2\text{O}$ , triclinic,  $P\bar{1}$ ,  $a = 8.381(5)$ ,  $b = 9.367(2)$ ,  $c = 16.855(3)$  Å,  $\alpha = 97.70(2)$ ,  $\beta = 104.99(2)$ ,  $\gamma = 86.19(2)^\circ$ ,  $D_o = 3.29(3)$ ,  $Z = 1$ ,  $D_c = 3.136$  Mg  $\text{m}^{-3}$ ;  $R = 0.084$  for 2056 diffractometer data [ $I > 4\sigma(I)$ ]. Two types of anions are present in the crystal structure, octahedral  $[\text{BiBr}_6]^{3-}$  anions and binuclear  $[\text{Bi}_2\text{Br}_{10}]^{4-}$  anions with two  $\text{BiBr}_6$  octahedra sharing an edge. The water molecules as well as some of the Br atoms of both types of anions are coordinated to the Na atoms.

**Introduction.** The results of the systematic structural investigation of halobismuthate(III) compounds (Lazarini, 1977*a,b,c,d*, 1978; Lazarini & Leban, 1980) show a great variety of different halobismuthate(III) anions, most of them bi- or polynuclear, to occur in the crystalline state. The main purpose of the present investigation was to establish the influence of a smaller cation on the structural behaviour of hexabromobismuthate(III) groups.

Yellow crystals of the title compound were grown by slow evaporation from an aqueous solution obtained by dissolving  $\text{Bi}(\text{OH})_3$  and  $\text{Na}_2\text{CO}_3$  in a 1:1 molar ratio in a dilute HBr solution. Three solid phases can be obtained under nearly the same experimental conditions:  $\text{Na}_2\text{BiBr}_5\cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_4\text{BiBr}_7\cdot 4\text{H}_2\text{O}$  and the title compound. The empirical formula of the title compound was determined by standard chemical analytical methods (calculated: 26.22% Bi, 53.48% Br, 13.57%  $\text{H}_2\text{O}$ ; found: 26.1% Bi, 52.9% Br, 14.1%  $\text{H}_2\text{O}$ ). The crystal, selected for the diffraction measurements, was characterized by the following planes (in parentheses are the distances from the crystal faces to an arbitrary origin inside the crystal):  $\pm(001)$  (0.10 mm),  $\pm(010)$  (0.15 mm) and  $\pm(101)$  (0.41 mm).

The intensity data were collected at 293 (1) K with an Enraf–Nonius CAD-4 diffractometer. Experimental conditions were: graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\omega$ - $2\theta$  scan,  $\theta_{\min} = 1^\circ$ ,  $\theta_{\max} = 28^\circ$ ,  $2\theta$  scan width =  $(0.8 + 0.3 \tan \theta)^\circ$ , aperture =  $(2.5 + 0.9 \tan \theta)$  mm, maximum scan time 40 s, background =  $\frac{1}{4}$  of the scan time at each of the scan limits. 6068 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 2056 reflexions were used in the refinement. Corrections were applied for Lorentz and polarization effects and for absorption [ $\mu(\text{Mo } K\alpha) = 23.37$   $\text{mm}^{-1}$ ]. The transmission factors, calculated from the measured crystal dimensions (Gaussian-grid method, 500 grid points, crystal volume 0.0636  $\text{mm}^3$ ), range from 0.001 to 0.049. The unit-cell parameters were calculated from a least-squares fit of the  $\theta$  values of 25 reflexions measured on the diffractometer. The space group  $P\bar{1}$  was confirmed by successful refinement.

The positions of all Bi and Br atoms were determined from the three-dimensional Patterson map and refined together with the isotropic temperature factors in both possible space groups  $P1$  and  $P\bar{1}$ . The centrosymmetric space group was considered to be correct because of the slightly lower  $R$  value and much more reasonable temperature factors. Then the Na atoms and the O atoms of the water molecules were located from a difference Fourier summation. The structure was refined by the full-matrix least-squares technique with anisotropic thermal parameters for Bi and Br atoms, isotropic for Na and O atoms and with an anomalous-dispersion correction for Bi and Br. The function minimized in the least-squares procedure was  $\sum w(|F_o| - |F_c|)^2$ . The empirical weighting scheme applied was as follows: for  $|F_o| < 130$ ,  $w_F = (|F_o|/130)^{1.1}$ ; for  $130 \leq |F_o| \leq 200$ ,  $w_F = 1.0$ ; for  $|F_o| > 200$ ,  $w_F = (200/|F_o|)^{2.5}$ ; for  $\sin \theta < 0.32$ ,  $w_S = (\sin \theta/0.32)^{2.9}$ ; for  $0.32 \leq \sin \theta \leq 0.40$ ,  $w_S = 1.0$ ; for  $\sin \theta > 0.40$ ,  $w_S = (0.40/\sin \theta)^{1.1}$ ;  $w = 0.01 w_F w_S$ . An isotropic extinction parameter (Larson, 1967) was also included in the final stage of the refinement [ $g = 6.6(4) \times 10^{-3}$ ]. Final  $R$  values are:  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.084$  and  $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.103$  for 2056 reflexions and 138 parameters. The average parameter shift-to-error ratio was 0.15 in the final cycle. A final difference Fourier map revealed no peaks greater than  $1.2 \text{ e } \text{Å}^{-3}$ .

All calculations were performed on the CDC Cyber © 1980 International Union of Crystallography

Table 1. Final positional parameters ( $\times 10^4$  for Bi and Br,  $\times 10^3$  for Na and O) and thermal parameters ( $\text{\AA}^2 \times 10^3$ ) with standard deviations in parentheses

For Bi and Br atoms the equivalent isotropic thermal parameter is given [calculated as  $U_{eq} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$ ], for Na and O atoms the isotropic thermal parameter is given.

	x	y	z	$U_{eq}$ or U
Bi(1)	0	0	0	25 (3)
Bi(2)	4322 (4)	4504 (3)	3670 (2)	26 (2)
Br(1)	128 (17)	2867 (10)	-342 (11)	53 (7)
Br(2)	-1962 (14)	931 (10)	1160 (7)	40 (5)
Br(3)	2964 (14)	437 (11)	1283 (7)	43 (5)
Br(4)	4577 (13)	7412 (9)	3487 (8)	48 (5)
Br(5)	4034 (14)	1561 (9)	3946 (8)	40 (4)
Br(6)	1505 (16)	4375 (11)	2439 (8)	51 (5)
Br(7)	6257 (14)	3676 (10)	2587 (7)	50 (5)
Br(8)	2402 (13)	5407 (11)	4954 (8)	46 (6)
Na(1)	500	500	0	36 (8)
Na(2)	89 (7)	118 (6)	255 (4)	77 (16)
Na(3)	-57 (4)	-40 (4)	392 (2)	54 (8)
Na(4)	562 (8)	820 (7)	156 (4)	113 (15)
O(1)	765 (8)	450 (6)	84 (4)	50 (14)
O(2)	437 (11)	241 (9)	-14 (6)	66 (21)
O(3)	413 (11)	611 (9)	123 (6)	77 (21)
O(4)	61 (6)	-112 (5)	279 (3)	41 (10)
O(5)	-14 (7)	204 (6)	369 (4)	33 (13)
O(6)	-115 (9)	-283 (7)	397 (5)	74 (16)
O(7)	-332 (7)	-13 (6)	278 (4)	41 (13)
O(8)	197 (10)	-52 (7)	501 (5)	70 (17)
O(9)	809 (10)	690 (8)	206 (5)	83 (18)

172 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) were applied together with the values of  $f'$  and  $f''$  for the anomalous-dispersion correction of Cromer & Liberman (1970).

The positional and thermal parameters are listed in Table 1.\* Equivalent isotropic thermal parameters are

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35457 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

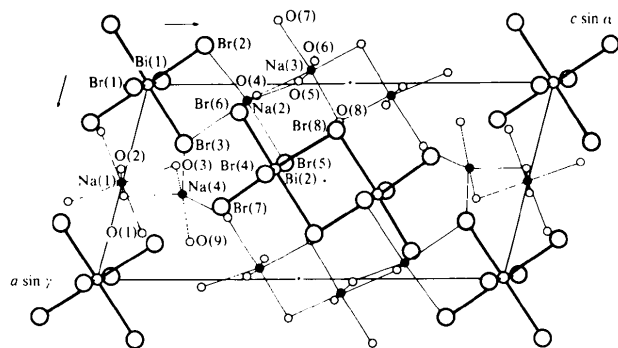


Fig. 1. A projection of the structure along  $b$ .

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with standard deviations in parentheses

Bi(1)-Br(1), Br(1 <sup>i</sup> )	2.84 (1)	Br(1)-Bi(1)-Br(2)	91.3 (4)
Bi(1)-Br(2), Br(2 <sup>i</sup> )	2.88 (1)	Br(1)-Bi(1)-Br(3)	89.1 (4)
Bi(1)-Br(3), Br(3 <sup>i</sup> )	2.85 (1)	Br(1)-Bi(1)-Br(1 <sup>i</sup> )	180.0 (5)
Bi(2)-Br(4)	2.81 (1)	Br(1)-Bi(1)-Br(2 <sup>i</sup> )	88.7 (4)
Bi(2)-Br(5)	2.89 (1)	Br(1)-Bi(1)-Br(3 <sup>i</sup> )	90.9 (4)
Bi(2)-Br(6)	2.71 (1)	Br(2)-Bi(1)-Br(3)	90.7 (3)
Bi(2)-Br(7)	2.75 (1)	Br(2)-Bi(1)-Br(1 <sup>i</sup> )	88.7 (4)
Bi(2)-Br(8)	3.02 (1)	Br(2)-Bi(1)-Br(2 <sup>i</sup> )	180.0 (3)
Bi(2)-Br(8 <sup>ii</sup> )	3.10 (1)	Br(2)-Bi(1)-Br(3 <sup>i</sup> )	89.3 (3)
		Br(3)-Bi(1)-Br(3 <sup>i</sup> )	180.0 (3)
Na(1)-O(1), O(1 <sup>iii</sup> )	2.35 (6)	Br(4)-Bi(2)-Br(5)	176.9 (4)
Na(1)-O(2), O(2 <sup>iii</sup> )	2.48 (8)	Br(4)-Bi(2)-Br(6)	89.6 (3)
Na(1)-O(3), O(3 <sup>iii</sup> )	2.46 (10)	Br(4)-Bi(2)-Br(7)	90.4 (4)
Na(2)-Br(2)	2.88 (5)	Br(4)-Bi(2)-Br(8)	89.9 (3)
Na(2)-Br(3)	3.07 (7)	Br(4)-Bi(2)-Br(8 <sup>ii</sup> )	91.0 (3)
Na(2)-Br(5)	3.05 (5)	Br(5)-Bi(2)-Br(6)	91.7 (3)
Na(2)-Br(6)	3.10 (6)	Br(5)-Bi(2)-Br(7)	92.3 (3)
Na(2)-O(4)	2.27 (8)	Br(5)-Bi(2)-Br(8)	87.2 (4)
Na(2)-O(5)	2.33 (9)	Br(5)-Bi(2)-Br(8 <sup>ii</sup> )	87.8 (3)
Na(3)-O(4)	2.51 (7)	Br(6)-Bi(2)-Br(7)	92.5 (4)
Na(3)-O(5)	2.47 (7)	Br(6)-Bi(2)-Br(8)	91.3 (4)
Na(3)-O(6)	2.34 (8)	Br(6)-Bi(2)-Br(8 <sup>ii</sup> )	178.3 (4)
Na(3)-O(7)	2.50 (6)	Br(7)-Bi(2)-Br(8)	176.1 (3)
Na(3)-O(8)	2.54 (8)	Br(7)-Bi(2)-Br(8 <sup>ii</sup> )	85.9 (3)
Na(3)-O(8 <sup>iv</sup> )	2.34 (10)	Br(8)-Bi(2)-Br(8 <sup>ii</sup> )	90.3 (3)
Na(4)-Br(3 <sup>v</sup> )	2.94 (6)		
Na(4)-O(3)	2.33 (11)	Bi(2)-Br(8)-Bi(2 <sup>ii</sup> )	89.7 (3)
Na(4)-O(9)	2.35 (10)		
Na(4)-O(7 <sup>v</sup> )	2.43 (8)		
Na(4)-O(2 <sup>iii</sup> )	2.38 (12)		
Br(2)-Br(7 <sup>vi</sup> )	3.78 (2)		
Br(4)-Br(5 <sup>v</sup> )	3.88 (1)		

Symmetry code

(i)	$-x, -y, -z$	(ii)	$1-x, 1-y, 1-z$
(iii)	$1-x, 1-y, -z$	(iv)	$-x, -y, 1-z$
(v)	$x, 1+y, z$	(vi)	$1+x, 1+y, z$
(vii)	$-1+x, y, z$		

given for Bi and Br atoms and isotropic thermal parameters for Na and O atoms. A projection of the structure along  $b$  is shown in Fig. 1. Some important interatomic distances and angles are listed in Table 2.

**Discussion.** The crystal structure of Na<sub>7</sub>[BiBr<sub>6</sub>][Bi<sub>2</sub>Br<sub>10</sub>].18H<sub>2</sub>O represents the first known example of a halobismuthate(III) containing two types of anions, octahedral [BiBr<sub>6</sub>]<sup>3-</sup> anions and binuclear [Bi<sub>2</sub>Br<sub>10</sub>]<sup>4-</sup> anions with two BiBr<sub>6</sub> octahedra sharing an edge. The water molecules and some of the Br atoms of both anions are coordinated to the Na atoms.

The distances and angles within the [BiBr<sub>6</sub>]<sup>3-</sup> anion agree completely with those found in Rb<sub>3</sub>BiBr<sub>6</sub> (Lazarini, 1978) which contains isolated octahedral hexabromobismuthate(III) anions [with Bi-Br distances between 2.824 (5) and 2.884 (7) Å]. The geometry of the [Bi<sub>2</sub>Br<sub>10</sub>]<sup>4-</sup> anion is also in good agreement with those in K<sub>4</sub>[Bi<sub>2</sub>Br<sub>10</sub>].4H<sub>2</sub>O (Lazarini, 1977a) and [Sr(H<sub>2</sub>O)<sub>8</sub>]<sub>2</sub>[Bi<sub>2</sub>Br<sub>10</sub>] - see the Discussion in the preceding paper (Lazarini & Leban, 1980).

Some contacts shorter than the sum of the van der Waals radii (3.90 Å; Wells, 1975) are present between Br atoms of different anions [Br(2)–Br(7<sup>vi</sup>) 3.78 (2), Br(4)–Br(5<sup>v</sup>) 3.88 (1) Å].

Both anions in the title compound seem to be interconnected through the Na(2) atoms into chains parallel to [111]. This is probably the reason for the existence of two kinds of anions. The Na(2) atom is octahedrally coordinated by four Br atoms of both anions and by two H<sub>2</sub>O molecules (in *cis* positions). The Na(1) as well as the Na(3) atoms are coordinated by six H<sub>2</sub>O molecules. The coordination polyhedra are distorted octahedra. The remaining Na(4) atom is coordinated by four H<sub>2</sub>O molecules and by one Br atom in a very irregular polyhedron. The cationic polyhedra are linked into a three-dimensional network through common edges and vertices. Hydrogen bonds do not seem to be important in this structure; there are no contacts between O atoms of different H<sub>2</sub>O molecules shorter than 2.80 Å.

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## Single-Crystal Refinement of the Structure of Carbon Dioxide

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**Abstract.** CO<sub>2</sub>, *Pa3*, *a*<sub>0</sub> = 5.624 (2) Å. The structure refinement was based on 57 observed reflections of a single crystal at 150 K (*R* = 0.041). The C–O distance is determined as 1.155 (1) Å.

**Introduction.** The crystal structure of carbon dioxide has been determined by Mark & Pohland (1925, 1926), de Smedt & Keesom (1925) and Krüner (1926) using X-ray powder methods. According to these investigations, CO<sub>2</sub> crystallizes in space group *Pa3*, the C atom occupying position 4(*a*) and the O atoms 8(*c*). In spite of considerable differences in the oxygen *x* parameter in the original papers, it is generally accepted to be *x* ≈ 0.11 (Wyckoff, 1963).

Single crystals of CO<sub>2</sub> were grown from a solution in CH<sub>2</sub>SF<sub>4</sub> (Simon, Peters, Lentz & Seppelt, 1980). A miniaturized Bridgman technique was used (Simon,

Deiseroth, Westerbeck & Hillenkötter, 1976) which has proved helpful in numerous cases of low-temperature crystal growth from gases and liquids. In the case of CO<sub>2</sub>, a 150/300 K temperature gradient was slowly shifted along the axis of a glass capillary (diameter 0.2 mm) filled with the solution. Several attempts finally led to a single crystal of length *ca* 2 mm. Crystal-growth and intensity measurements were carried out on a Syntex P2<sub>1</sub> four-circle diffractometer. The results are based on 71 independent reflections using the *XTL* system [57 reflections with *I* > 2σ(*I*); originally 281 measured reflections in the range 0 ≤ *h, k, l* ≤ 7; 7° < 2θ < 55°; Mo Kα, ω scan at 0.5 to 29° min<sup>-1</sup> with Δω = 1.0°]. No absorption correction was applied.

The final  $R = \sum (|F_o| - |F_c|) / \sum |F_o| = 0.041$ . Refinement including unobserved reflections yielded  $R' = 0.065$ . Using the general weighting scheme  $R_w = \sum w^{1/2} (|F_o| - |F_c|) / \sum w^{1/2} |F_o|$ , where  $w = 1/\sigma^2$ , the