

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306, Oak Ridge, Tennessee.
- CODA, A., GIUSEPPE, C. & TADINI, C. (1967). *Atti Accad. Nazl. Lincei Rend. Classe Sci. Fis. Mat. Nat.* **43**, 212–224.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KOSTINER, E. & REA, J. R. (1974). *Acta Cryst.* **B30**, 2901–2903.
- REA, J. R. & KOSTINER, E. (1972). *Acta Cryst.* **B28**, 2525–2529.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
- WALDROP, L. (1969). *Z. Kristallogr.* **130**, 1–14.
- WALDROP, L. (1970). *Z. Kristallogr.* **131**, 1–20.
- WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed. Oxford Univ. Press.
- ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A23**, 558–564.

Acta Cryst. (1976). **B32**, 1947

The Crystal Structure of $\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{Br}_3$

BY KONSTANTIN MARIOLACOS

Mineralogisch-Kristallographisches Institut der Universität, D-34 Göttingen, Germany (BRD)

(Received 3 September 1975; accepted 23 November 1975)

$\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{Br}_3$ is hexagonal, space group $P6_3$, with $a_0 = 15.545$ (3), $c_0 = 4.019$ (1) Å, $Z = \frac{3}{2}$. The structure investigation was undertaken on synthetic material and refined by full-matrix least-squares methods to a final R of 0.086. The 1332 independent reflexions were collected on a four-circle automatic diffractometer using monochromatized Mo $K\alpha$ radiation. The structure consists of $(\text{Bi}_4\text{S}_6)_\infty$ chains which run parallel to the z direction; these chains are connected to each other by the Br atoms which lie on the threefold axis and the Bi(1) atoms which lie on the 6_3 axis.

Introduction

Krämer (1973) first reported $\text{Bi}_{19}\text{S}_{27}\text{Br}_3$ and gave the lattice constants and powder data. Very few crystal structures of Bi sulphohalogenides have been investigated so far (Lewis & Kupčik, 1974; Ohmasa & Mariolacos, 1974; Mariolacos & Kupčik, 1975). Miehé & Kupčik (1971) have solved the crystal structure of the isotypical $\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{I}_3$, but they could not ascertain whether a centre of inversion exists in this compound. Since by absence of a symmetry centre the Bi-containing sulphohalogenides may be ferroelectric materials, it was interesting to synthesize the Br analog and to investigate its structure in order to answer the question of the existence of a symmetry centre. Furthermore it was of interest to investigate the statistical occupation of the sixfold axis.

Experimental

The crystals were synthesized by chemical transport using the method of Rabenau & Rau (1969) under the following conditions: starting materials were 1 part Bi_2S_3 , 1 part Cu_2S , 2 parts PbS ; transport material: 0.1 $N\text{HBr}$ solution; reaction and crystallization took place in a 140 mm long and 7 mm diameter silica glass tube; $T = 420 \pm 10^\circ\text{C}$; $\Delta T = 15^\circ\text{C}$; filling extent about 15%; time 12 d. After this reaction time the tube was taken away and was slowly cooled in air. Black, metallic, shiny prismatic crystals of $\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{Br}_3$ formed in

the cold part of the tube. Their maximum dimensions were about $0.05 \times 0.08 \times 7$ mm. The chemical composition of the compound was determined by semi-quantitative microprobe analysis and was confirmed after the structure determination. A crystal of size $0.018 \times 0.028 \times 5$ mm was selected for this investigation. The systematic absences $000l$ with $l = 2n + 1$ and the observed Laue group $6/m$ indicated $P6_3$ (No. 173) or $P6_3/m$ (No. 176) as possible space groups; the space group confirmed from the structure analysis is the former. The intensities were collected on an automatic four-circle diffractometer (STADI-4 system of Stoe) using graphite-crystal monochromatized Mo $K\alpha$ radiation and a θ - 2θ scan mode. Two standard reflexions were each monitored 27 times during the data collection and used to calculate the standard deviation of the intensity. Their intensities varied by less than $\pm 3.7\%$ throughout. The lattice constants were determined with the aid of 15 reflexions and refined by least-squares methods.

Crystal data

$\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{Br}_3$, hexagonal, space group $P6_3$; $a_0 = 15.545$ (3), $c_0 = 4.019$ (1) Å; ($\lambda = 0.7114$ Å); $Z = \frac{3}{2}$; $D_{\text{calc}} = 6.69$ g cm $^{-3}$; $\mu = 662$ cm $^{-1}$. For the layers $hk0$ to $hk5$ in the range $\sin \theta / \lambda \leq 0.805$ Å $^{-1}$ 1332 independent reflexions were obtained which were corrected for the Lorentz-polarization effect and for absorption, the prismatic shape being approximated by nine boundary planes in the absorption correction. Individual weights,

Table 1. Fractional atomic coordinates ($\times 10^5$), occupancies, and anisotropic thermal parameters ($\times 10^5$)

Thermal parameters in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	Site	<i>N</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bi(1)	0	0	10562 (504)	2(a)	0.333	15 (8)	15 (8)	3598 (292)	8 (4)	0	0
Bi(2)	29703 (6)	24345 (7)	25022 (162)	6(c)	1.0	169 (4)	319 (4)	2090 (46)	115 (3)	-14 (48)	57 (50)
Bi(3)	38912 (6)	51582 (6)	74974 (152)	6(c)	1.0	193 (4)	172 (4)	2469 (45)	99 (3)	77 (46)	40 (46)
S(1)	16806 (39)	18798 (39)	73576 (541)	6(c)	1.0	111 (21)	156 (22)	1094 (465)	84 (19)	-157 (157)	-307 (172)
S(2)	26238 (37)	39965 (38)	24635 (532)	6(c)	1.0	107 (21)	126 (23)	1578 (336)	37 (19)	73 (228)	-332 (221)
S(3)	45215 (37)	38930 (37)	73943 (572)	6(c)	1.0	112 (21)	117 (21)	1232 (412)	39 (18)	-285 (192)	-211 (190)
Br	66666	33333	74371 (512)	2(b)	1.0	194 (11)	194 (11)	3585 (357)	97 (6)	0	0

$1/\sigma^2(F_o)$ based on counting statistics were used for the refinements. 159 reflexions with $I < 2\sigma(F)$ were classified as unobserved. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1968) were used.

Structure determination

The basis of the present work was the atom parameters of $\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{I}_3$. A refinement with isotropic temperature factors in the centrosymmetric space group $P6_3/m$ yielded $R = 11.4\%$. A refinement in three sub-

sequent steps with isotropic temperature factors in the non-centrosymmetric space group $P6_3$, in which the *z* coordinate of one of the three Bi atoms was in turn held constant, yielded $R = 11.0\%$. Secondly the *z* coordinates of the three atoms S(1), S(3) and Br became 0.733 (5), 0.736 (5) and 0.724 (4) respectively, that is to say, even after consideration of the standard deviations (in parentheses), not the value 0.75 which is necessary for the space group $P6_3/m$. This fact indicated space group $P6_3$ as being correct. Subsequent refinement with anisotropic temperature factors in this space group gave for all reflexions $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.086$ and for observed reflexions $R' = 0.071$. The weighted R_w indices $[R_w = \{\sum w(|F_o| - |F_c|)^2\}^{1/2} / \{\sum w|F_o|^2\}^{1/2}]$ yielded the values 0.055 and 0.054 respectively. The final positional and thermal parameters together with the corresponding standard deviations and their occupancies are reported in Table 1.

Table 3. Bond lengths and angles with standard deviations in parentheses

Symmetry code				
Superscript (i)	<i>x</i> ,	<i>y</i> ,	<i>z</i> + 1	
(ii)	\bar{y} ,	<i>x</i> - <i>y</i> ,	<i>z</i> - 1	
(iii)	\bar{x} ,	\bar{y} ,	<i>z</i> - $\frac{1}{2}$	
(iv)	<i>y</i> ,	<i>y</i> - <i>x</i> ,	<i>z</i> - $\frac{1}{2}$	
(v)	<i>y</i> - <i>x</i> ,	\bar{x} ,	<i>z</i> - 1	
(vi)	<i>x</i> - <i>y</i> ,	<i>x</i> ,	<i>z</i> - $\frac{1}{2}$	
(vii)	<i>x</i> ,	<i>y</i> ,	<i>z</i> - 1	
(viii)	<i>x</i> - <i>y</i> ,	<i>x</i> ,	<i>z</i> + $\frac{1}{2}$	
(ix)	1 - <i>x</i> ,	1 - <i>y</i> ,	<i>z</i> + $\frac{1}{2}$	
(x)	1 - <i>x</i> ,	1 - <i>y</i> ,	<i>z</i> - $\frac{1}{2}$	

Bond lengths (Å)				
	S(1)	S(2)	S(3)	Br
Bi(1)	2.830 (11) (3 ×) 3.154 (15) (3 ×)			
Bi(2)	2.616 (18) 2.704 (18) 3.011 (5)	2.738 (7)	3.059 (16) 3.116 (16)	
Bi(3)		2.752 (17) 2.771 (17)	2.600 (7) 2.916 (17) 2.972 (17)	3.497 (12) 3.525 (12)

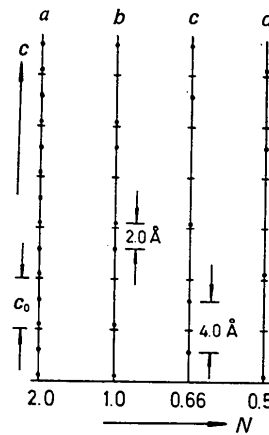
Fig. 1. Explanation of the statistical occupancy ($N = 0.333$) of the Bi(1) atom.

Table 3 (cont.)

Bond angles (°)			
S(1 ⁱⁱ)—Bi(1)—S(1 ^{vii})	99.59 (50)	S(2)—Bi(3)—S(2 ⁱ)	93.39 (48)
S(1 ⁱⁱⁱ)—Bi(1)—S(1 ^{viii})	162.53 (100)	S(2)—Bi(3)—S(3)	84.80 (43)
S(1 ^{iv})—Bi(1)—S(1 ^{ix})	69.74 (35)	S(2)—Bi(3)—S(3 ^{ix})	165.65 (189)
S(1 ⁱⁱ)—Bi(1)—S(1 ^v)	116.66 (33)	S(2)—Bi(3)—Br ^{vi}	71.40 (42)
S(1)—Bi(2)—S(1 ^{iv})	74.78 (37)	S(2)—Bi(3)—Br ^{viii}	121.17 (44)
S(1)—Bi(2)—S(2)	80.70 (41)	S(3)—Bi(3)—S(3 ^{ix})	81.35 (41)
S(1)—Bi(2)—S(3 ^{viii})	156.69 (119)	S(3 ^{ix})—Bi(3)—Br ^{vi}	118.72 (41)
S(1 ^{iv})—Bi(2)—S(2)	140.97 (28)	S(3 ^{ix})—Bi(3)—Br ^{viii}	73.05 (40)
S(1 ^{iv})—Bi(2)—S(3 ^{viii})	127.72 (40)	Br ^{vi} —Bi(3)—Br ^{viii}	69.83 (29)
S(2)—Bi(2)—S(3 ^{viii})	76.98 (36)		
S(3)—Bi(2)—S(3 ^{viii})	81.22 (42)		

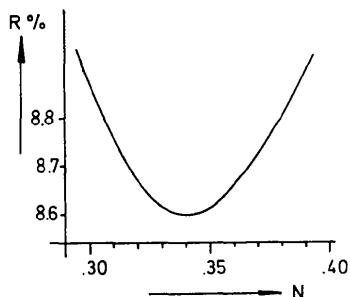


Fig. 2. The R index as a function of the occupancy N of the Bi(1) atom.

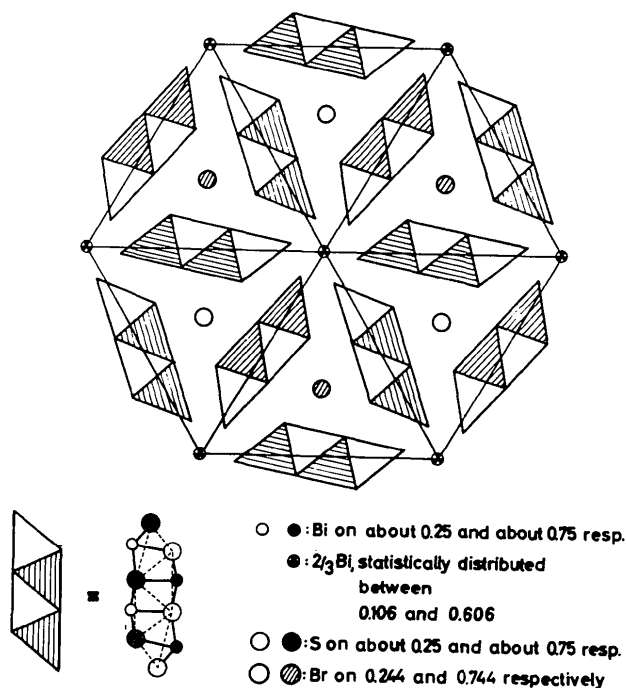


Fig. 3. Projection of the structure along the c axis.

Discussion

The statistical occupation $N=0.333$ of Bi(1) can be explained as follows. If the site $2(a)$ in the space group $P6_3$ were fully occupied, an interatomic distance of about 2.0 \AA between two Bi atoms is required for a lattice constant of about 4.0 \AA , Fig. 1(a). Since the shortest Bi-Bi distance in the metallic state is found to be 3.095 \AA , the full occupation of this position is forbidden. Reducing the occupancy to $N=\frac{1}{2}$ there are possible models which do require local distances of about 2.0 \AA between two Bi atoms, Fig. 1(b). When an occupancy of $N=\frac{1}{3}$ is assumed, at which every third unit cell has to remain statistically unoccupied, the resulting Bi-Bi distances have the usual values, Fig. 1(c). The correctness of this assumption is shown (Fig.

2) by a minimum in the residual R in the neighbourhood of $N=\frac{1}{3}$. Observed and calculated structure factors are listed in Table 2.* Fig. 3 shows the structure along the c axis. Bi(1) has $(3S+3S)$ neighbours forming a flat trigonal antiprism, while Bi(2) is surrounded by $(3S+3S)$ atoms in the form of a strongly distorted tetragonal pyramid with an additional bond to S(1). The $(3S+2S+2Br)$ around the Bi(3) form a slightly distorted tetragonal pyramid whose base is formed by two S(2) and two S(3) atoms and whose apex is occupied by the third S(3) atom. The configuration is completed by two additional bonds to the Br atom. The same coordination was also found in $\text{Bi}_2\text{Cu}_3\text{S}_4\text{Br}$. Bond lengths and angles are given in Table 3. Around the Bi(2) and Bi(3) atoms arise $(\text{Bi}_4\text{S}_6)_\infty$ chains, which run parallel to the z direction and which are connected together through the Bi(1) and Br atoms respectively. Thus around the threefold axis spacious channels result, which run along $[001]$.

The following programs were used in this work: (a) *ORFLS*, (b) *DATAPH* (a local version), (c) Institute's internal programs.

The author expresses his gratitude to Professor Dr V. Kupčik for his continuous encouragement and support. Thanks are due to Drs E. Matzat and G. Miede for interesting discussions. All calculations were carried out on a Univac 1108 computer in the Gesellschaft für wissenschaftliche Datenverarbeitung in Göttingen. The Deutsche Forschungsgemeinschaft provided part of the apparatus. I also thank Mr M. Machin for his help in improving the English of this paper.

* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31575 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- COPPENS, P. (1968). *DATAPH*. Dept. of Chem. Brookhaven National Laboratory (local version by G. Miede). *International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed., Table 3.3.1. Birmingham: Kynoch Press.
- KRÄMER, V. (1973). *J. Appl. Cryst.* **6**, 499.
- LEWIS, J. JR & KUPČIK, V. (1974). *Acta Cryst.* **B30**, 848-852.
- MARIOLACOS, K. & KUPČIK, V. (1975). *Acta Cryst.* **B31**, 1762-1763.
- MIEHE, G. & KUPČIK, V. (1971). *Naturwissenschaften*, **4**, 219.
- OHMASA, M. & MARIOLACOS, K. (1974). *Acta Cryst.* **B30**, 2640-2643.
- RABENAU, A. & RAU, H. (1969). *Philips Tech. Rev.* **30**, 89.