

Bi₅O₇Br and its structural relation to α -Bi₅O₇I

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Pentabismuth heptoxide bromide, Bi₅O₇Br, crystallizes in the space group *Cmca*. Its structure is compared with the closely related *Ibca* structure of α -Bi₅O₇I. The change in the space group is assumedly the result of a compromise between the different spatial needs of Br and I and the rigidity of the $\{\infty\}[\text{Bi}, \text{O}]$ frameworks into which they are embedded. A detailed procedure for the synthesis of Bi₅O₇Br is given.

Comment

In the quasi-binary system Bi₂O₃–BiBr₃, five well established compounds, namely BiOBr (1:1), Bi₄O₅Br₂ (2.5:1), Bi₂₄O₃₁Br₁₀ (3.1:1), Bi₃O₄Br (4:1) and Bi₁₂O₁₇Br₂ (8.5:1), are known (see, for example, Oppermann *et al.*, 1996). A sixth compound, of composition Bi₅O₇Br (7:1), has been described by Ketterer & Krämer (1984). It was obtained by reaction of aqueous solutions of HBiBr₄ and NaOH; details of the synthesis were not given. It should be noted that the compound could hitherto not be synthesized by ceramic methods (Ketterer, 1985; Oppermann *et al.*, 1996). In the following, a procedure for the synthesis of Bi₅O₇Br from aqueous solutions will be presented in detail (see *Experimental*). The structure (Fig. 1) has been determined. The model obtained is similar (but not identical) to the model described by Ketterer (1985), the latter leading to *R* = 0.16 on refinement of our reflection data.

In the following, the structure of Bi₅O₇Br will be compared with that of closely related α -Bi₅O₇I (Eggenweiler *et al.*, 2001). In Bi₅O₇Br, the Bi1 and Br1 atoms lie at sites with imposed mirror symmetry, while O2 is at a site with twofold symmetry. Both structures contain a $\{\infty\}[\text{Bi}, \text{O}]$ framework into which $\{\infty\}$ double columns ('zigzag rows') of halogen atoms aligned parallel to [010] are embedded. The three-dimensional frameworks consist of $\{\infty\}[\text{BiO}]^+$ sheets aligned parallel to (001), which are mutually connected by folded $\{\infty\}[\text{Bi}_4\text{O}_8]^{4-}$ ribbons aligned parallel to [010]. The 'folded ribbon' (Fig. 2) description implies that Bi–O bonds of lengths greater than 3 Å (see below) are neglected.

Bond-distance ranges in Bi₅O₇Br (Table 1) are as found in other bismuth oxide bromides (see, for example, Keller *et al.*, 2001) and (with respect to Bi–O) in α -Bi₅O₇I. Owing to the electron lone pair (LP) of Bi^{III}, one can distinguish between 'primary' and 'secondary' Bi–X bonds (Alcock, 1972). The Bi–O bonds with lengths in the range 2.1–2.4 Å (3.2–3.3 Å) can be classified as primary (secondary), while those in the range 2.5–2.7 Å may play an intermediate role. The Bi–Br bond lengths (in the range 3.4–3.6 Å) can be assigned to secondary bonding (as in BiSBr; Keller & Krämer, 2006b). Another Bi···Br distance of 4.163 (4) Å is clearly non-bonding. As usual for 'ions' with an LP, in all three cases (Bi1, Bi2 and Bi3) the atoms bonded by primary bonds occupy one side of the coordination sphere, while the other 'ligand atoms' gather at the other side, *i.e.* that side to which the LP is pointing. In the context of the crystal structure, the LPs of all Bi atoms are directed into the space that is occupied by the halogen atoms. These latter findings also apply to the structure of α -Bi₅O₇I.

While the symmetries of Bi₅O₇Br and α -Bi₅O₇I are different (*Cmca* versus *Ibca*), their lattice constants differ only slightly ($\Delta a = 0.18$ Å, $\Delta b = 0.05$ Å and $\Delta c = 0.00$ Å). The similarity of the two structures becomes especially obvious when their two projections on to (010) are superimposed with a mutual *z* shift of $\frac{1}{4}$ (Fig. 3). It is also reflected in the fact that the space groups

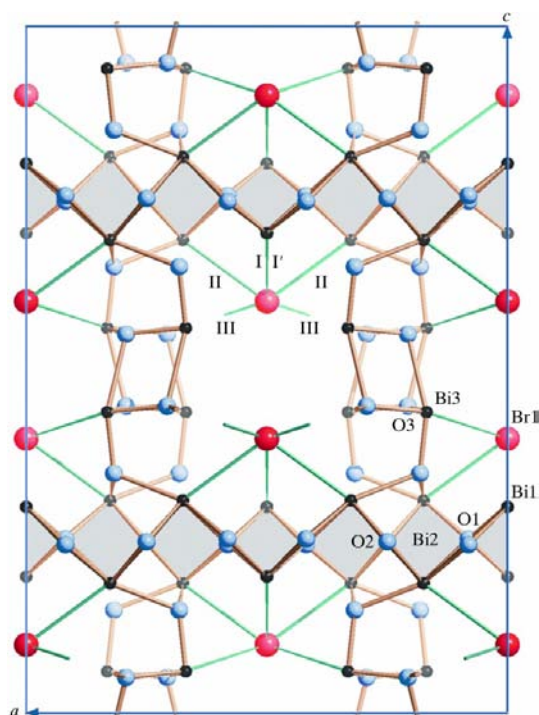


Figure 1

The structure of Bi₅O₇Br as seen from [010]. Bi, Br and O atoms are symbolized by small black, large (red in the electronic version of the paper) and medium-sized (light blue) spheres. Atoms/bonds in the 'background' have been drawn paler. $\{\infty\}[\text{BiO}]^+$ sheets (seen side-on) are emphasized. Secondary Bi–O bonds are not visualized. Symbols I, II, III and I' denote groups of Bi–X bonds (see *Comment*).

Cmca and *Ibca* have the common minimal supergroup *Cmma* ($2c' = c$). While the (010) projections are nearly identical, small differences in the ‘heights’ of corresponding atoms occur [0.2 (2) Å for the Bi and halogen atoms], which lead to the most important structural difference (Fig. 2); with respect to their overall folding pattern, two of the aforesaid ribbons which are vicinal in the [100] direction appear to be ‘in phase’ in the I compound, while there is a ‘phase shift’ of π in the Br compound (all details accounted for, the two ribbons are related to one another by an $a_{(001)}$ operation in the I and an $m_{(100)}$ operation in the Br compound).

The similarity of the lattice constants shows that the three-dimensional [Bi, O] framework, held together by strong Bi–O bonds, hardly adjusts itself with respect to size when the Br atoms in $\text{Bi}_5\text{O}_7\text{Br}$ are replaced by the larger I atoms. This is similar to the case of $\text{ABi}_6\text{O}_9\text{X}$ compounds ($A = \text{Na, K and Rb}$, and $X = \text{Cl, Br and I}$), which also contain $\{\infty\}[\text{Bi, O}]$ frameworks almost insensitive to changes in A and X (Keller & Krämer, 2006b; Keller *et al.*, 2007). In contrast to these compounds, however, the experimental size difference between Br and I in $\text{Bi}_5\text{O}_7\text{X}$, as retrievable from the bond lengths, is 0.18 (6) Å (but see below), which is much closer to the ‘isotypic’ size difference expectation value ($\rho_{\text{Br/I}}$) of 0.22 Å (Keller & Krämer, 2006a) than the corresponding value of 0.05 Å in $\text{KBi}_6\text{O}_9\text{X}$ ($X = \text{Br and I}$). A very similar size difference of 0.19 Å is found in BiOX ($X = \text{Br and I}$), the [Bi, O] substructure of which consists of the aforesaid $\{\infty\}[\text{BiO}]^+$ building blocks only (Keller & Krämer, 2006b).

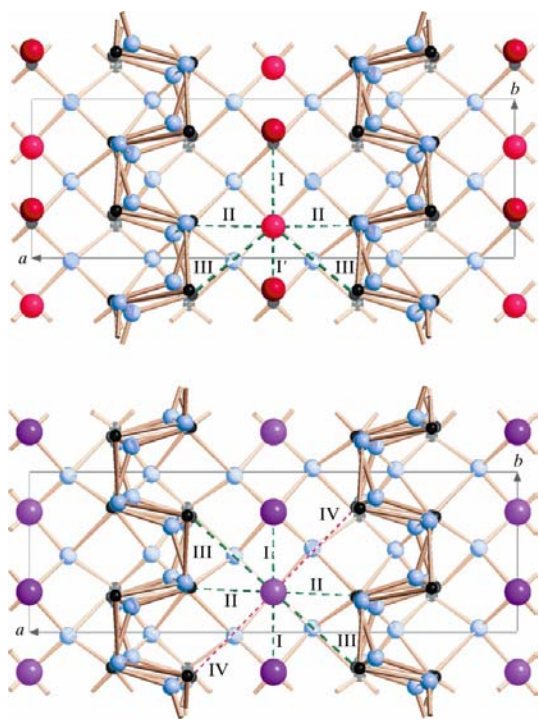


Figure 2
Parts of the structures of $\text{Bi}_5\text{O}_7\text{Br}$ (above) and $\alpha\text{-Bi}_5\text{O}_7\text{I}$ (below), as seen from [00 $\bar{1}$].

Similar to those in BiOX , the X coordination polyhedra in $\text{Bi}_5\text{O}_7\text{X}$ are more or less one-sided, as is visible in Figs. 1 and 2. Thus, when the I atoms are replaced by the smaller Br atoms, the latter can retreat to one side in the [001] direction, thereby enabling bonds I and II (Figs. 1 and 2) to shorten without a necessity for the [Bi, O] framework to change. Things are different in the [100] direction, where $X\text{--Bi}$ bonds are equally present on both sides, such that the framework actually gives way to some extent ($\Delta a = 0.18$ Å). For [010], a special solution has been found; enabled by the different arrangement of the $\{\infty\}[\text{Bi}_4\text{O}_8]^{4-}$ ribbons, the distances between vicinal Br atoms in a Br column become alternating (in contrast to the $\text{I}\cdots\text{I}$ distances), such that the Br coordination polyhedron becomes partially one-sided also in the [010] direction, as visible from Fig. 2, thus allowing the remaining $\text{Bi}\text{--}X$ bonds to shorten as well. Seen the other way around, it is presumably the difference in the spatial requirements of the halogen atoms which induces the rearrangement of the ribbons (and, as a consequence, the change in space group).

It should be noted that, as the two $\text{Bi}_5\text{O}_7\text{X}$ structures are not isotypic, the calculation of the experimental Br/I size difference is not unambiguous; the above value of 0.18 (6) Å is rather an estimation. Firstly, to have the coordination numbers (CN) of Br and I both equal to 6 we have to neglect the two weak secondary $\text{I}\text{--}\text{Bi}3$ bonds IV (Fig. 2) of lengths 4.01 Å. The assignment of CN 8 to both X atoms would be an alternative, but it would imply the existence of two additional very long $\text{Br}\text{--}\text{Bi}3$ bonds of length 4.16 Å (see above) and the unreasonable assumption that these two $\text{Bi}\text{--}X$ bonds elongate in the transition from I to Br. Secondly, while bonds I ($X\text{--}\text{Bi}1$) and II ($X\text{--}\text{Bi}2$) exist analogously in both compounds, the remaining two bonds III ($X\text{--}\text{Bi}3$), when seen from [001] (Fig. 2), have a *cisoid* (*transoid*) configuration for $X = \text{Br}$ (I) owing to the different symmetries of the coordi-

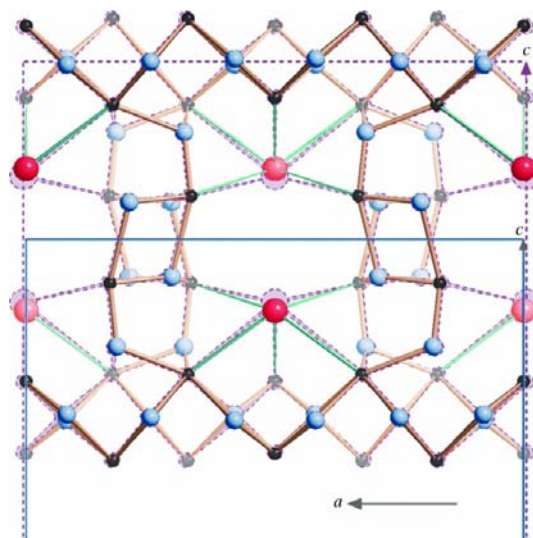


Figure 3
Superposition of the corresponding parts of the structures of $\text{Bi}_5\text{O}_7\text{Br}$ and $\alpha\text{-Bi}_5\text{O}_7\text{I}$ (dashed lines).

nation polyhedra [m (2) for $X = \text{Br}$ (1)]. This latter difference matters neither in the light of the bond valence nor in that of the ionic radii concept, however, as the connectivity schemes and X coordination numbers are identical for both compounds. On the other hand, the implied neglect of the two Bi—I bonds IV in this case means that the experimental size difference of 0.18 (6) Å (calculated from the six pairs of corresponding bonds) is presumably slightly overestimated.

Experimental

In a 100 ml polypropylene flask, distilled and freshly filtered water was added to NaOH (9.2 g, 0.23 mol) until the volume of the solution was 32 ml. The solution was heated to about 313 K from below but not stirred. Three 16.5 ml portions of a 0.0035 *M* filtered solution of Bi₂O₃ in 1.5 *N* aqueous HBr were added dropwise from a burette (approximately one drop every 2 min), each portion on one of three successive days (partitioning helped to keep the dropping rate approximately constant). Colourless (sometimes slightly yellow) needles of Bi₅O₇Br (with lengths of up to 1 mm) grew during the second and third day. The by-products were white amorphous 'microflakes' and minor amounts of yellow Bi₂O₃, and colourless NaBi₆O₉Br crystals. The mother liquor and reaction products were filtered through a plastic sieve (pore size 70 μ and diameter 25 mm) to separate the Bi₅O₇Br needles from the by-products. Still in the sieve, the needles were washed about ten times with about 20 ml of water and dried (yield 80 mg, 65 μmol, 93%). Chemical analyses: Bi (AAS): 85.5% (theory 84.5%); Br (ion-selective electrode): 7.4% (theory 6.5%).

Crystal data

Bi ₅ O ₇ Br	$V = 1961.6$ (6) Å ³
$M_r = 1236.81$	$Z = 8$
Orthorhombic, <i>Cmca</i>	Mo $K\alpha$ radiation
$a = 16.087$ (3) Å	$\mu = 93.49$ mm ⁻¹
$b = 5.2965$ (10) Å	$T = 293$ (2) K
$c = 23.022$ (4) Å	$0.26 \times 0.02 \times 0.01$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	5805 measured reflections
Absorption correction: integration (<i>SHELXTL</i> ; Bruker, 2000)	1251 independent reflections
$T_{\min} = 0.043$, $T_{\max} = 0.553$	789 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.080$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	46 parameters
$wR(F^2) = 0.094$	$\Delta\rho_{\text{max}} = 3.78$ e Å ⁻³
$S = 1.08$	$\Delta\rho_{\text{min}} = -3.21$ e Å ⁻³
1251 reflections	

Table 1

Selected bond lengths (Å).

Bi1—O1 ⁱ	2.219 (17)	Bi2—O4 ^v	2.511 (16)
Bi1—O1 ⁱⁱ	2.184 (16)	Bi2—O4 ^{vi}	3.214 (16)
Bi1—O4	3.157 (17)	Bi2—O3	3.214 (18)
Bi1—Br1	3.412 (5)	Bi2—Br1	3.485 (3)
Bi1—Br1 ⁱⁱⁱ	3.588 (5)	Bi3—O4	2.074 (15)
Bi2—O2	2.154 (11)	Bi3—O3 ^{vii}	2.105 (16)
Bi2—O4	2.390 (16)	Bi3—O3	2.125 (16)
Bi2—O2 ^{iv}	2.407 (13)	Bi3—O3 ^{viii}	2.714 (18)
Bi2—O1	2.309 (17)	Bi3—O3 ⁱⁱⁱ	3.340 (17)
Bi2—O1 ^{iv}	2.571 (17)	Bi3—Br1	3.643 (3)

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXD* (Sheldrick, 2006); program(s) used to refine structure: *SHELXTL* (Bruker, 2000); molecular graphics: *SCHAKAL99* (Keller, 2004); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3029). Services for accessing these data are described at the back of the journal.

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