Synthesis and Crystal Structure of Penthylenediammonium pentabromobismutate(III) $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{BiBr}_5$

Mohsen OULED MOHAMED SGHAIER,^{*,†} Mohamed ABDELHEDI,^{**,†} and Slaheddine CHAABOUNI^{*}

^{*}Laboratoire des Sciences des Matériaux et d'Environnement, Faculté des sciences de Sfax, route de soukra BP 1171, 3000 Sfax, Tunisia

^{**}Laboratoire de Chimie Inorganique Faculté des sciences de Sfax, route de soukra BP 1171, 3000 Sfax, Tunisia

X-ray studies on $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{BiBr}_5$ show that it crystallizes in the orthorhombic $P2_12_12_1$ space group with the following unit-cell dimensions: $a = 7.9580(4)\text{\AA}$, $b = 14.0110(16)\text{\AA}$, $c = 14.0960(14)\text{\AA}$. The structure was refined to $R = 0.0492$. It consists of penthylenediammonium cations and one-dimensional $[\text{BiBr}_5]_n^{2-}$ polyanionic zig-zag chains composed of deformed BiBr_6 octahedra connected by two cis vertices. These chains are themselves interconnected by means of the N-H...Br hydrogen bonds.

(Received May 28, 2011; Accepted October 21, 2011; Published on web January 10, 2012)

The structures of halogenoantimonates(III) and halogenobismuthates(III) with organic cations, a new group of ferroic crystals, are best described as molecular-ionic, organic inorganic hybrid materials. They consist of organic cations within anionic inorganic frameworks. Differences in the size, symmetry and ability to form hydrogen bonds of the various possible organic cations, together with the many different possible metal-halogen atom configurations, provide a rich family of compounds. The anionic structures that have been reported so far range from simple isolated $[\text{MX}_6]^{3-}$ octahedra and $[\text{MX}_5]^{2-}$ square pyramids (M-Sb^{III}, Bi^{III}; X-Br, Cl, I) through isolated units containing octahedra/square pyramids, connected by corners, edges or faces, to infinite one- or two-dimensional polyanionic structures.^{1,2}

Single crystals of $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{BiBr}_5$ were obtained in the reaction of $\text{Bi}(\text{NO}_3)_3$ with $\text{NH}_2(\text{CH}_2)_5\text{NH}_2$ with a large excess of HBr. The synthesized compound was purified by repeated crystallizations. Yellow and transparent single crystals were grown at room temperature, and had the form of flat needles.

The crystal and experimental data are given in Table 1. The positional parameters for the bismuth atoms were obtained from a three-dimensional Patterson map, while the remaining atoms were found from a successive difference Fourier map. After introducing anisotropic thermal displacement parameters for the

non-hydrogen atoms, the hydrogen atoms were localized and optimized to fixed positions. Their contributions were isotropically introduced into the calculation, but not refined. The final anisotropic full-matrix least squares resulted in the convergence of the R factor to 0.0492 ($R_w = 0.0547$), incorporating the weighting scheme

$$w = 1/[\sigma^2(F_o)^2 + (0.0289.P)^2], \text{ where } P = \text{Max}[(F_o^2, 0) + 2 F_c^2]/3.$$

A projection along the a axis of the atomic arrangement of the

Table 1 Crystal and experimental data

Chemical formula: $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{BiBr}_5$
Formula weight (g mol^{-1}) = 712.70
$T = 298$
Crystal system: orthorhombic Space group: $P2_12_12_1$
$a = 7.9580(4)\text{\AA}$
$b = 14.0110(16)\text{\AA}$
$c = 14.0960(14)\text{\AA}$
$V = 1571.7(3)\text{\AA}^3$
$D_x = 3.012 \text{ g/cm}^3$
Radiation: Mo K_α , $\lambda = 0.71073$
(Mo K_α) = 0.827 mm^{-1} $F(000) = 1272$
Crystal size (mm^3) = $0.35 \times 0.20 \times 0.15$
No. of reflections collected = 11917
No. of independent reflections = 4401
θ Range for data collection: 3.236 to 29.997°
Data/Restraints/Parameters = 4401/235/120
Goodness-of-fit on $F^2 = 1.1721$
R indices [$I > 2\sigma(I)$]: $R1 = 0.0492$, $wR2 = 0.0547$
R indices [all data]: $R1 = 0.0492$, $wR2 = 0.0547$
$(\Delta/\sigma)_{\text{max}} = 0.057$
$(\Delta\rho)_{\text{max}} = 3.60 \text{ e/\AA}^{-3}$ $(\Delta\rho)_{\text{min}} = -1.59 \text{ e/\AA}^{-3}$
Measurement: Enraf-Nonius CAD4
Program system: SHELXL-97
Structure determination: SHELXS-97
CCDC deposit number: 799634

Fig. 1 Chemical diagram of the title compound.

[†] To whom correspondence should be addressed.
E-mail: mohsenesghaier@yahoo.fr

Fig. 2 $[\text{BiBr}_5]^{2-}$ chain structure viewed from the (b) top and (a) sides. Symmetry code: i = $1/2+x, 3/2-y, 1-z$, ii = $-1/2+x, 3/2-y, 1-z$, iii = $1+x, y, z$, iv = $-1+x, y, z$.

Table 2 Selected bond distances (Å) and angles (°)

Atoms	Distance	Atoms	Distance
Bi-Br ⁱ	3.013(5)	N1-C1	1.47(5)
Bi-Br1	2.709(5)	N2-C5	1.50(6)
Bi-Br2	2.697(5)	C1-C2	1.61(6)
Bi-Br3	2.827(5)	C2-C3	1.47(5)
Bi-Br4	2.863(4)	C3-C4	1.60(6)
Bi-Br5	3.035(5)	C4-C5	1.37(6)
Atoms	Angle	Atoms	Angle
Br5 ⁱ -Bi-Br1	92.0(2)	N1-C1-C2	106(3)
Br5 ⁱ -Bi-Br2	170.57(18)	C1-C2-C3	112(4)
Br1-Bi-Br2	94.84(16)	C2-C3-C4	113(4)
Br5 ⁱ -Bi-Br3	87.77(16)	C3-C4-C5	120(3)
Br2-Bi-Br3	98.01(18)	N2-C5-C4	119(3)
Angles diedres			
Br1-Bi-Br4	92.84(16)	N1-C1-C2-C3	179.16(1)
Br2-Bi-Br4	88.87(16)	C1-C2-C3-C4	176.62(1)
Br3-Bi-Br4	168.86(15)	C2-C3-C4-C5	71.17(1)
Br5 ⁱ -Bi-Br5	84.62(5)	C3-C4-C5-N2	177.46(1)
Br1-Bi-Br5	175.9(16)		
Br2-Bi-Br5	88.77(19)		
Br3-Bi-Br5	82.25(15)		
Br4-Bi-Br5	89.20(15)		
Br1-Bi-Br3	95.27(18)		

i = $x+0.5, -y+1.5, -z$.

complex is depicted in (Fig. 2). An examination shows a layer arrangement parallel to the [011] direction: polyanionics of $[\text{BiBr}_5]^{2-}$ alternated with planes of the $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]^{2+}$ group.

The mid planes $[\text{BiBr}_5]^{2-}$ chains are located at $a = 0$ and $a = 0.5$ (Fig. 3S). Each Bi atom is surrounded by six Br atoms, with a Bi-Br distance ranging from 2.6953(2) to 3.022(2) Å. These values are comparable with those reported to date.³ Each $[\text{BiBr}_5]^{2-}$ anion is related to another by a twofold screw axis along the a axis, giving a Bi-Brⁱ contact distance of 3.013(5) Å. Thus, Br5 forms a lopsided bridge between two bismuth centres, and the longer Bi-Br5 distance, 3.035(5) Å, is typical for a Bi-Br asymmetric bridging bond. The terminal bonds located opposite to the bridging are shortened, while those neither bridging nor terminal opposite to bridging should not generally change. Additional deformation to the bond lengths may be introduced by hydrogen bonds.⁴ The involvement of any particular bromine atom in hydrogen bonding leads to a shift of the lone electron pair of Bi atoms in the direction of H atom, which generally results in a shift of the respective Br atom out of the Bi position. This leads to an increase in the Bi-Br bond length.

Four of the hydrogen bondings are relatively stronger. The longest distances, Bi-Br4 = 2.863(4) Å, Bi-Br5 = 3.035(5) Å, and Bi-Brⁱ = 3.013(5) Å, are particularly due to the presence of the Bi(III) lone electron pair (LEP). The LEP is responsible for the deformation of the octahedron coordination of Bi(III).^{5,6} In our case, the lone electron pair of Bi(III) points in for opposite direction to the Br3 atoms. The orientation of octahedral chains indicates that these LEP point in [011] direction. Table 2 reports the principal geometrical features of the $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]^{2+}$ cations. The C-N and C-C bond lengths vary from 1.47(6) to 1.50(5) Å and from 1.37(6) to 1.61(6) Å, respectively. The intermolecular hydrogen bonding contacts N-H...Br provide a linkage between the $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]^{2+}$ entities and $[\text{BiBr}_5]^{2-}$ chains. All these hydrogen bonds give rise to a three-dimensional network in the structure and add of stability to this compound. The dihedral rotational angles, [N-C-C-C], [C-C-C-C] and [C-C-C-N], of the chain (Fig. 3S) are listed in Table 3S. According to results obtained by a calculation with molecular mechanism method of dihedral angles in the organic chain $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]^{2+}$ (Table 3S),⁷ we assumed that our cation presents a TTGT conformation (*Trans Trans Gauche Trans*).

References

- G. A. Fischer and N. C. Norman, *Adv. Inorg. Chem.*, **1994**, 41.
- M. Bujak and J. Zaleski, *J. Solid State Chem.*, **2004**, 177, 3202.
- T. Okuda, N. Tanaka, S. Ichiba, and K. Yamada, *Z. Naturforsch.*, **1986**, A41, 319.
- J. Zaleski and A. Pietraszko, *Acta Cryst.*, **1996**, B52, 287.
- J. Olivier-Fourcade, A. Ibanez, J. C. Jumas, M. Maurin, I. Lefebvre, P. Lippens, M. Lannoo, and G. Allan, *J. Solid State Chem.*, **1990**, 87, 366.
- X. Wang and F. Liebau, *Acta Cryst.*, **1996**, B52, 7.
- N. Fourati, Y. Abid, S. Kamoun, A. Daoud, and W. Depmeir, *Ann. Chim. Sci., Mat.*, **1998**, 23, 181.