

Synthesis and Crystal Structure of

3-3'-Diaminomethyldipropylammonium Hexachlorobismuthate (III)

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Abstract

Synthesis and crystal structure of 3-3'-diamino-N-methyldipropylammonium hexachlorobismuthate (III) are reported. The compound crystallizes in the triclinic system with space group P1. The unit cell dimensions are: $a = 7.5580(5)$, $b = 7.8710(6)$, $c = 8.3709(7)$ Å with $Z=1$. The crystal is built up of separated $[\text{BiCl}_6]^{3-}$ octahedral anions and 3-3'-diamino-N-methyldipropylammonium cations. The organic layers are arranged in sandwich between the anionic ones. The crystal packing is governed by means of the ionic N-H...Cl hydrogen bonds, forming a three dimensional network.

Keywords:

Organic-inorganic hybrid material; Crystal structure; Halogenobismuthates(III).

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I. Introduction

Recently, much attention has been focused on organic–inorganic hybrid materials based on metal–halide units; those materials are frequently characterized by their various physical and chemical properties that could lead to technological innovations like magnetic or ferroelectric transitions, conductivity (super conductivity), electroluminescence and photoluminescence [1–6]. To date, numerous metal–halide systems involving Sn, Pb, Sb, Bi, and Te have been synthesized and structurally characterized [7–12]. The anionic metal–halide species has been observed to range in dimensionality from two-dimensional or one dimensional polymeric anions to discrete anions of various sizes. The polyhedral may be linked by corner-, edge-, or face-sharing into numerous different arrangements; and consequently, halometallate compounds exhibit very great structural diversity [8, 10, 13]. The identity of the anions formed has been found to depend on the specific reaction conditions employed including the size, shape, the reagent stoichiometry, and ability to form the hydrogen bond system by the cations. The bismuth compounds represent a potential class of materials with unusual structural arche-types, due to the fact that the Bi(III) ion exhibits a variety of coordination modes, depending on crystal packing and on ligands: octahedral coordination being observed.

The polyhedra may be linked by corner-, edge-, or face sharing into numerous different arrangements, leading to an extensive family of bismuth(III) halogenoanions ($[\text{BiX}_4]$, $[\text{BiX}_5]^{2-}$, $[\text{BiX}_6]^{3-}$, $[\text{Bi}_2\text{X}_9]^{3-}$, $[\text{Bi}_2\text{X}_{11}]^{5-}$, $[\text{Bi}_3\text{X}_{12}]^{3-}$, $[\text{Bi}_4\text{X}_{18}]^{6-}$, $[\text{Bi}_6\text{X}_{22}]^{4-}$, and $[\text{Bi}_8\text{X}_{30}]^{4-}$) [14–19]. The structure of the anionic form is related to the size and symmetry of the organic counter-ions and their ability to form hydrogen bonds as well. In fact, besides the rich structural diversity displayed by these systems, some interest has been directed towards halobismuthate(III) compounds in combination with organic cations, due to their very interesting physical properties caused by active lone pairs [20].

In an attempt to study the effects of the size and the coordination mode of the cation in this class of compounds, we have successfully synthesized a new compound of formula $[\text{C}_7\text{H}_{22}\text{N}_3]\text{BiCl}_6$.

In the present paper, we report the synthesis and the structural characterization by X-ray diffraction of the 3-3'-diamino-N-methyldipropylammonium hexachlorobismuthate (III).

II. Experimental section

II.1.Synthesis

Single crystals of the title compound were prepared at 300 K by slow evaporation of a saturated aqueous solution obtained by dissolving $\text{C}_7\text{H}_{19}\text{N}_3$ and BiCl_3 (molar ratio 3/1) in 36% HCl. The resulting solution is kept under ambient conditions which were allowed to evaporate slowly. A few days later prismatic crystals were obtained.

II.2.Single crystal structure determination

The X-ray data collection was carried out on Enraf-Nonius Kappa CCD diffractometer using Ag K α radiation. The positional parameters for the heavy atoms were obtained from a three-dimensional Patterson map, while the non-H atoms were found from successive difference Fourier Maps. The structure was refined by full-matrix least squares using anisotropic temperature factors for all non-hydrogen atoms and the hydrogen atoms were localized and optimized to restrained positions. Calculations were performed with the programs SHELXS [21], using the scattering factors enclosed therein. The crystal data, collected reflections and parameters of the final refinement are reported in Table 1.

Table 1. Crystal and experimental data

Chemical formula	$[\text{C}_7\text{H}_{22}\text{N}_3]\text{BiCl}_6$
Formula weight	440.37(6)
Crystal system	Triclinic
Space group	$P1$
T	293(2) K
Cell constants	
<i>a</i>	7,5580(5)Å
<i>b</i>	7,8710(6)Å
<i>c</i>	17.3168(13)Å
β	89,169(5)°
Cell volume (Å ³)	3005.5(4)
Z	1
Dx	2,15g/cm ³
Diffractometer/scan	Enraf-Nonius Kappa CCD



Radiation,	
graphite monochromator	Mo K α ($\lambda = 0.71073 \text{ \AA}$)
μ_{cal}	$10,905 \text{ mm}^{-1}$
R_{int}	0,0269
No. of reflections collected	1993
No. of independent reflections	3994
Range of h, k, l	-10 \rightarrow 10, -10 \rightarrow 11, -12 \rightarrow 11
$F(000)$	1067,7
θ range for data collection	$2,44 \leq \theta \leq 30,95$
Weights	$w = 1/[r^2(F_o^2) + (0.0433P)^2]$ where $P = \text{Max} [(F_o^2, 0) + 2F_c^2]/3$
$R = \sum F_o - F_c / \sum F_o $	0,0424
wR	0,1322
Goodness-of-fit (GOF) = S	1.04

III. Results and discussion

The final atomic coordinates obtained from the single crystal refinement with Ueq are given in Table 2. Table 3 shows the anisotropic displacement parameters. Interatomic distances and bond angles schemes are listed in Table 4.

The title compound crystallizes in the non-centrosymmetric triclinic space group P1. The crystallographic analysis of the title compound reveals that the crystal structure of $[\text{C}_7\text{H}_{22}\text{N}_3]\text{BiCl}_6$ consists of the monomeric $[\text{BiCl}_6]^{3-}$ anion and one crystallographically independent triprotonated 3-3'-diamino-N-methyldipropylammonium cation, as shown in Figure 1.

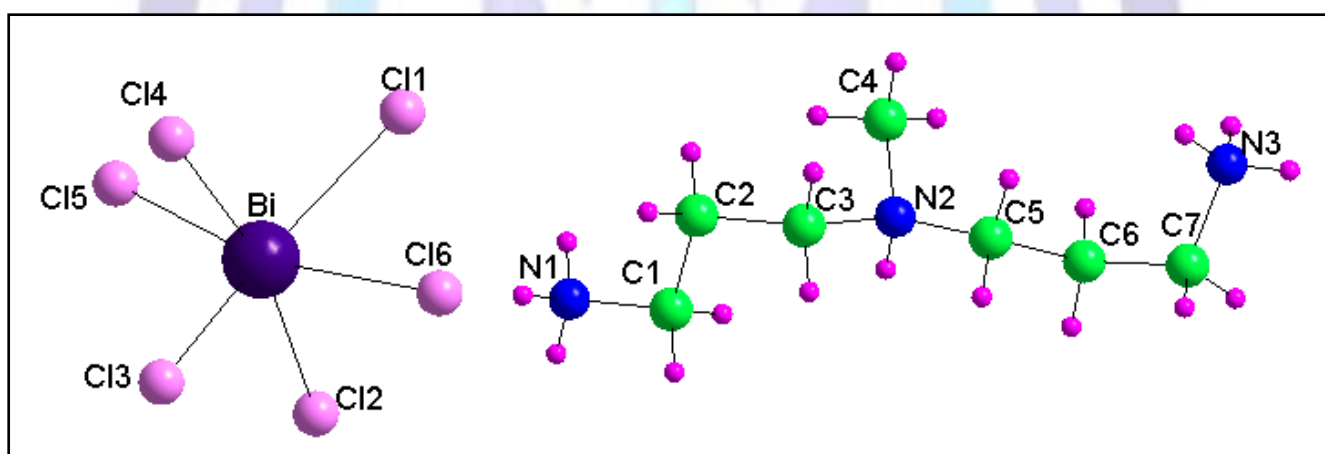


Fig 1: Atom numbering scheme for the title compound $[\text{C}_7\text{H}_{22}\text{N}_3]\text{BiCl}_6$

Table 2 . Atomic coordinates and U_{eq} or U_{iso} for $[C_7H_{22}N_3] BiCl_6$

Atomes	X/a	Y/b	Z/c	U_{eq} ou U_{iso}
Bi	-0,0877	-0,0867	-0,0788	0,02492 (11)
Cl1	-0,4010 (5)	0,0629 (5)	0,1204 (4)	0,0407 (7)
Cl2	-0,2031 (9)	0,2085 (8)	-0,3160 (6)	0,0553 (12)
Cl3	0,3009 (5)	-0,2504 (7)	-0,1459 (5)	0,0477 (8)
Cl4	-0,2566 (6)	-0,2675 (5)	-0,2373 (4)	0,0368 (6)
Cl5	0,0978 (8)	-0,4189 (7)	0,1099 (7)	0,0521 (11)
Cl6	-0,0346 (8)	0,1401 (8)	0,1127 (8)	0,0717 (17)
C1	-0,442(2)	-0,372(2)	0,1143 (17)	0,038(3)
H1A	-0,5607	-0,2488	0,0954	0,046*
H1B	-0,3270	-0,3506	0,0929	0,046*
C2	-0,432(3)	-0,452(3)	0,2918 (18)	0,040(3)
H2A	-0,5449	-0,4777	0,3125	0,049*
H2B	-0,3111	-0,5720	0,3123	0,049*
C3	-0,436(2)	-0,311(3)	0,4006 (19)	0,041(3)
H3A	-0,3285	-0,2798	0,3717	0,049*
H3B	-0,4066	-0,3733	0,5092	0,049*
C4	-0,802(3)	-0,161(3)	0,435(2)	0,045(3)
H4A	-0,8031	-0,2459	0,3600	0,068*
H4B	-0,9243	-0,0431	0,4227	0,068*
H4C	-0,7885	-0,2202	0,5421	0,068*
C5	-0,605(3)	0,007(2)	0,499(2)	0,044(4)*
H5A	-0,4764	0,0024	0,4774	0,053*
H5B	-0,6018	-0,0396	0,6112	0,053*
C6	-0,772(3)	0,224(2)	0,473(2)	0,043(4)
H6A	-0,7593	0,2770	0,3669	0,051*
H6B	-0,9014	0,2262	0,4758	0,051*
C7	-0,769(3)	0,352(3)	0,590(3)	0,052(4)
H7A	-0,6339	0,3316	0,6047	0,062*
H7B	-0,8501	0,4842	0,5475	0,062*
N1	-0,447(2)	-0,5025 (18)	0,0071 (15)	0,039(2)
HN1A	-0,4528	-0,4538	-0,0940	0,058*
HN1B	-0,5545	-0,5199	0,0254	0,058*
HN1C	-0,3382	-0,6146	0,0235	0,058*
N2	-0,632(2)	-0,1186 (18)	0,4022 (15)	0,037(3)
HN2	-0,6525	-0,0610	0,3001	0,045*
N3	-0,844(2)	0,319(2)	0,744(2)	0,057(4)
HN3A	-0,8398	0,3993	0,8100	0,085*
HN3B	-0,7680	0,1984	0,7843	0,085*
HN3C	-0,9686	0,3390	0,7309	0,085*

The atomic arrangement of the complex is depicted in Figure 2. An examination shows a layer arrangement paralleled to the b direction: octahedral of $[\text{BiCl}_6]^{3-}$ alternate with planes of 3-3'-diamino-N-méthylidipropylammonium groups. The monomeric $[\text{BiCl}_6]^{3-}$ anions are located in the (b, c) plane at $z = 0$ and $z = 1$ and those for organic groups at $z = 1/2$.

Table 3. Anisotropic displacement parametrs(\AA^2) for $[\text{C}_7\text{H}_{22}\text{N}_3] \text{BiCl}_6$

Atomes	U11	U22	U33	U23	U13	U12
Bi	0,02398(14)	0,02008(15)	0,02926(16)	-0,00296(9)	-0,00009(10)	-0,00875(10)
Cl1	0,0389(15)	0,0403(17)	0,0446(17)	-0,0110(13)	0,0116(13)	-0,0188(13)
Cl2	0,061(3)	0,048(3)	0,053(2)	0,022(2)	-0,012(2)	-0,027(2)
Cl3	0,0345(14)	0,062(2)	0,0412(17)	0,0043(15)	0,0002(13)	-0,0196(16)
Cl4	0,0413(16)	0,0361(16)	0,0370(15)	-0,0036(12)	-0,0037(12)	-0,0210(14)
Cl5	0,055(2)	0,042(2)	0,063(3)	0,011(2)	-0,014(2)	-0,027(2)
Cl6	0,052(2)	0,056(3)	0,092(4)	-0,043(3)	-0,023(3)	-0,004(2)
N2	0,050(7)	0,025(5)	0,028(5)	-0,010(4)	0,003(5)	-0,009(5)
C3	0,036(6)	0,041(9)	0,035(7)	0,012(6)	-0,013(5)	-0,012(6)
C5	0,056(9)	0,040(8)	0,046(8)	0,016(7)	-0,028(7)	-0,032(8)
C4	0,056(9)	0,051(9)	0,045(7)	-0,013(6)	0,011(7)	-0,037(8)
C2	0,054(9)	0,032(8)	0,030(6)	0,000(5)	-0,008(6)	-0,016(7)
C6	0,045(8)	0,019(6)	0,056(10)	0,002(6)	0,000(7)	-0,009(6)
C1	0,049(7)	0,031(6)	0,040(6)	-0,004(5)	0,004(6)	-0,023(6)
C7	0,051(9)	0,041(10)	0,064(11)	-0,016(8)	-0,003(8)	-0,019(8)
N1	0,041(6)	0,032(6)	0,038(6)	-0,011(4)	0,000(5)	-0,012(5)
N3	0,043(7)	0,049(8)	0,060(9)	-0,025(7)	-0,004(6)	-0,002(6)

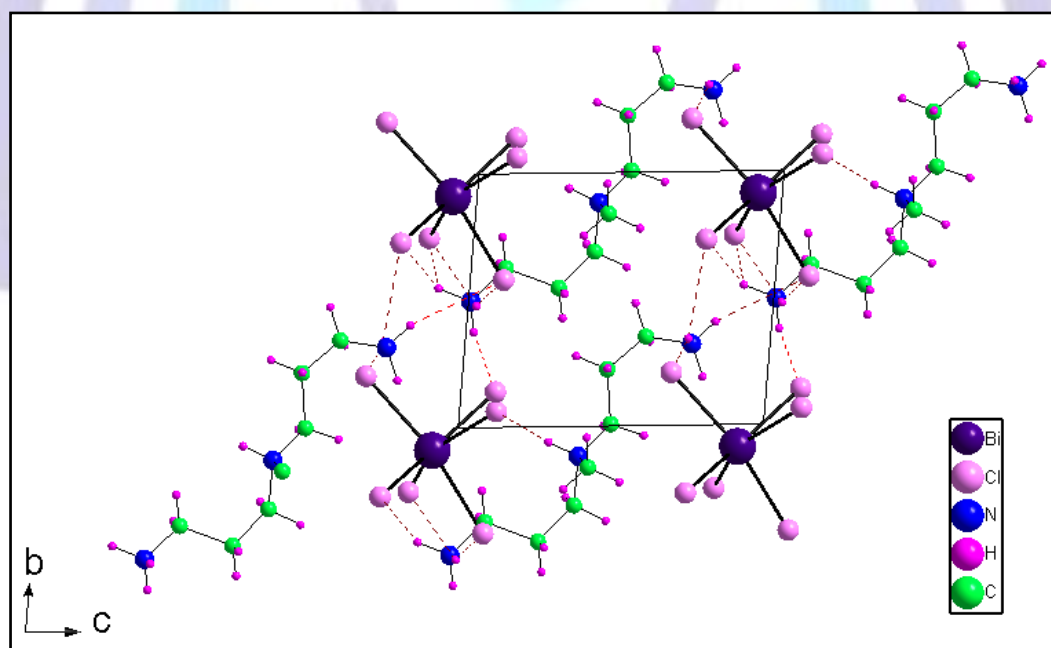


Fig 2: Projection in the plane (b,c) of the atomic arrangement of $[\text{C}_7\text{H}_{22}\text{N}_3]\text{BiCl}_6$

Each Bi atom is surrounded by six Cl atoms, forming a distorted octahedral configuration, with Bi–Cl bond lengths ranging from 2,668(4) to 2,734(3) \AA (Table 4) and a mean value of 2,727(2) \AA , and Cl–Bi–Cl bond angles ranging from 71.87(2) to 97.91(3) $^\circ$ for cis and from 100.21(2) to 166.56(2) $^\circ$ for trans arrangements. These values are comparable with those reported to date [20].



In addition to the bond length differences, the Cl–Bi–Cl bond angles (Table 2) deviate from 90°, with the biggest difference [97.91(3)°] occurring for the Cl(6)–Bi–Cl(5) angle and the lowest one [71.87(2)°] occurring for the Cl(3)–Bi–Cl(5) angle, which incorporates the two shortest Bi–Cl bonds. This distortion is correlated both to primary deformations resulting from the stereochemical activity of the Bi lone electron pair [20,22] and to secondary deformations resulting from hydrogen bond interactions [23].

The involvement of any particular chlorine atom in hydrogen bonding brings about the shift of the lone electron pair of the Bi atom in the direction of the H atom, which generally results in the shift of the respective Cl atom out of the Bi position. This leads to an increase in the Bi–Cl bond length (Bi–Cl1: 2.73(3), Bi–Cl5: 2.730(4) and Bi–Cl4: 2.734(3) Å) compared to the others.

Figure 2 shows that the 3-3'-diamino-N-methyldipropylammonium cations are interspersed between the anionic plans at $z = 1/2$. The C–N and C–C bond lengths vary respectively from 1.442(2) to 1.56(2) and 1.47(3) to 1.59(2) Å. These values are comparable with those reported by other researchers [24].

Table 4. Principal intramolecular distances (Å), bond angles (°) in [C₇H₂₂N₃] BiCl₆

Atoms	Distance	Atoms	Distance
Bi - Cl1	2,730(3)	C3- C2	1,49 (3)
Bi - Cl2	2,730(4)	C5- C6	1,59 (2)
Bi - Cl3	2,686(4)	C2- C1	1,550(2)
Bi - Cl4	2,734(3)	C6 - C7	1,47 (3)
Bi - Cl5	2,692(5)	C1- N1	1,440(2)
Bi - Cl6	2,668(4)	C7 - N3	1,44 (3)
		N2 - C5	1,42(2)
		N2 - C4	1,48(2)
		N2 - C3	1,56(2)
		N2 - C3	1,56(2)
		N2 - C5	1,42(2)
C11 -Bi - Cl4	92,70 (2)	C5 - N2 -C4	118,3(2)
Cl2 - Bi - Cl1	100,21 (2)	C5 - N2 -C3	110,3(3)
Cl2 - Bi - Cl4	92,46 (2)	C4 - N2 -C3	109,5(3)
Cl3 - Bi - Cl2	95,91 (4)	C2 - C3 - N2	117,3(2)
Cl3 - Bi - Cl1	153,90 (3)	N2 - C5 - C6	114,4(2)
Cl5 - Bi - Cl2	166,56 (2)	C3 - C2 - C1	110,0(1)
Cl3 - Bi - Cl5	71,87 (2)	C7 - C6 - C5	116,0(2)
Cl3 - Bi - Cl4	107,04 (3)	N1 - C1 -C2	110,9(2)
Cl5 - Bi - Cl1	93,20 (2)	N3- C7 -C6	112,5(1)
Cl5 - Bi - Cl4	86,04 (3)		
Cl6 - Bi - Cl1	69,95 (4)		
Cl6 - Bi - Cl2	87,6 (2)		
Cl6 - Bi - Cl3	90,52 (2)		
Cl6 - Bi - Cl4	162,33 (2)		
Cl6 - Bi - Cl5	97,91 (3)		

In [C₇H₂₂N₃]BiCl₆, the organic species interact with the inorganic chains via N-H...Cl hydrogen bonds, forming a three dimensional network (Table 4) such that all the hydrogen atoms bonded to nitrogen atoms participate in the



formation of these hydrogen bonds, with distances between 2.310 and 3.76 Å. Two of these bonds are considered as strong, whilst the others are weak [25]. Details of the hydrogen bonding scheme are reported in Table 5.

Table 5: Main inter-atomic distances (Å) and bond angles (°) involved in the hydrogen Bonds of [C₇H₂₂N₃] BiCl₆ compounds.

D-H...A	d(D-H)	d(H...A)	d(D...A)	d(DHA)
N ₂ -H ₂ ... Cl ₁	0,910	2,860	127,85	3,493
N ₂ -H ₂ ... Cl ₆ ^a	0,910	2,964	127,63	3,593
N ₁ -H _{1a} ... Cl ₃ ^a	0,890	1,838	110,91	3,310
N ₁ -H _{1a} ... Cl ₄	0,890	2,722	130,64	3,370
N ₁ -H _{1b} ... Cl ₅ ^a	0,890	2,484	153,88	3,306
N ₁ -H _{1c} ... Cl ₆ ^b	0,890	2,296	164,60	3,163
N ₁ -H _{1c} ... Cl ₁ ^b	0,890	2,837	115,88	3,323
N ₃ -H _{3a} ... Cl ₅ ^c	0,890	2,928	156,29	3,760
N ₃ -H _{3c} ... Cl ₂ ^d	0,890	2,473	148,90	3,268
N ₃ -H _{3c} ... Cl ₄ ^c	0,890	2,889	112,63	3,334

Symmetry codes:

a : [x-1, y, z], b : [x, y-1, z], c : [x-1, y+1, z+1], d : [x-1, y, z+1]

Conclusion

The 3-3'-diamino-N-methyldipropylammonium hexachlorobismuthate (III) belongs to the triclinic system with P1 space group. The crystal structure consists of the monomeric [BiCl₆]³⁻ and one crystallographically independent triprotonated 3-3'-diamino-N-methyldipropylammonium cation. The structure of this compound consists of alternation organic and inorganic layers. These layers are themselves interconnected by means of the ionic N-H...Cl hydrogen bonds.

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