Synthesis and Crystal Structure of Tris(2-amino-indolinium)-hexachlorobismuthate(III) monohydrate

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The salt tris(2-amino-indolinium)hexachlorobismuthate(III) monohydrate $[\text{C}_8\text{H}_9\text{N}_2]_3\text{BiCl}_6 \cdot \text{H}_2\text{O}$ crystallizes at room temperature in the monoclinic system with space group $P2_1/n$. The unit-cell dimensions are: $a = 15.1853(14)$, $b = 11.7761(9)$, $c = 17.3168(13)\text{\AA}$, $\beta = 103.937(8)^\circ$ with $Z = 4$. The crystal structure of this salt was solved by Patterson methods and refined by full-matrix least squares on F^2 to final values of $R = 0.0293$ and $wR = 0.0786$. The structure consists of monomeric BiCl_6^{3-} anions, monoprotonated 2-amino-indolinium cations and water molecules. These entities are interconnected by means of hydrogen bonding contacts $[\text{N}-\text{H}\cdots\text{O}(\text{Cl})]$ and $[\text{O}(\text{W})-\text{H}\cdots\text{Cl}]$, forming a three-dimensional network.

(Received May 25, 2009; Accepted November 26, 2009; Published on web March 10, 2010)

Several studies have been made in the solid state on complexes between bismuth(III) and bromide or iodide; however, only few complexes of bismuth(III) chlorides with organic cations have been investigated. The alkylammonium halogenobismuthates(III) can form a variety of polychlorinated anions, including (BiCl_4^-) ,¹ (BiCl_5^{2-}) ,² (BiCl_6^{3-}) ,³ $(\text{Bi}_2\text{Cl}_{10}^{4-})$,⁴ $(\text{Bi}_2\text{Cl}_{11}^{5-})$ and $(\text{Bi}_4\text{Cl}_{18}^{6-})$.⁵ These compounds are interesting because they exhibit ferro-paraelectric phase transitions related to the motions of the ammonium cations. Taking these considerations into account, we report on the synthesis and crystal structure of tris(2-amino-indolinium)hexachlorobismuthate(III) monohydrate $[\text{C}_8\text{H}_9\text{N}_2]_3\text{BiCl}_6 \cdot \text{H}_2\text{O}$.

The crystals of the title compound were obtained by dissolving in a concentrated HCl (36%) solution a stoichiometric mixture of 2-amino-indolinium $\text{C}_8\text{H}_8\text{N}_2$ and BiCl_3 (molar ratio 3/1). The resulting aqueous solution was then kept at room temperature. After several weeks of evaporation, parallelepiped-shaped monocrystals appeared in the solution.

A single-crystal study was performed by using an Enraf-Nonius Kappa CCD diffractometer. The main crystal data and a summary of the parameters related to intensity data collection and structure refinement are reported in Table 1. The positional parameters for the bismuthate atoms were obtained from a three-dimensional Patterson map, while the remaining atoms were found from successive difference Fourier maps. After introducing thermal displacement parameters for the non-

hydrogen atoms, the hydrogen atoms were localized and optimized to restraint positions. Their thermal displacement contributions were isotropically introduced into the calculation and fixed. Corrections were applied for Lorentz and polarization effects and for absorptions. The final anisotropic full-matrix least squares resulted in a convergence of the R factor at 0.0293, $Rw = 0.0786$ incorporating the weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0044 P)^2 + 17.5587 P]$, where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$.

The asymmetric unit of the title compound is depicted in Fig.

Table 1 Crystal and experimental data

Chemical formula: $[\text{C}_8\text{H}_9\text{N}_2]_3\text{BiCl}_6 \cdot \text{H}_2\text{O}$	
Formula weight = 839.21	
$T = 298\text{ K}$	
Crystal system: monoclinic	Space group: $P2_1/n$
$a = 15.1853(14)\text{\AA}$	
$b = 11.7761(9)\text{\AA}$	$\beta = 103.937(8)^\circ$
$c = 17.3168(13)\text{\AA}$	
$V = 3005.5(4)\text{\AA}^3$	$Z = 4$
$D_x = 1.855\text{ g/cm}^3$	
Radiation: ($\lambda = 0.71073\text{ \AA}$)	
$\mu(\text{Mo K}\alpha) = 6.430\text{ mm}^{-1}$	$F(0\ 0\ 0) = 1632$
crystal size = $0.04 \times 0.06 \times 0.08\text{ mm}^3$	
No. of reflections collected = 40776	
No. of independent reflections = 6814	
θ range for data collection: 3.96 to 27.54°	
Data/Restraints/Parameters = 6814/3/354	
Goodness-of-fit on $F^2 = 1.272$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0293$, $wR2 = 0.0565$	
R indices [all data]: $R1 = 0.0643$, $wR2 = 0.0786$	
$(\Delta/\sigma)_{\text{max}} = 0.002$	
$(\Delta\rho)_{\text{max}} = 1.704\text{ e/\AA}^{-3}$	$(\Delta\rho)_{\text{min}} = -1.319\text{ e/\AA}^{-3}$
Measurement: Enraf-Nonius Kappa CCD	
Program system: SHELXL-97	
Structure determination: SHELXS-97	
CCDC deposit number: 705448

Fig. 1 Chemical diagram of the title compound.

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Fig. 2 Asymmetric unit of $[\text{C}_8\text{H}_9\text{N}_2]_3\text{BiCl}_6 \cdot \text{H}_2\text{O}$. Displacement ellipsoids are at the 30% probability level.

Fig. 3 Projection along the b axis of the atomic arrangements of $[\text{C}_8\text{H}_9\text{N}_2]_3\text{BiCl}_6 \cdot \text{H}_2\text{O}$.

2. The structure consists of monoprotonated 2-amino-indolinium cations, monomeric BiCl_6^{3-} anions and water molecules. The BiCl_6^{3-} configuration is a distorted octahedral; the bismuth atom is surrounded by six chlorine atoms with Bi-Cl bonds lengths ranging from 2.6115(16) to 2.8220(16) Å. These values are comparable with those reported by other researchers.²⁻⁴ The angles involving atoms mutually *cis* range from 84.77(6) to 97.49(6)°, while the *trans* angles vary from 173.93(6) to 177.07(6)°. The deviations of these bond angles from the ideal values of 90 and 180° are consistent with the presence of long bonds. The largest deviations from 90° involve the more weakly bonded chlorine atoms: Cl3-Bi-Cl5 = 84.77(6)° and Cl3-Bi-Cl2 = 97.49(6)°. Distortion from octahedral geometry in the BiCl_6^{3-} anion may also be ascribed to the strong hydrogen bonding, which involves 5 of the 6 coordinated chlorine atoms.

The organic group A is located in the (b,c) plane, whereas the others (B and C) exist in the (a,c) plane (Fig. 3). Table 2 reports on the principal geometrical features of the $[\text{C}_8\text{H}_9\text{N}_2]^+$ cations. They are in agreement with those found in related compounds.¹⁻³

The C-C perpendicular interplanar distances range from 3.663 to 8.582 Å, indicating the existence of a strong interaction by

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

BiCl ₆ Octahedron						
Bi	Cl(1)	Cl(2)	Cl(3)	Cl(4)	Cl(5)	Cl(6)
Cl(1)	2.7020(15)	3.7601(2)	3.9852(1)	5.3710(3)	3.9361(2)	3.801(2)
Cl(2)	87.49(6)	2.7367(18)	4.1790(1)	3.7864(1)	5.4031(2)	3.6990(1)
Cl(3)	92.32(5)	97.49(6)	2.8220(16)	3.7521(1)	3.7021(1)	5.4261(2)
Cl(4)	175.75(7)	88.82(6)	86.07(5)	2.6733(15)	3.7601(3)	3.7561(6)
Cl(5)	94.30(7)	177.07(6)	84.77(6)	89.48(7)	2.6681(19)	3.7374(2)
Cl(6)	91.35(6)	87.49(6)	173.93(6)	90.60(6)	90.13(6)	2.6115(16)

Organic group			
N(1A)–C(1A)	: 1.315(8)	C(1A)–C(2A)–C(3A)	: 110.0(5)
C(1A)–C(2A)	: 1.312(7)	C(1A)–N(2A)–C(8A)	: 108.5(3)
C(2A)–C(3A)	: 1.383(9)	C(2A)–C(1A)–N(1A)	: 127.8(5)
C(3A)–C(8A)	: 1.377(9)	C(2A)–C(1A)–N(2A)	: 108.2(3)
N(2A)–C(1A)	: 1.366(8)	N(1A)–C(1A)–N(2A)	: 123.9(4)
N(2A)–C(8A)	: 1.384(9)	C(8A)–C(3A)–C(2A)	: 106.8(7)
N(1B)–C(1B)	: 1.316(9)	C(3A)–C(8A)–N(2A)	: 106.5(6)
C(1B)–C(2B)	: 1.332(8)	C(1B)–C(2B)–C(3B)	: 109.3(5)
C(3B)–C(8B)	: 1.383(9)	C(1B)–N(2B)–C(8B)	: 108.8(6)
N(2B)–C(8B)	: 1.399(8)	C(2B)–C(1B)–N(1B)	: 125.3(6)
N(2B)–C(1B)	: 1.339(9)	C(2B)–C(1B)–N(2B)	: 109.0(6)
N(1C)–C(1C)	: 1.334(9)	N(1B)–C(1B)–N(2B)	: 125.7(7)
C(1C)–C(2C)	: 1.318(10)	C(8B)–C(3B)–C(2B)	: 106.2(6)
C(2C)–C(3C)	: 1.380(9)	C(3B)–C(8B)–N(2B)	: 106.6(6)
C(3C)–C(8C)	: 1.384(10)	C(1C)–C(2C)–C(3C)	: 108.5(6)
N(2C)–C(8C)	: 1.382(10)	C(1C)–N(2C)–C(8C)	: 108.8(6)
N(2C)–C(1C)	: 1.342(10)	C(2C)–C(1C)–N(1C)	: 125.5(8)
		C(2C)–C(1C)–N(2C)	: 109.0(7)
		N(1C)–C(1C)–N(2C)	: 125.5(7)
		C(8C)–C(3C)–C(2C)	: 106.2(6)
		C(3C)–C(8C)–N(2C)	: 106.6(6)

van der Waals contacts between $[\text{C}_8\text{H}_9\text{N}_2]^+$ cations. The intermolecular hydrogen bonding contacts N–H...Cl and N–H...O(W) provide a linkage between the $[\text{C}_8\text{H}_9\text{N}_2]^+$ entities, the BiCl_6^{3-} anions and the water molecules. All of these hydrogen bonds [N–H...O(Cl)] and O(W)–H...Cl give rise to a three-dimensional network in the structure, and add stability of this compound.

Supporting Information

Table S1 shows the atomic coordinates and temperature factors for $[\text{C}_8\text{H}_9\text{N}_2]_3\text{BiCl}_6 \cdot \text{H}_2\text{O}$.

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