



# Crystal structure of the new hybrid material bis(1,4-diazoniabicyclo[2.2.2]octane) di- $\mu$ -chlorido-bis[tetrachloridobismuthate(III)] dihydrate

Marwen Chouri and Habib Boughzala\*

Received 14 October 2015

Accepted 21 October 2015

Laboratoire de Matériaux et Cristallographie, Faculté des Sciences de Tunis, Université de Tunis El Manar, 2092 Manar II Tunis, Tunisia. \*Correspondence e-mail: [habib.boughzala@ipein.rnu.tn](mailto:habib.boughzala@ipein.rnu.tn)

Edited by A. Van der Lee, Université de Montpellier II, France

**Keywords:** crystal structure; hybrid material; DABCO

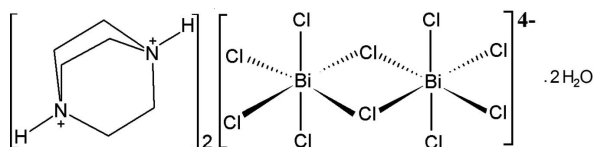
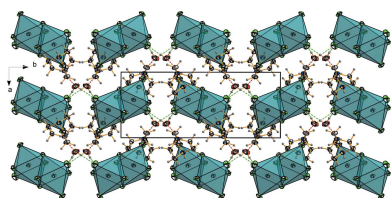
**CCDC reference:** 971956

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The title compound bis(1,4-diazoniabicyclo[2.2.2]octane) di- $\mu$ -chlorido-bis[tetrachloridobismuthate(III)] dihydrate,  $(C_6H_{14}N_2)_2[Bi_2Cl_{10}] \cdot 2H_2O$ , was obtained by slow evaporation at room temperature of a hydrochloric aqueous solution (pH = 1) containing bismuth(III) nitrate and 1,4-diazabicyclo[2.2.2]octane (DABCO) in a 1:2 molar ratio. The structure displays a two-dimensional arrangement parallel to (100) of isolated  $[Bi_2Cl_{10}]^{4-}$  bioctahedra (site symmetry  $\bar{1}$ ) separated by layers of organic 1,4-diazoniabicyclo[2.2.2]octane dication  $[(DABCOH_2)^{2+}]$  and water molecules.  $O-H \cdots Cl$ ,  $N-H \cdots O$  and  $N-H \cdots Cl$  hydrogen bonds lead to additional cohesion of the structure.

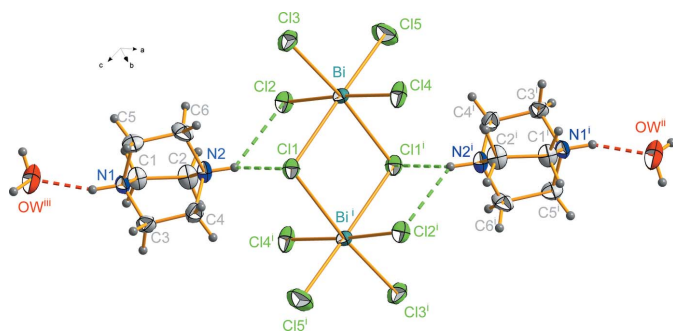
## 1. Chemical context

In recent years, many new organic–inorganic hybrid compounds have been synthesized because of their interesting physical behaviour and applications in optoelectronics (Jakubas & Sobczyk, 1990). The main interesting optical activity observed in this kind of compounds is generally the result of the presence of an active  $ns^2$  lone pair (Chaabouni *et al.*, 1998) in the inorganic parts. It can also be the result of an important structural distortion in the organic cations (Ishihara *et al.*, 1990; Lacroix *et al.*, 1994). The combination of the particular properties of the organic and inorganic moieties can induce interesting new properties. In particular for the halogenated bismuth or antimony anionic networks (Ahmed *et al.*, 2001; Jakubas *et al.*, 2005), the anionic arrangement leads to four kinds of dimensionalities: quantum dots (zero-dimensional, 0D) observed in hybrids such as  $(C_6H_{14}N_2)_2[Sb_2Cl_{10}] \cdot 2H_2O$  (Ben Rhaïem *et al.*, 2013), quantum wires (one-dimensional, 1D) as is the case in the structure of  $(C_2H_7N_4O)_2[BiCl_5]$  (Ferjani *et al.*, 2012), quantum wells (two-dimensional, 2D) and a bulk (three-dimensional, 3D) topology. The organic cations are usually filling the empty space left by the inorganic network. Here we report the structure of a new hybrid bismuthate compounds having a 0D dimensionality with respect to its inorganic part.

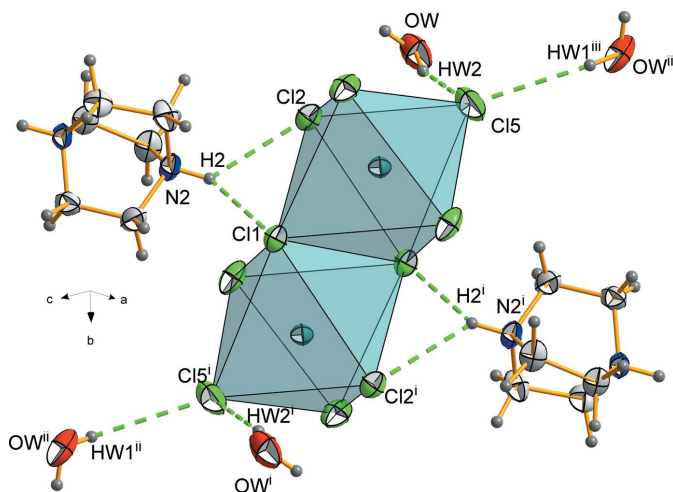


## 2. Structural commentary

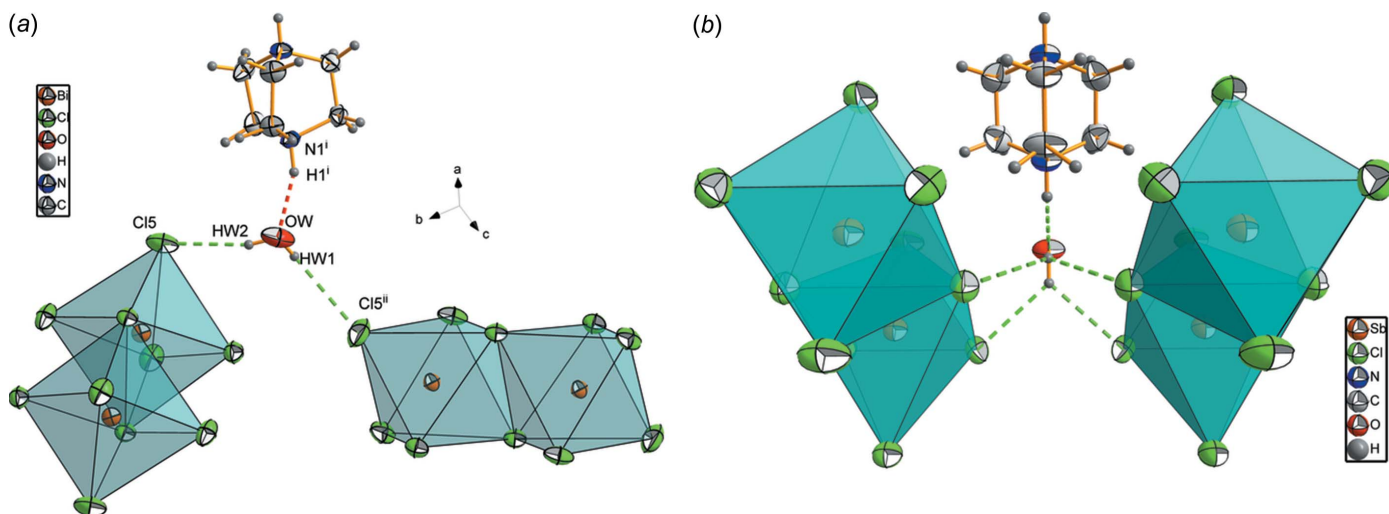
The structural unit (Fig. 1) of the compound is built up by an isolated dimeric decachloridobismuthate(III)  $[Bi_2Cl_{10}]^{4-}$


**Figure 1**

Plot of the molecular entities of  $(C_6H_{14}N_2)_2[Bi_2Cl_{10}] \cdot 2H_2O$ , showing the atom numbering scheme. Atomic displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. [Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + 2, y + 0.5, -z + 0.5$ ; (iii)  $x - 1, -y + 0.5, z + 0.5$ .]


**Figure 2**

Hydrogen-bonding environment of the anionic part of the structure. [Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 1.5$ ; (iii)  $x, -y + 0.5, z - 0.5$ .]


**Figure 3**

Water-molecule hydrogen-bonding interaction between organic and inorganic parts: (a) in the title compound [symmetry codes: (i)  $x + 1, -y + 0.5, z - 0.5$ ; (ii)  $x, -y + 0.5, z + 0.5$ ]; (b) in the structure of  $(C_6H_{14}N_2)_2[Sb_2Cl_{10}] \cdot 2H_2O$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ).

Bi—Cl5	2.588 (2)	N1—C5	1.504 (9)
Bi—Cl3	2.601 (2)	N2—C4	1.489 (10)
Bi—Cl2	2.6611 (19)	N2—C2	1.492 (9)
Bi—Cl4	2.704 (2)	N2—C6	1.494 (10)
Bi—Cl1	2.8610 (19)	C1—C2	1.517 (11)
Bi—Cl1 <sup>i</sup>	2.884 (2)	C6—C5	1.531 (11)
N1—Cl	1.485 (9)	C3—C4	1.493 (11)
N1—C3	1.503 (9)		

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

anion, two organic 1,4-diazoniabicyclo[2.2.2]octane dications  $[(DABCOH_2)^{2+}]$  and two water molecules. These components are linked by strong hydrogen bonds. The inorganic moiety is an edge-sharing dioctahedron located site with symmetry  $\bar{1}$ . The two  $(DABCOH_2)^{2+}$  dications (Fig. 4) in the structural unit are related to the dimeric  $[Bi_2Cl_{10}]^{4-}$  units by means of  $N2-H2 \cdots Cl2$  and  $N2-H2 \cdots Cl1$  interactions.

The bond lengths and angles of the dication are within normal ranges and are comparable to those observed in similar structures. Table 1 summarizes the most important distances in these molecules. The C—N bond lengths vary from 1.479 (11) to 1.508 (12)  $\text{\AA}$ . The C—C bond lengths vary from 1.500 (13) to 1.535 (13)  $\text{\AA}$ . The angles in this molecule are between 109.8 (7) and 110.7 (8) $^\circ$  for C—N—C and between 108.1 (8) and 109.2 (8) $^\circ$  for N—C—C.

As listed in Table 1, the bond lengths of bismuth to terminal chlorides [2.587 (5)–2.704 (5)  $\text{\AA}$ ] are shorter than the bridging ones [2.863 (4) and 2.884 (4)  $\text{\AA}$ ]. The Cl—Bi—Cl angles vary from 84.46 (12) to 95.4 (2) $^\circ$  for the *cis* and 173.25 (15) to 176.64 (15) $^\circ$  for the *trans* arrangement. Using Shannon's method (Shannon, 1976), the distortion index of  $1.87 (9) \times 10^{-3}$  reveals only a small distortion in the  $BiCl_6$  octahedron. The bismuth  $6s^2$  electron pair has stereochemical activity and the hydrogen-bond orientation can be related to the bismuth

Table 2

Comparison of the cell parameters of the structures of  $[\text{Bi}_2\text{Cl}_{10}](\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$  and  $[\text{Sb}_2\text{Cl}_{10}](\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$ .

	$[\text{Bi}_2\text{Cl}_{10}](\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$	$[\text{Sb}_2\text{Cl}_{10}](\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$	Parameter variation (%) $[(X_{\text{Bi}} - X_{\text{Sb}})/(X_{\text{Sb}})] \cdot 100$
Crystal system	monoclinic	orthorhombic	-
Space group	$P2_1/c$	$Pnmm \rightarrow Pnmm$ (cba)	-
$a$ (Å)	7.875 (3)	9.162 (1) => 7.566 (2)	4.08 (2)
$b$ (Å)	18.379 (5)	20.689 (7) => 20.689 (7)	-11.16 (3)
$c$ (Å)	10.444 (4)	7.566 (2) => 9.162 (1)	13.99 (2)
$\beta$ (Å)	105.95 (3)	90.00	-
$V$ (Å <sup>3</sup> )	1453.4 (9)	1446.8 (7)	0.45 (7)

Table 3

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{Ow}-\text{Hw}2 \cdots \text{Cl}5$	0.91	2.63	3.458 (8)	163
$\text{N}1-\text{H}1 \cdots \text{Ow}^{\text{ii}}$	0.91	1.87	2.739 (10)	159
$\text{Ow}-\text{Hw}1 \cdots \text{Cl}5^{\text{iii}}$	0.91	2.80	3.475 (9)	138
$\text{N}2-\text{H}2 \cdots \text{Cl}1$	0.91	2.73	3.352 (6)	127
$\text{N}2-\text{H}2 \cdots \text{Cl}2$	0.91	2.65	3.325 (7)	132

Symmetry codes: (ii)  $x - 1, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .

polyhedra distortion. The final Fourier difference map reveals four large peaks at approximately 1 Å from the bismuth atom that can be attributed to the delocalization of the  $6s^2$  electron pair as is the case in most other bismuth-based structures.

The  $(\text{C}_6\text{H}_{14}\text{N}_2)_2[\text{Bi}_2\text{Cl}_{10}] \cdot 2\text{H}_2\text{O}$  structure is very close to that of  $(\text{C}_6\text{H}_{14}\text{N}_2)_2[\text{Sb}_2\text{Cl}_{10}] \cdot 2\text{H}_2\text{O}$  (Ben Rhaïem *et al.*, 2013). The cell parameters of both structures can be compared after making a necessary transformation (cba) in the  $Pnmm$  antimony unit cell to be comparable to the bismuth one (Table 2). Apart from the higher symmetry of the antimony structure, an important distortion is noted in the  $\text{SbCl}_6$  octahedra confirmed by the Shannon's distortion index (Shannon, 1976)  $[6.20 (9) \times 10^{-3}]$ , more than three times larger than the one for the title bismuth compound  $[1.87 (9) \times 10^{-3}]$ . It is worth noting that the water molecule plays a more efficient role in the bismuth

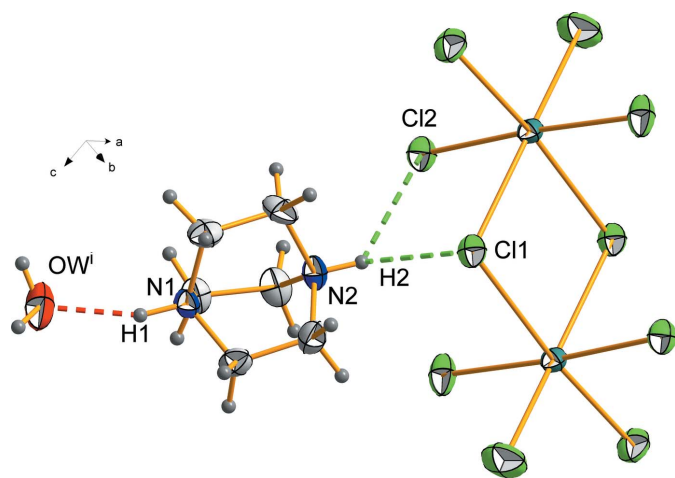


Figure 4

Hydrogen-bonding environment of the cationic organic part of the title compound.

based compound. In  $(\text{C}_6\text{H}_{14}\text{N}_2)_2[\text{Sb}_2\text{Cl}_{10}] \cdot 2\text{H}_2\text{O}$ , the  $\text{H}_2\text{O}$  molecules are only linked to  $(\text{DABCOH}_2)^{2+}$  and in the  $(\text{C}_6\text{H}_{14}\text{N}_2)_2[\text{Bi}_2\text{Cl}_{10}] \cdot 2\text{H}_2\text{O}$  structure they are directly hydrogen bonded to both the organic and inorganic parts (Fig. 3). The atomic radius of bismuth is larger than that for antimony, and thus an increase of the cell volume is expected. In fact, the main increase is observed for the  $c$  axis [13.99 (2) Å] because the metallic coordination polyhedra are aligned along this axis. On the other hand, a roughly equivalent decrease of the  $b$  parameter is observed causing the unit-cell volume of the two compounds approximately to be the same. A general comparison of the two structures reveals that they have a similar 3D pattern, built up by isolated bioctahedra,  $(\text{DABCOH}_2)^{2+}$  cations and water molecules leaving empty the same voids. On the other hand, the water molecule immediate environment is more regular in the Sb structure (Fig. 3b) and the  $(\text{DABCOH}_2)^{2+}$  cation is more distorted in the Bi structure (Fig. 3a) explaining the lowering of the symmetry in the title compound.

### 3. Supramolecular features

As shown in Fig. 2, every anionic unit is linked to four water molecules and two organic cations. The water molecules (Fig. 3) are strongly hydrogen bonded to the inorganic part by means of  $\text{O}-\text{Hw}1 \cdots \text{Cl}5^{\text{ii}}$  [symmetry code: (ii)  $x, -y + 0.5, z + 0.5$ ] and  $\text{O}-\text{Hw}2 \cdots \text{Cl}5$  interactions. The DABCO cations are hydrogen bonded to water molecules, leading to chains composed of organic moieties, inorganic clusters and  $\text{H}_2\text{O}$  molecules running along the  $b$  direction (Fig. 1). The water

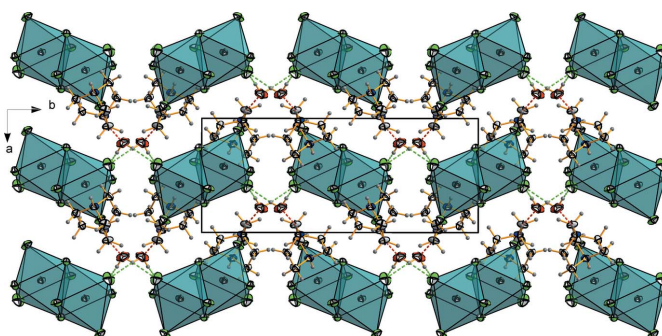


Figure 5

Projection of the crystal structure of the bismuthate hybrid compound along the  $c$  axis, showing the alternation of organic and inorganic layers.

molecules stabilize the structure by playing a bridge role between organic and inorganic parts. Furthermore, they ensure the link in the other directions leading to a hydrogen-bond-based three-dimensional network. The structure can be seen (Fig. 5) as an alternation of organic and inorganic layers parallel to (100) which are linked by a strong hydrogen-bond pattern (Table 3).

#### 4. Synthesis and crystallization

(C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>)<sub>2</sub>[Bi<sub>2</sub>Cl<sub>10</sub>]·2H<sub>2</sub>O crystals were obtained at ambient conditions by dissolving Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and DABCO (C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>) in water in a 1:2 molar ratio. The pH of the solution was adjusted to 1 with HCl. The mixture was stirred and kept for several days. Colourless crystals were obtained after a few weeks.

#### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The isotropic displacement parameter of the hydrogen atoms for the water molecule were fixed to be restrained to be approximately 1.5 times those of the parent atom and the water molecule geometries were regularised using distance restraints

**Table 4**  
Experimental details.

Crystal data	
Chemical formula	(C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> ) <sub>2</sub> [Bi <sub>2</sub> Cl <sub>10</sub> ]·2H <sub>2</sub> O
<i>M</i> <sub>r</sub>	1036.88
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> /c
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.875 (3), 18.379 (5), 10.444 (4)
β (°)	105.95 (3)
<i>V</i> (Å <sup>3</sup> )	1453.4 (9)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	13.03
Crystal size (mm)	0.5 × 0.3 × 0.2
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Absorption correction	ψ scan (North <i>et al.</i> , 1968)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.013, 0.074
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	3159, 3159, 2681
<i>R</i> <sub>int</sub>	0.035
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.638
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.036, 0.102, 1.06
No. of reflections	3159
No. of parameters	142
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	3.48, -2.57

Computer programs: *CAD-4 EXPRESS* (Enraf–Nonius, 1994), *XCAD4* (Harms & Wocadlo, 1995), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2006) and *pubCIF* (Westrip, 2010).

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## supporting information

*Acta Cryst.* (2015). E71, 1384-1387 [https://doi.org/10.1107/S2056989015019933]

## Crystal structure of the new hybrid material bis(1,4-diazoniabicyclo[2.2.2]octane) di- $\mu$ -chlorido-bis[tetrachloridobismuthate(III)] dihydrate

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### Computing details

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

### Bis(1,4-diazoniabicyclo[2.2.2]octane) di- $\mu$ -chlorido-bis[tetrachloridobismuthate(III)] dihydrate

#### Crystal data

(C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>)<sub>2</sub>[Bi<sub>2</sub>Cl<sub>10</sub>]·2H<sub>2</sub>O

$M_r = 1036.88$

Monoclinic,  $P2_1/c$

$a = 7.875$  (3) Å

$b = 18.379$  (5) Å

$c = 10.444$  (4) Å

$\beta = 105.95$  (3)°

$V = 1453.4$  (9) Å<sup>3</sup>

$Z = 2$

$F(000) = 968$

$D_x = 2.369$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3158 reflections

$\theta = 2.2$ – $2.7$ °

$\mu = 13.03$  mm<sup>-1</sup>

$T = 293$  K

Prism, colourless

$0.5 \times 0.3 \times 0.2$  mm

#### Data collection

Enraf–Nonius CAD-4  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega/2\theta$  scans

Absorption correction:  $\psi$  scan

North *et al.* (1968). Number of  $\psi$  scan sets used was 5. Theta correction was applied. Averaged transmission function was used. No Fourier smoothing was applied.

$T_{\min} = 0.013$ ,  $T_{\max} = 0.074$

3159 measured reflections

3159 independent reflections

2681 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 27.0$ °,  $\theta_{\min} = 2.2$ °

$h = -10 \rightarrow 1$

$k = -1 \rightarrow 23$

$l = -12 \rightarrow 13$

2 standard reflections every 120 min

intensity decay: 10%

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.102$

$S = 1.06$

3159 reflections

142 parameters

2 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 4.4831P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 3.48 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -2.57 \text{ e } \text{\AA}^{-3}$$

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi	0.42097 (3)	0.42073 (2)	0.34670 (2)	0.02518 (11)
Cl1	0.2576 (2)	0.50934 (10)	0.50438 (18)	0.0329 (4)
Cl2	0.4635 (3)	0.32483 (10)	0.54389 (18)	0.0361 (4)
Cl3	0.1117 (3)	0.36755 (11)	0.2279 (2)	0.0441 (5)
Cl4	0.3821 (3)	0.52442 (12)	0.1571 (2)	0.0438 (5)
Cl5	0.5941 (4)	0.33648 (14)	0.2288 (3)	0.0635 (7)
OW	0.7852 (9)	0.2151 (4)	0.4798 (8)	0.0609 (18)
HW1	0.701 (11)	0.194 (6)	0.501 (12)	0.070*
HW2	0.732 (14)	0.251 (4)	0.434 (10)	0.070*
N1	0.0157 (8)	0.3538 (3)	0.8660 (6)	0.0291 (12)
H1	-0.0668	0.3405	0.9173	0.035*
N2	0.2250 (8)	0.3886 (3)	0.7369 (6)	0.0319 (13)
H2	0.3082	0.4026	0.6866	0.038*
C1	0.1780 (10)	0.3089 (4)	0.9111 (8)	0.0340 (16)
H1A	0.1513	0.2584	0.8867	0.041*
H1B	0.2238	0.3117	1.0072	0.041*
C6	0.0703 (11)	0.3511 (5)	0.6456 (7)	0.0403 (19)
H6A	0.1062	0.3045	0.6179	0.048*
H6B	0.0224	0.3805	0.5668	0.048*
C3	0.0613 (10)	0.4331 (4)	0.8868 (8)	0.0344 (16)
H3A	-0.0457	0.4618	0.8708	0.041*
H3B	0.1310	0.4413	0.9778	0.041*
C4	0.1641 (11)	0.4551 (4)	0.7924 (8)	0.0385 (17)
H4A	0.0904	0.4841	0.7209	0.046*
H4B	0.2650	0.4843	0.8386	0.046*
C5	-0.0695 (11)	0.3398 (5)	0.7206 (7)	0.0386 (17)
H5A	-0.1673	0.3731	0.6874	0.046*
H5B	-0.1147	0.2905	0.7078	0.046*
C2	0.3144 (11)	0.3374 (4)	0.8454 (8)	0.0385 (17)
H2A	0.4078	0.3625	0.9105	0.046*
H2B	0.3663	0.2973	0.8090	0.046*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Bi	0.02361 (17)	0.02675 (16)	0.02414 (16)	-0.00230 (9)	0.00482 (11)	-0.00228 (8)

Cl1	0.0253 (8)	0.0374 (9)	0.0354 (9)	0.0006 (7)	0.0073 (7)	0.0026 (7)
Cl2	0.0343 (9)	0.0360 (9)	0.0374 (9)	0.0016 (7)	0.0087 (7)	0.0066 (7)
Cl3	0.0352 (10)	0.0522 (11)	0.0396 (10)	-0.0140 (9)	0.0011 (8)	0.0003 (8)
Cl4	0.0282 (9)	0.0570 (12)	0.0434 (10)	-0.0072 (8)	0.0052 (8)	0.0165 (9)
Cl5	0.0703 (16)	0.0640 (15)	0.0643 (15)	0.0110 (12)	0.0319 (13)	-0.0197 (12)
OW	0.045 (4)	0.073 (5)	0.067 (5)	0.017 (3)	0.019 (3)	-0.016 (4)
N1	0.024 (3)	0.037 (3)	0.030 (3)	-0.001 (2)	0.013 (2)	-0.002 (2)
N2	0.027 (3)	0.035 (3)	0.037 (3)	0.003 (2)	0.016 (3)	0.005 (3)
C1	0.032 (4)	0.034 (4)	0.036 (4)	0.010 (3)	0.009 (3)	0.011 (3)
C6	0.044 (5)	0.054 (5)	0.021 (3)	0.002 (4)	0.005 (3)	-0.003 (3)
C3	0.032 (4)	0.030 (3)	0.043 (4)	0.002 (3)	0.012 (3)	-0.007 (3)
C4	0.038 (4)	0.030 (4)	0.050 (5)	-0.003 (3)	0.017 (4)	0.001 (3)
C5	0.033 (4)	0.050 (4)	0.028 (4)	-0.005 (3)	-0.001 (3)	-0.005 (3)
C2	0.034 (4)	0.041 (4)	0.040 (4)	0.012 (3)	0.010 (3)	0.014 (3)

*Geometric parameters (Å, °)*

Bi—Cl5	2.588 (2)	N2—H2	0.9800
Bi—Cl3	2.601 (2)	C1—C2	1.517 (11)
Bi—Cl2	2.6611 (19)	C1—H1A	0.9700
Bi—Cl4	2.704 (2)	C1—H1B	0.9700
Bi—Cl1	2.8610 (19)	C6—C5	1.531 (11)
Bi—Cl1 <sup>i</sup>	2.884 (2)	C6—H6A	0.9700
Cl1—Bi <sup>i</sup>	2.884 (2)	C6—H6B	0.9700
OW—HW1	0.850 (10)	C3—C4	1.493 (11)
OW—HW2	0.850 (10)	C3—H3A	0.9700
N1—C1	1.485 (9)	C3—H3B	0.9700
N1—C3	1.503 (9)	C4—H4A	0.9700
N1—C5	1.504 (9)	C4—H4B	0.9700
N1—H1	0.9800	C5—H5A	0.9700
N2—C4	1.489 (10)	C5—H5B	0.9700
N2—C2	1.492 (9)	C2—H2A	0.9700
N2—C6	1.494 (10)	C2—H2B	0.9700
Cl5—Bi—Cl3	95.45 (9)	C2—C1—H1B	110.0
Cl5—Bi—Cl2	90.07 (8)	H1A—C1—H1B	108.4
Cl3—Bi—Cl2	91.28 (7)	N2—C6—C5	108.1 (6)
Cl5—Bi—Cl4	92.39 (9)	N2—C6—H6A	110.1
Cl3—Bi—Cl4	90.73 (7)	C5—C6—H6A	110.1
Cl2—Bi—Cl4	176.66 (6)	N2—C6—H6B	110.1
Cl5—Bi—Cl1	173.58 (7)	C5—C6—H6B	110.1
Cl3—Bi—Cl1	88.74 (7)	H6A—C6—H6B	108.4
Cl2—Bi—Cl1	84.97 (6)	C4—C3—N1	108.6 (6)
Cl4—Bi—Cl1	92.41 (7)	C4—C3—H3A	110.0
Cl5—Bi—Cl1 <sup>i</sup>	91.38 (8)	N1—C3—H3A	110.0
Cl3—Bi—Cl1 <sup>i</sup>	173.16 (6)	C4—C3—H3B	110.0
Cl2—Bi—Cl1 <sup>i</sup>	88.44 (6)	N1—C3—H3B	110.0
Cl4—Bi—Cl1 <sup>i</sup>	89.25 (6)	H3A—C3—H3B	108.4

Cl1—Bi—Cl1 <sup>i</sup>	84.43 (6)	N2—C4—C3	109.0 (6)
Bi—Cl1—Bi <sup>i</sup>	95.57 (6)	N2—C4—H4A	109.9
HW1—OW—HW2	102 (10)	C3—C4—H4A	109.9
C1—N1—C3	110.0 (6)	N2—C4—H4B	109.9
C1—N1—C5	109.4 (6)	C3—C4—H4B	109.9
C3—N1—C5	109.5 (6)	H4A—C4—H4B	108.3
C1—N1—H1	109.3	N1—C5—C6	108.0 (6)
C3—N1—H1	109.3	N1—C5—H5A	110.1
C5—N1—H1	109.3	C6—C5—H5A	110.1
C4—N2—C2	110.9 (6)	N1—C5—H5B	110.1
C4—N2—C6	109.5 (6)	C6—C5—H5B	110.1
C2—N2—C6	109.1 (6)	H5A—C5—H5B	108.4
C4—N2—H2	109.1	N2—C2—C1	108.5 (6)
C2—N2—H2	109.1	N2—C2—H2A	110.0
C6—N2—H2	109.1	C1—C2—H2A	110.0
N1—C1—C2	108.6 (5)	N2—C2—H2B	110.0
N1—C1—H1A	110.0	C1—C2—H2B	110.0
C2—C1—H1A	110.0	H2A—C2—H2B	108.4
N1—C1—H1B	110.0		

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
Ow—Hw2...C15	0.91	2.63	3.458 (8)	163
N1—H1...Ow <sup>ii</sup>	0.91	1.87	2.739 (10)	159
Ow—Hw1...C15 <sup>iii</sup>	0.91	2.80	3.475 (9)	138
N2—H2...Cl1	0.91	2.73	3.352 (6)	127
N2—H2...Cl2	0.91	2.65	3.325 (7)	132

Symmetry codes: (ii)  $x-1, -y+1/2, z+1/2$ ; (iii)  $x, -y+1/2, z+1/2$ .