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

Tarek Ben Rhaiem, Habib Boughzala\* and Ahmed Driss

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

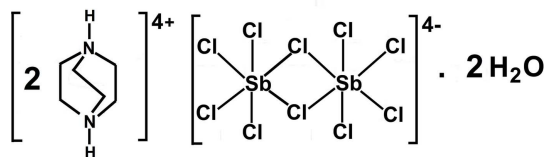
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å; H-atom completeness 88%;  $R$  factor = 0.023;  $wR$  factor = 0.061; data-to-parameter ratio = 20.7.

The title salt,  $(\text{C}_6\text{H}_{14}\text{N}_2)_2[\text{Sb}_2\text{Cl}_{10}]\cdot 2\text{H}_2\text{O}$ , was obtained by slow evaporation of an acidic solution of 1,4-diazabicyclo[2.2.2]octane and  $\text{SbCl}_3$ . The crystal structure consists of  $(\text{C}_6\text{H}_{14}\text{N}_2)^{2+}$  cations,  $[\text{Sb}_2\text{Cl}_{10}]^{4-}$  double octahedra and lattice water molecules. All molecular components are situated on special positions. The cation and the lattice water molecule exhibit mirror symmetry, whereas the anion has site symmetry  $2/m$ . The cations, anions and water molecules are alternately arranged into columns along [010]. Individual columns are joined into layers extending along (001). Intralayer  $\text{N}-\text{H}\cdots\text{O}$  and interlayer  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen-bonding interactions lead to the formation of a three-dimensional network.

## Related literature

For background to this class of compounds, see: Pietraszko *et al.* (2001); Feng *et al.* (2007); Bujak & Zaleski (1999); Knodler *et al.* (1988); Baker & Williams (1978). For a related structure, see: Qu & Sun (2005).



## Experimental

### Crystal data

$(\text{C}_6\text{H}_{14}\text{N}_2)_2[\text{Sb}_2\text{Cl}_{10}]\cdot 2\text{H}_2\text{O}$

$M_r = 862.46$

Orthorhombic,  $Pnmm$

$a = 9.162$  (1) Å

$b = 20.869$  (7) Å

$c = 7.566$  (2) Å

$V = 1446.8$  (7) Å<sup>3</sup>

$Z = 2$

Mo  $K\alpha$  radiation

$\mu = 2.81$  mm<sup>-1</sup>

$T = 298$  K

$0.50 \times 0.43 \times 0.36$  mm

### Data collection

Enraf-Nonius CAD-4 diffractometer

Absorption correction:  $\psi$  scan (North *et al.*, 1968)

$T_{\text{min}} = 0.334$ ,  $T_{\text{max}} = 0.431$

2797 measured reflections

1700 independent reflections

1488 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

2 standard reflections every 120 min

intensity decay: 1%

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.061$

$S = 1.08$

1700 reflections

82 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.59$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.37$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{Cl2}$	0.91	2.59	3.340 (4)	140
$\text{N1}-\text{H1}\cdots\text{Cl3}$	0.91	2.77	3.390 (3)	126
$\text{N1}-\text{H1}\cdots\text{Cl3}^i$	0.91	2.77	3.390 (3)	126
$\text{N2}-\text{H2}\cdots\text{O}$	0.91	2.00	2.780 (4)	143

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

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2740).

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## supporting information

*Acta Cryst.* (2013). E69, m330 [doi:10.1107/S160053681301307X]

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

Tarek Ben Rhaïem, Habib Boughzala and Ahmed Driss

### S1. Comment

Halogenidoantimonates(III) and halogenidobismuthates(III) with organic cations defined by the general formula  $R_aM_bX_{3b+ta}$  (where  $R$  is an organic cation;  $M$  is  $Sb^{III}$  or/and  $Bi^{III}$  and  $X$  is Cl, Br or/and I) are an interesting group of compounds due to their ferroelectric properties (Pietraszko *et al.*, 2001). Halogenidoantimonates(III) constitute a group of salts in which a number of compounds have a similar structural arrangement (Feng *et al.*, 2007; Bujak & Zaleski, 1999; Knodler *et al.*, 1988; Baker & Williams, 1978). Recently, the new chloridoantimonate(III),  $(C_6H_{14}N_2)_2[Sb_2Cl_{10}]2H_2O$ , has been synthesized in our laboratory. The synthesis and the structure determination are presented here.

The crystal structure of the title compound is formed by an alternating packing of layers along [001] (Fig. 1). Each layer spreads parallel to (001) and is located at  $x = 0$  and  $x = 0.5$  and consists of columns extending along [010] of alternating cations, anions and water molecules (Fig. 2).

The  $[Sb_2Cl_{10}]^{4-}$  anion has site symmetry  $2/m$  and is composed of two distorted, edge-sharing  $SbCl_6$  octahedra. The *cis* Sb–Cl–Sb angles vary from 81.11 (2) to 104.42 (1)°, whereas the *trans* angles are between 164.64 (4) and 173.84 (1)°. The longest Sb1–Cl14 bond length (2.9107 (8) Å) corresponds to the bridging chlorine atom while the shortest one, Sb1–Cl3 (2.4904 (7) Å) is terminal and located in opposite direction to the bridging one (Fig. 2). The anionic charge is balanced by organic  $(C_6H_{14}N_2)^{2+}$  (DABCO) cations that exhibit mirror symmetry. Bond lengths and angles in the  $(C_6H_{14}N_2)^{2+}$  cation are within normal ranges and are comparable with those observed in a related structure (Qu & Sun, 2005).

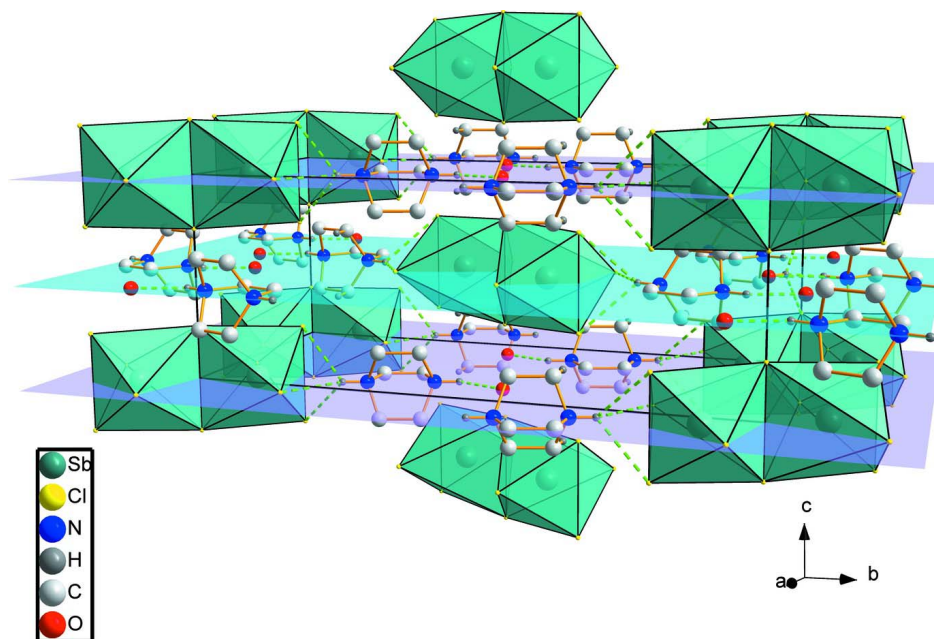
The cohesion of the layers is ensured by N—H $\cdots$ O and N—H $\cdots$ Cl hydrogen bonds between organic cations, inorganic anions and the water molecules (Fig. 2, Table 1).

### S2. Experimental

A mixture of  $SbCl_3$  (0.23 g, 1 mmol) and DABCO (0.11 g, 1 mmol) was dissolved in an aqueous solution of hydrochloric acid and stirred for several minutes at room temperature. Colorless crystals suitable for X-ray diffraction analysis were obtained by slow evaporation at room temperature over 2 weeks.

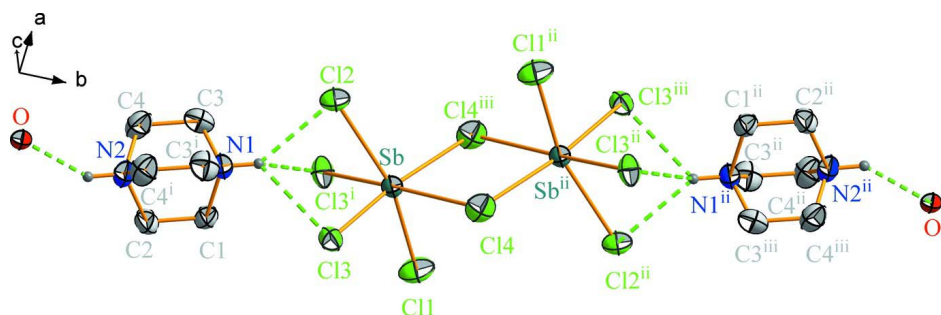
### S3. Refinement

Hydrogen positions of the water molecule could not be located reliably and were eventually omitted from refinement. The C—H and N—H hydrogen atom positions were placed geometrically. They were included in the refinement using the riding-model approximation, with distance constraints of C—H = 0.97 Å, N—H = 0.91 and with  $U_{iso}(H) = 1.2U_{eq}(C,N)$ .



**Figure 1**

Three-dimensional view of  $(C_6H_{14}N_2)_2[Sb_2Cl_{10}] \cdot 2H_2O$  showing the crystal packing. H atoms not involved in hydrogen bonding (dashed lines) have been omitted for clarity.



**Figure 2**

An ORTEP plot of the molecular entities of  $(C_6H_{14}N_2)_2[Sb_2Cl_{10}] \cdot 2H_2O$ , showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. [Symmetry code: (i)  $x, y, 1 - z$ ; (ii)  $1 - x, 1 - y, z$ ; (iii)  $1 - x, 1 - y, 1 - z$ .]

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

*Crystal data*

$(C_6H_{14}N_2)_2[Sb_2Cl_{10}] \cdot 2H_2O$

$M_r = 862.46$

Orthorhombic,  $Pnmm$

Hall symbol:  $-P 2 2n$

$a = 9.162 (1) \text{ \AA}$

$b = 20.869 (7) \text{ \AA}$

$c = 7.566 (2) \text{ \AA}$

$V = 1446.8 (7) \text{ \AA}^3$

$Z = 2$

$F(000) = 840$

$D_x = 1.980 \text{ Mg m}^{-3}$

Melting point: 571 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1700 reflections

$\theta = 2.4\text{--}27.0^\circ$

$\mu = 2.81 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Prism, colourless

$0.50 \times 0.43 \times 0.36 \text{ mm}$

Data collection

Enraf–Nonius CAD-4  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

non-profiled  $\omega/2\theta$  scans

Absorption correction:  $\psi$  scan  
(North *et al.*, 1968)

$T_{\min} = 0.334$ ,  $T_{\max} = 0.431$

2797 measured reflections

1700 independent reflections

1488 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 27.0^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -1 \rightarrow 11$

$k = -26 \rightarrow 1$

$l = -9 \rightarrow 3$

2 standard reflections every 120 min

intensity decay: 1%

Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.061$

$S = 1.08$

1700 reflections

82 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2 + 1.1425P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.59 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0099 (5)

Special details

**Experimental.** Number of psi-scan sets used was 5 Theta correction was applied. Averaged transmission function was used. No Fourier smoothing was applied.

**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.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Sb	0.40193 (3)	0.407356 (11)	0.5000	0.03327 (11)	
Cl1	0.16885 (14)	0.46510 (7)	0.5000	0.0678 (4)	
Cl2	0.62462 (11)	0.31027 (6)	0.5000	0.0471 (3)	
Cl3	0.30372 (8)	0.33776 (3)	0.26053 (10)	0.04669 (19)	
Cl4	0.5000	0.5000	0.23812 (14)	0.0534 (3)	
N1	0.3554 (4)	0.20234 (16)	0.5000	0.0406 (8)	
H1	0.3861	0.2438	0.5000	0.049*	
N2	0.2710 (4)	0.09024 (15)	0.5000	0.0443 (8)	
H2	0.2394	0.0489	0.5000	0.053*	
C1	0.1931 (4)	0.20125 (18)	0.5000	0.0433 (9)	
H1A	0.1563	0.2231	0.3961	0.052*	0.50
H1B	0.1563	0.2231	0.6039	0.052*	0.50

C2	0.1428 (5)	0.1332 (2)	0.5000	0.0537 (12)	
H2A	0.0836	0.1251	0.6039	0.064*	0.50
H2B	0.0836	0.1251	0.3961	0.064*	0.50
C3	0.4100 (3)	0.17034 (16)	0.6617 (5)	0.0535 (8)	
H3A	0.3730	0.1921	0.7657	0.064*	
H3B	0.5158	0.1720	0.6646	0.064*	
C4	0.3595 (4)	0.10141 (15)	0.6615 (5)	0.0541 (8)	
H4A	0.4432	0.0729	0.6626	0.065*	
H4B	0.3013	0.0929	0.7660	0.065*	
O	0.3071 (4)	-0.04203 (13)	0.5000	0.0522 (8)	

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Sb	0.03290 (16)	0.02973 (15)	0.03718 (16)	-0.00263 (10)	0.000	0.000
C11	0.0468 (6)	0.0716 (8)	0.0850 (9)	0.0239 (6)	0.000	0.000
C12	0.0379 (5)	0.0543 (6)	0.0492 (6)	0.0080 (4)	0.000	0.000
C13	0.0517 (4)	0.0401 (4)	0.0483 (4)	-0.0104 (3)	-0.0131 (3)	0.0003 (3)
C14	0.0639 (7)	0.0548 (6)	0.0414 (5)	0.0027 (5)	0.000	0.000
N1	0.0392 (17)	0.0292 (15)	0.053 (2)	-0.0064 (13)	0.000	0.000
N2	0.050 (2)	0.0268 (15)	0.056 (2)	0.0011 (14)	0.000	0.000
C1	0.036 (2)	0.0315 (18)	0.062 (3)	0.0061 (16)	0.000	0.000
C2	0.0314 (19)	0.039 (2)	0.091 (4)	-0.0053 (18)	0.000	0.000
C3	0.0447 (16)	0.0601 (19)	0.0557 (19)	-0.0037 (14)	-0.0143 (15)	-0.0024 (16)
C4	0.0640 (19)	0.0475 (16)	0.0508 (18)	0.0084 (14)	-0.0059 (17)	0.0100 (15)
O	0.0487 (17)	0.0359 (15)	0.072 (2)	-0.0019 (13)	0.000	0.000

*Geometric parameters (Å, °)*

Sb—C11	2.4520 (12)	N2—H2	0.9100
Sb—C13 <sup>i</sup>	2.4904 (7)	C1—C2	1.492 (6)
Sb—C13	2.4904 (7)	C1—H1A	0.9700
Sb—C12	2.8755 (11)	C1—H1B	0.9700
Sb—C14	2.9107 (8)	C2—H2A	0.9700
N1—C3	1.481 (4)	C2—H2B	0.9700
N1—C3 <sup>i</sup>	1.481 (4)	C3—C4	1.511 (4)
N1—C1	1.487 (5)	C3—H3A	0.9700
N1—H1	0.9100	C3—H3B	0.9700
N2—C2	1.478 (5)	C4—H4A	0.9700
N2—C4 <sup>i</sup>	1.485 (4)	C4—H4B	0.9700
N2—C4	1.485 (4)		
C11—Sb—C13 <sup>i</sup>	88.39 (3)	N1—C1—H1A	109.9
C11—Sb—C13	88.39 (3)	C2—C1—H1A	109.9
C13 <sup>i</sup> —Sb—C13	93.37 (3)	N1—C1—H1B	109.9
C11—Sb—C12	164.64 (4)	C2—C1—H1B	109.9
C13 <sup>i</sup> —Sb—C12	81.11 (2)	H1A—C1—H1B	108.3
C13—Sb—C12	81.11 (2)	N2—C2—C1	109.4 (3)

C14—Sb—C13	90.19 (1)	N2—C2—H2A	109.8
C14—Sb—C13 <sup>i</sup>	173.84 (1)	C1—C2—H2A	109.8
C14—Sb—C11	86.69 (4)	N2—C2—H2B	109.8
C14—Sb—C12	104.42 (1)	C1—C2—H2B	109.8
C3—N1—C3 <sup>i</sup>	111.4 (3)	H2A—C2—H2B	108.2
C3—N1—C1	109.3 (2)	N1—C3—C4	109.0 (3)
C3 <sup>i</sup> —N1—C1	109.3 (2)	N1—C3—H3A	109.9
C3—N1—H1	108.9	C4—C3—H3A	109.9
C3 <sup>i</sup> —N1—H1	108.9	N1—C3—H3B	109.9
C1—N1—H1	108.9	C4—C3—H3B	109.9
C2—N2—C4 <sup>i</sup>	109.8 (2)	H3A—C3—H3B	108.3
C2—N2—C4	109.8 (2)	N2—C4—C3	108.5 (3)
C4 <sup>i</sup> —N2—C4	110.8 (4)	N2—C4—H4A	110.0
C2—N2—H2	108.8	C3—C4—H4A	110.0
C4 <sup>i</sup> —N2—H2	108.8	N2—C4—H4B	110.0
C4—N2—H2	108.8	C3—C4—H4B	110.0
N1—C1—C2	108.9 (3)	H4A—C4—H4B	108.4

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

*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>
N1—H1...C12	0.91	2.59	3.340 (4)	140
N1—H1...C13	0.91	2.77	3.390 (3)	126
N1—H1...C13 <sup>i</sup>	0.91	2.77	3.390 (3)	126
N2—H2...O	0.91	2.00	2.780 (4)	143

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