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# Doxofyllinium tetrachlorido-antimonate(III) monohydrate

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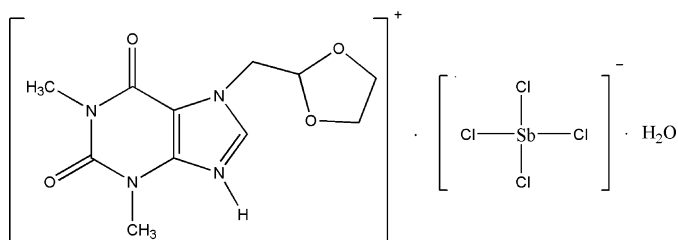
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 Key indicators: single-crystal X-ray study;  $T = 153$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.038;  $wR$  factor = 0.097; data-to-parameter ratio = 18.6.

The title compound,  $(\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_4)[\text{SbCl}_4]\cdot\text{H}_2\text{O}$ , comprises a protonated doxofyllinium cation [7-(1,3-dioxolan-2-ylmethyl)-1,3-dimethyl-2,6-dioxo-3,7-dihydro-1*H*-purin-9-ium], an  $[\text{SbCl}_4]^-$  anion and a water molecule linked by  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{Cl}$  hydrogen bonds: the  $[\text{SbCl}_4]^-$  anions form centrosymmetric dimers *via* weak  $\text{Sb}\cdots\text{Cl}$  interactions [ $\text{Sb}\cdots\text{Cl} = 3.1159$  (9) Å]. The geometrical arrangement in the crystal structure is characterized by slipped  $\pi$ - $\pi$  stacking of the parallel purine ring systems, with an interplanar separation of 3.32 Å.

## Related literature

For related literature, see: Chen, Tu, Shu *et al.* (2007); Chen, Tu & Jin (2007); Feng *et al.* (2007); Franzone *et al.* (1981, 1989); Villani *et al.* (1997); Zhao & Li (2001).



## Experimental

### Crystal data

 $(\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_4)[\text{SbCl}_4]\cdot\text{H}_2\text{O}$   
 $M_r = 548.85$ 

 Triclinic,  $P\bar{1}$   
 $a = 8.9783$  (5) Å

 $b = 10.4727$  (5) Å  
 $c = 11.0357$  (4) Å  
 $\alpha = 68.7550$  (10)°  
 $\beta = 82.671$  (2)°  
 $\gamma = 88.228$  (2)°  
 $V = 959.10$  (8) Å<sup>3</sup>
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.03$  mm<sup>-1</sup>  
 $T = 153$  (2) K  
 $0.33 \times 0.28 \times 0.27$  mm

### Data collection

 Bruker APEX diffractometer  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2000)  
 $T_{\text{min}} = 0.459$ ,  $T_{\text{max}} = 0.486$   
 (expected range = 0.547–0.579)

 9490 measured reflections  
 4399 independent reflections  
 4151 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.046$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.097$   
 $S = 1.05$   
 4399 reflections  
 236 parameters  
 3 restraints

 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 1.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -2.97$  e Å<sup>-3</sup>
**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O5}$	0.92 (4)	1.75 (4)	2.663 (4)	172 (4)
$\text{O5}-\text{H5C}\cdots\text{Cl1}$	0.81 (3)	2.65 (2)	3.332 (3)	142 (2)
$\text{O5}-\text{H5D}\cdots\text{Cl1}^i$	0.81 (3)	2.41 (2)	3.205 (3)	166 (5)
$\text{C3}-\text{H3A}\cdots\text{O1}$	0.97	2.45	3.145 (8)	128
$\text{C7}-\text{H7}\cdots\text{Cl3}^{ii}$	0.93	2.56	3.432 (3)	157

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG2051).

## References

- Bruker (2000). *SMART* (Version 5.618), *SADABS* (Version 2.05), *SAINTE* (Version 6.02a) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Chen, Z.-H., Tu, B. & Jin, Z.-M. (2007). *Acta Cryst.* **E63**, o2676–o2677.
- Chen, H.-X., Tu, B., Shu, Z., Ma, X.-J. & Jin, Z.-M. (2007). *Acta Cryst.* **E63**, o726–o727.
- Feng, W.-J., Ma, X.-J., Shu, Z. & Jin, Z.-M. (2007). *Acta Cryst.* **E63**, o3609.
- Franzone, J. S., Cirillo, R. & Biffignandi, P. (1989). *Eur. J. Pharmacol.* **165**, 269–277.
- Franzone, J. S., Reboani, C. & Fonzo, D. (1981). *Farmacol. Sci.* **36**, 201–219.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Villani, F., De Maria, P., Ronchi, E. & Galimberti, M. (1997). *Int. J. Clin. Pharmacol. Ther.* **35**, 107–111.
- Zhao, J. J. & Li, L. (2001). *J. N. Bethune Univ. Med. Sci.* **27**, 646–676.

## supporting information

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**Doxofyllinium tetrachloridoantimonate(III) monohydrate****Wan Xing Wei, Wen-Jie Feng, Bo-Jiöng Zheng, Ying Chen and Zhi-Min Jin****S1. Comment**

Doxofylline [7-(1,3-dioxolan-2-ylmethyl)-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione] is a therapeutic agent with anti-asthmatic (Franzone *et al.*, 1989), anti-inflammatory activities (Zhao *et al.*, 2001) and a bronchodilating effect on smooth muscle (Franzone *et al.*, 1981; Villani *et al.*, 1997). So far several organic compounds containing doxofylline have been synthesized (Chen, Tu, Shu *et al.*, 2007); Chen, Tu & Jin, 2007; Feng *et al.*, 2007), but the doxofylline complex containing metal has not been reported. All of the above studies provide important references to further research into doxofylline. Herein we present here the structure of the title compound (Scheme 1), (I).

As depicted in Fig. 1, the compound (I) is comprised of a doxofylline cation, a SbCl<sub>4</sub> anion and a water molecule. The N1 of doxofylline is protonated and links to the water molecule by N1—H1...O5 hydrogen bond, and the water molecule links the SbCl<sub>4</sub> anion by O5—H5C...Cl interactions. The dihedral angle between the plane of the purine ring and the approximate plane through C4/O3/C6/O4 is 68.5°. The pure compound is 8.42° (Chen, Tu, Shu *et al.*, 2007); Chen, Tu & Jin, 2007). In the purine ring, the bond length of N4—C11 [1.392 (3) Å] bond is somewhat longer than the corresponding N—C [1.374 (4) Å] bond length in the Chen's case (Chen *et al.*, 2007).

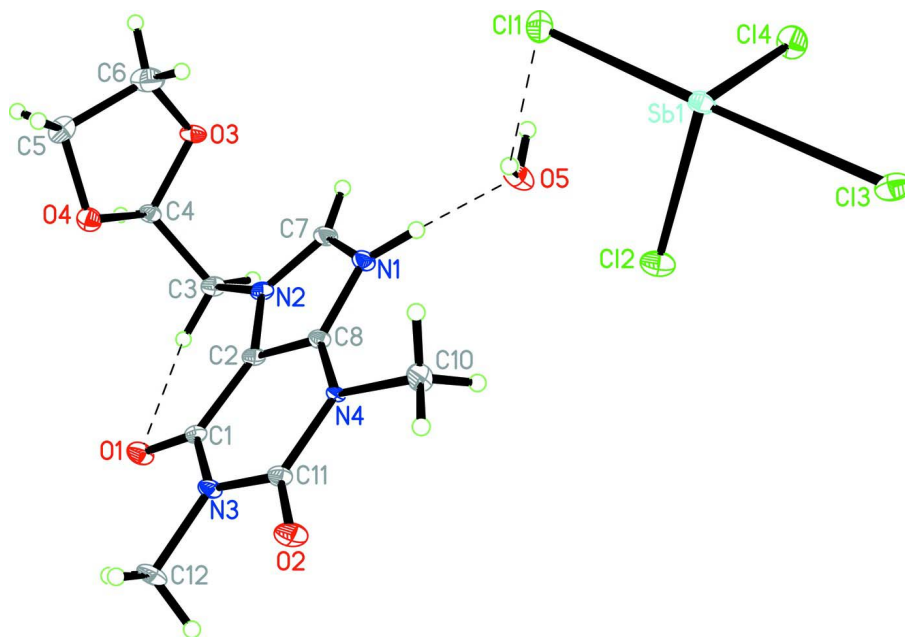
The symmetrically related SbCl<sub>4</sub> link into dimers *via* coordinated bonds of Sb1—Cl4 (-x + 1, -y + 2, -z + 2) [3.1159 (9) Å] (Fig. 2), which plays an important role in the formation of the crystal. In addition, there exists slipped  $\pi$ ... $\pi$  stacking between symmetrically related pyridines rings at (-x + 2, -y + 1, -z + 1), with a centroid to centroid distance equal to be 3.662 (6) Å. With intermolecular hydrogen bonds listed in Table 1, the stacking interactions further stabilize the crystal structure (Fig. 3).

**S2. Experimental**

Antimony trichloride, hydrochloride acid and doxofylline in a 1:1:1 molar ratio were mixed and dissolved in sufficient acetone by heating to a temperature at which a clear solution resulted. Crystals of (I) were formed by gradual evaporation of acetone over a period of three days at 298 K.

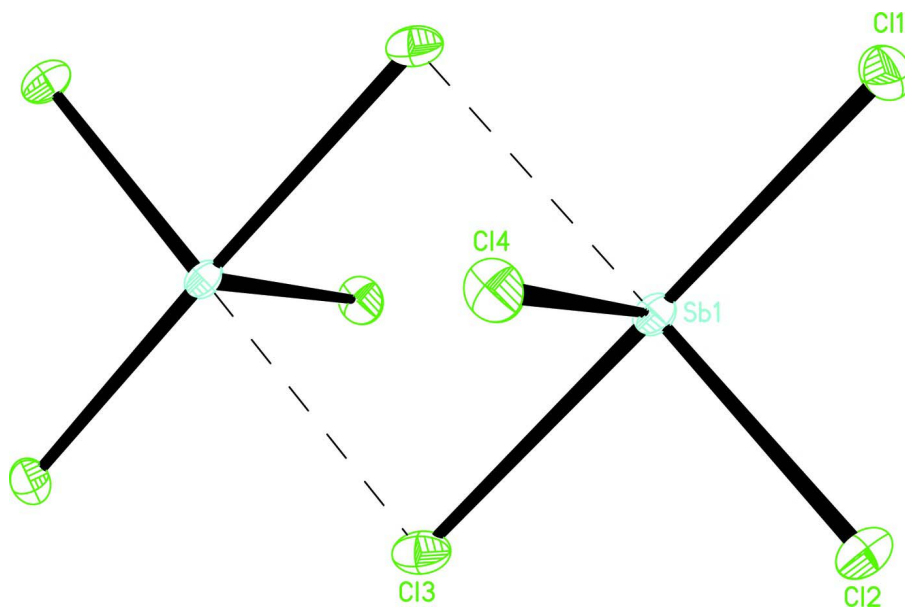
**S3. Refinement**

H atoms attaching to N atoms were deduced from difference Fourier maps, and incorporated in refinement freely. The water H atoms were located tentatively in difference Fourier maps and were refined with the O—H and H...H distances restrained to 0.82 (2) and 1.39 (2) Å. Others were placed in calculated positions and allowed to ride on their parent atoms at distances of 0.93 (C7—H7), 0.96 (methyl), 0.97 (methylene) and 0.98 Å (methine), with  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5 U_{\text{eq}}(\text{C})$ .



**Figure 1**

The molecular structure of (I), with 30% probability displacement ellipsoids is shown. Hydrogen bonds are illustrated as dashed lines.



**Figure 2**

The dimer of  $\text{SbCl}_4$  in the crystal lattice. Atoms which are not labeled are obtained by symmetry operation of  $(-x + 1, -y + 2, -z + 2)$ . Coordinated bonds of  $\text{Sb1—Cl4} (-x + 1, -y + 2, -z + 2)$  and  $\text{Cl4—Sb1} (-x + 1, -y + 2, -z + 2)$  are illustrated by dashed lines.

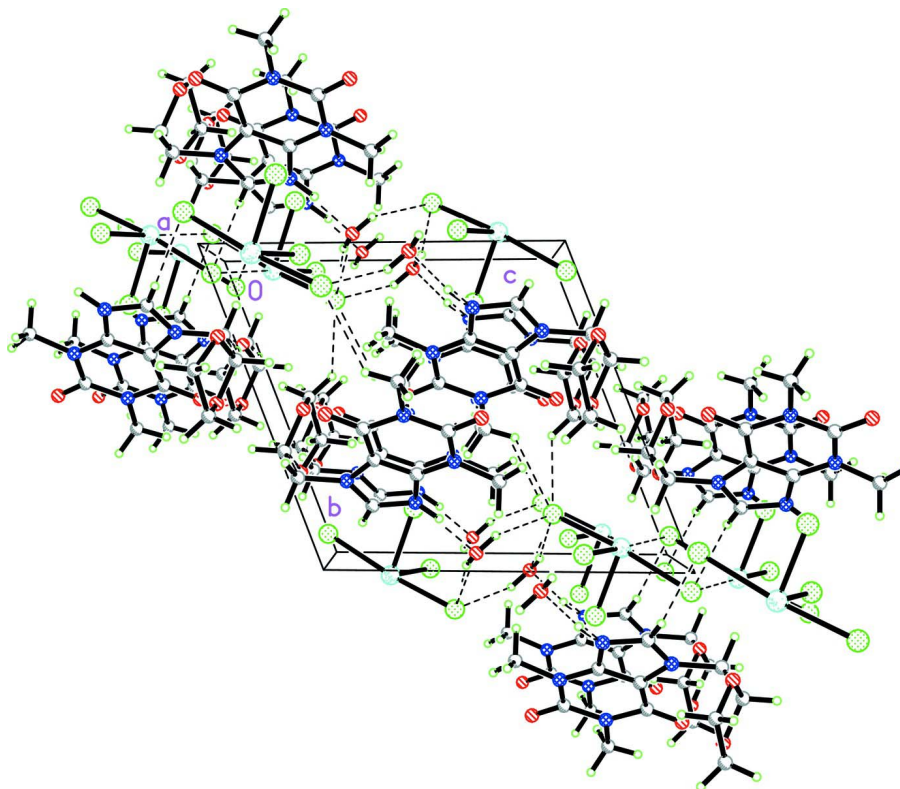


Figure 3

The packing diagram of (I) viewed down along the *c* axis. Hydrogen bonds are illustrated by dashed lines.

**7-(1,3-dioxolan-2-ylmethyl)-1,3-dimethyl-2,6-dioxo-3,7-dihydro-1H-purin-9-ium tetrachloridoantimonate(III) monohydrate**

*Crystal data*

(C<sub>11</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>)[SbCl<sub>4</sub>]·H<sub>2</sub>O

*M<sub>r</sub>* = 548.85

Triclinic, *P*1̄

Hall symbol: -P 1

*a* = 8.9783 (5) Å

*b* = 10.4727 (5) Å

*c* = 11.0357 (4) Å

α = 68.755 (1)°

β = 82.671 (2)°

γ = 88.228 (2)°

*V* = 959.10 (8) Å<sup>3</sup>

*Z* = 2

*F*(000) = 540

*D<sub>x</sub>* = 1.901 Mg m<sup>-3</sup>

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 4733 reflections

θ = 2.1–26.9°

μ = 2.03 mm<sup>-1</sup>

*T* = 153 K

Block, colourless

0.33 × 0.28 × 0.27 mm

*Data collection*

Bruker APEX  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scan

Absorption correction: multi-scan

(*SADABS*; Bruker, 2000)

*T<sub>min</sub>* = 0.459, *T<sub>max</sub>* = 0.486

9490 measured reflections

4399 independent reflections

4151 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.046

θ<sub>max</sub> = 27.5°, θ<sub>min</sub> = 3.1°

*h* = -11→11

*k* = -13→13

*l* = -14→14

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.097$   
 $S = 1.05$   
 4399 reflections  
 236 parameters  
 3 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.741P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.40 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -2.97 \text{ e } \text{\AA}^{-3}$

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.

**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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Sb1	0.603006 (19)	0.947081 (18)	0.845084 (16)	0.01708 (9)
Cl1	0.50253 (10)	0.84549 (9)	0.69342 (9)	0.03132 (19)
Cl2	0.85111 (8)	0.95551 (8)	0.72752 (7)	0.02636 (17)
Cl3	0.70926 (9)	1.07637 (8)	0.98807 (8)	0.02720 (17)
Cl4	0.53886 (10)	1.16845 (8)	0.70074 (8)	0.02833 (18)
O3	0.7285 (2)	0.7066 (2)	0.0265 (2)	0.0210 (4)
N4	1.0810 (3)	0.6651 (3)	0.4722 (2)	0.0167 (5)
N3	1.2424 (3)	0.5255 (2)	0.3864 (2)	0.0162 (5)
C11	1.1991 (3)	0.5734 (3)	0.4877 (3)	0.0173 (5)
C8	1.0212 (3)	0.7064 (3)	0.3567 (3)	0.0153 (5)
C1	1.1882 (3)	0.5670 (3)	0.2638 (3)	0.0153 (5)
C2	1.0676 (3)	0.6614 (3)	0.2569 (3)	0.0149 (5)
O1	1.2388 (2)	0.5233 (2)	0.1794 (2)	0.0226 (5)
N1	0.9061 (3)	0.7955 (3)	0.3204 (2)	0.0182 (5)
N2	0.9814 (3)	0.7279 (3)	0.1570 (2)	0.0164 (5)
O2	1.2588 (2)	0.5340 (2)	0.5875 (2)	0.0247 (5)
C7	0.8856 (3)	0.8068 (3)	0.1984 (3)	0.0199 (6)
H7	0.8145	0.8619	0.1501	0.024*
C12	1.3671 (3)	0.4282 (3)	0.4072 (3)	0.0233 (6)
H12A	1.3891	0.4014	0.3325	0.035*
H12B	1.3390	0.3488	0.4840	0.035*
H12C	1.4544	0.4711	0.4188	0.035*
O4	0.8543 (2)	0.5081 (2)	0.1080 (2)	0.0221 (4)
C3	0.9963 (3)	0.7182 (3)	0.0266 (3)	0.0186 (6)

H3A	1.0894	0.6729	0.0131	0.022*
H3B	1.0012	0.8097	-0.0395	0.022*
C4	0.8666 (3)	0.6396 (3)	0.0103 (3)	0.0170 (5)
H4	0.8816	0.6326	-0.0766	0.020*
C5	0.6971 (4)	0.4720 (3)	0.1295 (3)	0.0254 (6)
H5A	0.6695	0.4048	0.2166	0.030*
H5B	0.6713	0.4361	0.0652	0.030*
C6	0.6219 (4)	0.6067 (4)	0.1140 (4)	0.0362 (8)
H6A	0.5284	0.6123	0.0770	0.043*
H6B	0.6014	0.6188	0.1975	0.043*
C10	1.0375 (4)	0.7258 (3)	0.5723 (3)	0.0230 (6)
H10A	1.0918	0.6828	0.6458	0.035*
H10B	0.9316	0.7121	0.6004	0.035*
H10C	1.0607	0.8222	0.5359	0.035*
O5	0.7621 (3)	0.9581 (3)	0.4328 (2)	0.0308 (5)
H1	0.857 (4)	0.845 (4)	0.367 (4)	0.024 (9)*
H5C	0.731 (4)	0.907 (3)	0.5067 (18)	0.029*
H5D	0.699 (3)	1.004 (3)	0.390 (3)	0.029*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Sb1	0.01524 (12)	0.01761 (13)	0.01647 (12)	0.00463 (8)	-0.00456 (8)	-0.00337 (9)
Cl1	0.0308 (4)	0.0267 (4)	0.0434 (5)	0.0035 (3)	-0.0099 (3)	-0.0195 (4)
Cl2	0.0185 (3)	0.0339 (4)	0.0231 (3)	0.0024 (3)	-0.0001 (3)	-0.0070 (3)
Cl3	0.0209 (4)	0.0285 (4)	0.0289 (4)	-0.0004 (3)	-0.0088 (3)	-0.0045 (3)
Cl4	0.0357 (4)	0.0188 (4)	0.0285 (4)	0.0071 (3)	-0.0144 (3)	-0.0031 (3)
O3	0.0136 (9)	0.0262 (11)	0.0211 (10)	0.0040 (8)	-0.0060 (8)	-0.0051 (9)
N4	0.0172 (11)	0.0215 (12)	0.0123 (10)	0.0048 (9)	-0.0057 (9)	-0.0063 (9)
N3	0.0149 (11)	0.0191 (12)	0.0146 (10)	0.0056 (9)	-0.0061 (9)	-0.0052 (9)
C11	0.0158 (12)	0.0212 (14)	0.0148 (12)	0.0024 (10)	-0.0044 (10)	-0.0057 (11)
C8	0.0141 (12)	0.0180 (13)	0.0141 (12)	0.0029 (10)	-0.0055 (10)	-0.0050 (10)
C1	0.0124 (12)	0.0190 (13)	0.0140 (12)	-0.0004 (10)	-0.0038 (10)	-0.0048 (11)
C2	0.0133 (12)	0.0200 (13)	0.0115 (11)	0.0023 (10)	-0.0060 (9)	-0.0042 (10)
O1	0.0219 (11)	0.0312 (12)	0.0189 (10)	0.0091 (9)	-0.0056 (8)	-0.0139 (9)
N1	0.0171 (11)	0.0205 (12)	0.0188 (11)	0.0067 (9)	-0.0069 (9)	-0.0082 (10)
N2	0.0151 (11)	0.0206 (12)	0.0137 (10)	0.0026 (9)	-0.0075 (9)	-0.0047 (9)
O2	0.0234 (11)	0.0353 (13)	0.0155 (9)	0.0084 (9)	-0.0107 (8)	-0.0070 (9)
C7	0.0168 (13)	0.0237 (15)	0.0215 (13)	0.0053 (11)	-0.0084 (11)	-0.0093 (12)
C12	0.0209 (14)	0.0281 (16)	0.0201 (13)	0.0135 (12)	-0.0081 (11)	-0.0068 (12)
O4	0.0227 (11)	0.0215 (11)	0.0203 (10)	0.0024 (8)	-0.0035 (8)	-0.0052 (9)
C3	0.0171 (13)	0.0276 (15)	0.0117 (12)	0.0020 (11)	-0.0046 (10)	-0.0071 (11)
C4	0.0154 (13)	0.0218 (14)	0.0149 (12)	0.0049 (11)	-0.0056 (10)	-0.0071 (11)
C5	0.0277 (16)	0.0304 (17)	0.0179 (13)	-0.0070 (13)	0.0006 (12)	-0.0091 (13)
C6	0.0223 (16)	0.037 (2)	0.0401 (19)	-0.0003 (14)	-0.0018 (14)	-0.0035 (16)
C10	0.0269 (15)	0.0301 (17)	0.0159 (13)	0.0065 (12)	-0.0065 (11)	-0.0122 (12)
O5	0.0291 (12)	0.0417 (15)	0.0262 (11)	0.0164 (11)	-0.0078 (9)	-0.0176 (11)

*Geometric parameters (Å, °)*

Sb1—C14	2.3915 (7)	N2—C3	1.468 (3)
Sb1—C12	2.4176 (7)	C7—H7	0.9300
Sb1—C11	2.5460 (9)	C12—H12A	0.9600
Sb1—C13	2.6917 (9)	C12—H12B	0.9600
O3—C6	1.428 (4)	C12—H12C	0.9600
O3—C4	1.429 (3)	O4—C4	1.405 (3)
N4—C8	1.364 (3)	O4—C5	1.440 (4)
N4—C11	1.392 (3)	C3—C4	1.512 (4)
N4—C10	1.470 (4)	C3—H3A	0.9700
N3—C11	1.392 (4)	C3—H3B	0.9700
N3—C1	1.409 (3)	C4—H4	0.9800
N3—C12	1.473 (3)	C5—C6	1.507 (5)
C11—O2	1.216 (4)	C5—H5A	0.9700
C8—C2	1.362 (4)	C5—H5B	0.9700
C8—N1	1.369 (3)	C6—H6A	0.9700
C1—O1	1.213 (3)	C6—H6B	0.9700
C1—C2	1.434 (4)	C10—H10A	0.9600
C2—N2	1.388 (3)	C10—H10B	0.9600
N1—C7	1.344 (4)	C10—H10C	0.9600
N1—H1	0.92 (4)	O5—H5C	0.81 (3)
N2—C7	1.327 (4)	O5—H5D	0.81 (3)
C14—Sb1—C12	93.49 (3)	H12A—C12—H12B	109.5
C14—Sb1—C11	88.23 (3)	N3—C12—H12C	109.5
C12—Sb1—C11	88.95 (3)	H12A—C12—H12C	109.5
C14—Sb1—C13	86.84 (3)	H12B—C12—H12C	109.5
C12—Sb1—C13	90.02 (3)	C4—O4—C5	105.2 (2)
C11—Sb1—C13	174.90 (3)	N2—C3—C4	112.1 (2)
C6—O3—C4	108.5 (2)	N2—C3—H3A	109.2
C8—N4—C11	117.8 (2)	C4—C3—H3A	109.2
C8—N4—C10	122.3 (2)	N2—C3—H3B	109.2
C11—N4—C10	119.4 (2)	C4—C3—H3B	109.2
C11—N3—C1	127.4 (2)	H3A—C3—H3B	107.9
C11—N3—C12	115.5 (2)	O4—C4—O3	106.6 (2)
C1—N3—C12	116.9 (2)	O4—C4—C3	110.1 (2)
O2—C11—N3	121.5 (3)	O3—C4—C3	110.1 (2)
O2—C11—N4	121.2 (3)	O4—C4—H4	110.0
N3—C11—N4	117.3 (2)	O3—C4—H4	110.0
C2—C8—N4	124.1 (2)	C3—C4—H4	110.0
C2—C8—N1	108.2 (2)	O4—C5—C6	102.8 (3)
N4—C8—N1	127.7 (2)	O4—C5—H5A	111.2
O1—C1—N3	122.2 (2)	C6—C5—H5A	111.2
O1—C1—C2	126.7 (3)	O4—C5—H5B	111.2
N3—C1—C2	111.1 (2)	C6—C5—H5B	111.2
C8—C2—N2	106.7 (2)	H5A—C5—H5B	109.1
C8—C2—C1	122.1 (2)	O3—C6—C5	103.9 (3)

N2—C2—C1	131.2 (2)	O3—C6—H6A	111.0
C7—N1—C8	107.2 (2)	C5—C6—H6A	111.0
C7—N1—H1	125 (2)	O3—C6—H6B	111.0
C8—N1—H1	127 (2)	C5—C6—H6B	111.0
C7—N2—C2	107.7 (2)	H6A—C6—H6B	109.0
C7—N2—C3	125.6 (2)	N4—C10—H10A	109.5
C2—N2—C3	126.7 (2)	N4—C10—H10B	109.5
N2—C7—N1	110.1 (2)	H10A—C10—H10B	109.5
N2—C7—H7	125.0	N4—C10—H10C	109.5
N1—C7—H7	125.0	H10A—C10—H10C	109.5
N3—C12—H12A	109.5	H10B—C10—H10C	109.5
N3—C12—H12B	109.5	H5C—O5—H5D	116.0 (19)
C1—N3—C11—O2	-176.7 (3)	O1—C1—C2—N2	-1.4 (5)
C12—N3—C11—O2	-1.7 (4)	N3—C1—C2—N2	-180.0 (3)
C1—N3—C11—N4	5.3 (4)	C2—C8—N1—C7	-1.4 (3)
C12—N3—C11—N4	-179.7 (3)	N4—C8—N1—C7	179.5 (3)
C8—N4—C11—O2	179.0 (3)	C8—C2—N2—C7	-1.3 (3)
C10—N4—C11—O2	6.1 (4)	C1—C2—N2—C7	-178.8 (3)
C8—N4—C11—N3	-3.1 (4)	C8—C2—N2—C3	176.4 (3)
C10—N4—C11—N3	-175.9 (3)	C1—C2—N2—C3	-1.1 (5)
C11—N4—C8—C2	1.4 (4)	C2—N2—C7—N1	0.5 (3)
C10—N4—C8—C2	174.1 (3)	C3—N2—C7—N1	-177.3 (3)
C11—N4—C8—N1	-179.7 (3)	C8—N1—C7—N2	0.6 (3)
C10—N4—C8—N1	-7.0 (5)	C7—N2—C3—C4	-73.4 (4)
C11—N3—C1—O1	176.4 (3)	C2—N2—C3—C4	109.3 (3)
C12—N3—C1—O1	1.4 (4)	C5—O4—C4—O3	31.0 (3)
C11—N3—C1—C2	-5.0 (4)	C5—O4—C4—C3	150.4 (2)
C12—N3—C1—C2	-180.0 (3)	C6—O3—C4—O4	-12.6 (3)
N4—C8—C2—N2	-179.2 (3)	C6—O3—C4—C3	-132.0 (3)
N1—C8—C2—N2	1.7 (3)	N2—C3—C4—O4	-56.9 (3)
N4—C8—C2—C1	-1.4 (5)	N2—C3—C4—O3	60.4 (3)
N1—C8—C2—C1	179.5 (3)	C4—O4—C5—C6	-36.3 (3)
O1—C1—C2—C8	-178.6 (3)	C4—O3—C6—C5	-9.9 (4)
N3—C1—C2—C8	2.9 (4)	O4—C5—C6—O3	28.0 (3)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O5	0.92 (4)	1.75 (4)	2.663 (4)	172 (4)
O5—H5C $\cdots$ C11	0.81 (3)	2.65 (2)	3.332 (3)	142 (2)
O5—H5D $\cdots$ C11 <sup>i</sup>	0.81 (3)	2.41 (2)	3.205 (3)	166 (5)
C3—H3A $\cdots$ O1	0.97	2.45	3.145 (8)	128
C7—H7 $\cdots$ Cl3 <sup>ii</sup>	0.93	2.56	3.432 (3)	157

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