Tetragonal
$I4_1cd$
a = 14.795 (1) Å
c = 16.634 (2) Å
V = 3641.2 (6) Å^3
Z = 8
D_x = 1.542 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 31.59–39.73°
μ = 4.454 mm^{-1}
T = 293 (2) K
Prism
0.40 × 0.16 × 0.10 mm
Brown–red

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min}$ = 0.318, $T_{\max}$ = 0.634
9986 measured reflections
1354 independent reflections

1099 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.070
$\theta_{\max}$ = 60.07°
$h = -16 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = -18 \rightarrow 18$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.063
S = 0.923
1354 reflections
122 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.010
$\Delta\rho_{\max}$ = 0.229 e Å^{-3}
$\Delta\rho_{\min}$ = −0.206 e Å^{-3}

Extinction correction: *SHELXL*97
Extinction coefficient: 0.00015 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.01 (2)

Table 5. *Selected geometric parameters (Å, °) for (III)*

Cu1—N12	2.020 (3)	Cu1—Cl1	2.214 (1)
N12—Cu1—N12$^{\rm i}$	97.73 (15)	N12—Cu1—Cl1	96.12 (8)
N12—Cu1—Cl1$^{\rm i}$	138.42 (8)	Cl1$^{\rm i}$—Cu1—Cl1	98.97 (7)

Symmetry code: (i) $2 - x, 1 - y, z$.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX*3.1a (McArdle, 1995); software used to prepare material for publication: *PARST*97 (Nardelli, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1369). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Goslar, J., Szczaniecki, P. B. & Strawiak, M. M. (1987). *Solid State Commun.* **62**, 169–171.
Goslar, J., Szczaniecki, P. B., Strawiak, M. M. & Mroziński, J. (1988). *Transition Met. Chem.* **13**, 81–84.
Kostka, K. & Strawiak, M. M. (1982). *Pol. J. Chem.* **56**, 895–901.
McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Molecular Structure Corporation (1989*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1989*b*). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Nardelli, M. (1996). *J. Appl. Cryst.* **29**, 296–300.
Nasiadek, M. (1985). Diploma thesis, Institute of Chemistry, Faculty of Pharmacy, Medical University of Łódź, Poland.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–83.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1998). C**54**, 1773-1777

Bis(dimethylammonium) Pentachloroantimonate(III), on the Deformation of the Octahedral Coordination of Sb$^{\rm III}$

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Abstract

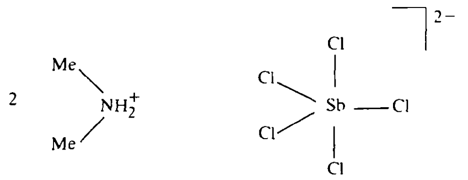
The structure of the title compound, $[\mathrm{NH_2(CH_3)_2}]_2$-$[\mathrm{SbCl_5}]$, was determined at 295 and 85 K. It consists of polymeric $(\mathrm{SbCl_5^{2-}})_n$ chains composed of deformed $\mathrm{SbCl_6^{3-}}$ octahedra connected by corners and dimethylammonium cations. The temperature dependence of the Sb—Cl bond lengths is discussed. It is argued that the deformation of the octahedral coordination of the Sb$^{\rm III}$ atom is caused by electrostatic interaction/hydrogen bonds.

Comment

Alkylammonium chloroantimonates are obtained by mixing amine hydrochloride and antimony trichloride in an organic solvent or aqueous hydrochloric acid. Depending on the ratio of the reactants used, the type of cation, the solvent and the experimental conditions one or more products of different stoichiometries may be obtained. They are defined by the general formula $R_a\mathrm{Sb}_b\mathrm{Cl}_c$ (R = alkylammonium cation, $c = 3b + a$). These compounds are attracting growing attention since many salts of this group undergo numerous phase transitions, some of them to polar ferroelectric, ferrielectric or pyroelectric phases (Sobczyk *et al.*, 1997, and references therein). They are ionic salts with anionic sublattices composed of deformed $SbCl_6^{3-}$ octahedra, isolated or connected to each other by corners, edges or faces. Alkylammonium cations are located in the anionic cavities and are connected to the anions by hydrogen bonds.

Dimethylammonium chloroantimonates are reported to crystallize in three different stoichiometries: $[NH_2(CH_3)_2]_3Sb_2Cl_9$ (DMACA), $[NH_2(CH_3)_2]_2SbCl_5$ and $[NH_2(CH_3)_2]_4SbCl_7$ (Ensinger *et al.*, 1982). The anionic sublattice of DMACA is composed of two-dimensional polyanionic $(Sb_2Cl_9^{3-})_n$ layers formed by $SbCl_6^{3-}$ octahedra connected by corners. The octahedra are arranged in such a way that they form a deformed honeycomb structure. At room temperature, there are two crystallographically independent disordered cations, one located inside the polyanionic cavities, the other between the layers. One phase transition from the paraelectric $P2_1/c$ phase to the ferroelectric Pc phase at 242 K has been reported. It was attributed to ordering of the dimethylammonium cation located inside the polyanionic cavities as the temperature was lowered. At the phase transition, the anionic sublattice is further deformed. This can be explained by the displacement of Cl atoms in the direction of the N atoms of the dimethylammonium cations (Zaleski & Pietraszko, 1996).

The anionic sublattice of $[NH_2(CH_3)_2]_4SbCl_7$ is composed of isolated $SbCl_6^{3-}$ units with three independent dimethylammonium cations (Knödler *et al.*, 1988). The crystal structure of $[NH_2(CH_3)_2]_2SbCl_5$ has not been reported so far. The goal of the present study was to determine the crystal structure of $[NH_2(CH_3)_2]_2SbCl_5$, (I), at 295 and 85 K, and study the temperature dependence of the Sb—Cl bond lengths.



(I)

The anionic sublattice of $[NH_2(CH_3)_2]_2SbCl_5$ is built of one-dimensional $(SbCl_5^{2-})_n$ chains composed of deformed $SbCl_6^{3-}$ octahedra connected by corners. Two Cl atoms of the coordination sphere of each Sb atom are bridging and four are terminal. The Sb atoms are linked by the bridging Cl atoms, forming characteristic zigzag chains. Dimethylammonium cations are located in the cavities formed by the polyanionic lattice. They are connected to Cl atoms by hydrogen bonds. The crystal packing of $[NH_2(CH_3)_2]_2SbCl_5$ is shown in Fig. 1.

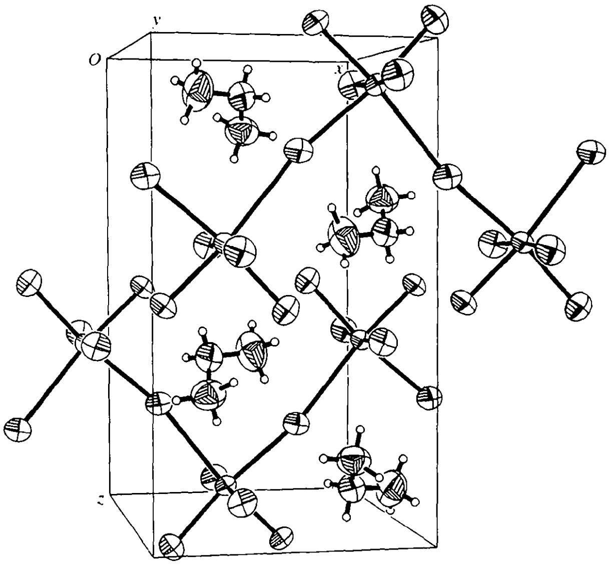


Fig. 1. Packing diagram of $[NH_2(CH_3)_2]_2SbCl_5$ at 295 K. Displacement ellipsoids are at 50% probability.

At 295 K, the lengths of the Sb—Cl bonds vary between 2.404 (1) and 3.257 (1) Å. The longest Sb—Cl bonds are characteristic of bridging Cl atoms [2.873 (1) and 3.257 (1) Å], while the shortest bonds are those to the terminal atoms opposite the bridging ones [2.475 (1) and 2.404 (1) Å]. Two other terminal bonds have intermediate lengths [2.616 (1) Å] (Table 2). It should be noted that the sum of the bond lengths between the Sb atom and the two opposite terminal Cl atoms is significantly lower (5.232 Å) than in the case of two other pairs comprising bridging/terminal atoms (5.348 and 5.661 Å). The Cl—Sb—Cl angles (for Cl atoms *cis* to one another in the octahedra) vary between 82.37 (4) and 97.38 (4)°.

At 85 K, the lengths of the Sb—Cl bonds to terminal chlorines (Cl1, Cl2 and Cl3) remain the same within one standard deviation, while bond lengths to bridging chlorine Cl4 ($Cl4^{ii}$) significantly increase;by 0.027 (2) (Sb1—Cl4) and by 0.049 (2) Å (Sb1—$Cl4^{ii}$) (Table 5). The Cl—Sb—Cl bond angles to Cl1 and Cl2 do not change, while the largest changes are observed for $Cl4^{ii}$ [up to 2.62 (8)° in $Cl4^{ii}$—Sb1—Cl2].

The shortest N· · ·Cl contacts fall in the range 3.266 (4)–3.353 (4) Å at 295 K and 3.236 (3)–3.275 (3) Å at 85 K (Tables 3 and 6), and correspond to hydrogen bonds of intermediate strength. A significant decrease of the distance between $Cl4^{i}$ and N1 at 85 K [0.078 (4) Å] should be noted.

The influence of the N—H· · ·Cl bonds on the octahedral coordination geometry of the Sb atom is shown in Fig. 2. As shown in the case of DMACA, when there are no hydrogen bonds to the bridging Cl atom this atom is located in the middle between Sb atoms with the Sb—Cl—Sb angle equal to 180° (Zaleski & Pietraszko, 1996). In the case of $[NH_2(CH_3)_2]_2SbCl_5$, the Sb1—

Cl4—Sb1^{iii} angle is 168.44 (4)° corresponding to the displacement of Cl4 by 0.30 (1) Å from the line joining the Sb atoms. At 85 K, the Sb1—Cl4—Sb1^{iii} angle decreases to 166.46 (4)° with the displacement of Cl4 increasing to 0.36 (1) Å. As a result of the shifting of Cl4 towards the N1^{iii} atom, the Cl2—Sb1—Cl4 angle decreases from 90 to 82.37 (4)°, while Cl3—Sb1—Cl4^{ii} increases to 97.38 (4)° at 295 K, and these deformations increase at 85 K to 81.52 (4) and 99.56 (4)°, respectively [symmetry code: (iii) $2-x$, $2-y$, $1-z$].

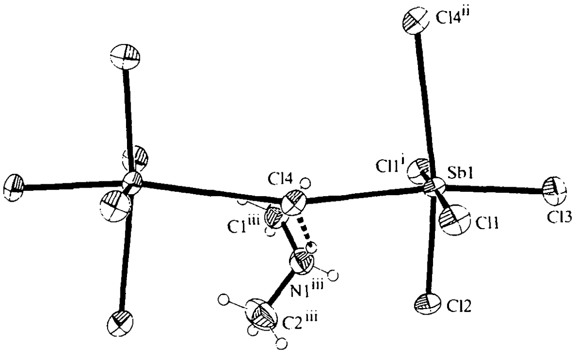


Fig. 2. Scheme of the hydrogen bonding involving the Cl4 atom at 85 K. Cl4 is displaced by 0.36 (1) Å from the line joining the Sb atoms in the direction of the N atom. (Out of two symmetry-related cations forming hydrogen bonds to Cl4, only one is shown for clarity.) Displacement ellipsoids are at 50% probability. [Symmetry codes: (i) x, $\frac{3}{2}-y$, z; (ii) $x-\frac{1}{2}$, y, $\frac{3}{2}-z$; (iii) $2-x$, $2-y$, $1-z$.]

Antimony(III) possesses a lone electron pair (LEP), which occupies the spherical 5*s* orbital. The LEP is responsible for the deformation of the octahedral coordination of Sb^{III} (Wang & Liebau, 1996*a*,*b*; Olivier-Fourcade *et al.*, 1990). The presence of the LEP makes the Sb^{III}—Cl bonds significantly longer than the corresponding bonds of Sb^{V} compounds. Assuming ideal octahedral coordination, the typical length of the Sb^{III}—Cl bond is 2.65 (1) Å, which is about 0.27 (2) Å longer than the corresponding Sb^{V}—Cl bond [2.38 (1) Å; Prassides *et al.*, 1985]. The LEP has a screening effect on the atomic charge on antimony leading to the weakening and therefore elongation of the Sb—Cl bonds. Electrostatic interactions together with hydrogen bonds easily deform the coordination of the Sb^{III} atoms. Only a very limited number of antimony(III) compounds possess almost ideal non-distorted octahedral coordination. All others are generally characterized by octahedral coordination deformed to various degrees. Generally, bridging chlorines form much longer (weaker) bonds in comparison with the terminal ones. They are generally quite easily displaced in the direction of a positive charge which in the case of alkylammonium compounds is located on the N atoms. In the case of terminal Cl atoms, these interactions lead to the deformation of Cl—Sb—Cl angles from 90°.

Experimental

The title compound was obtained by mixing dimethylamine and antimony trichloride (molar ratio 7:1) in aqueous hydrochloric acid. Crystals of suitable dimensions for X-ray structure analysis were grown by slow evaporation at room temperature.

Compound (I) at 295 K

Crystal data

$(C_2H_8N)_2[SbCl_5]$
$M_r = 391.19$
Orthorhombic
Pnma
$a = 8.599\,(2)$ Å
$b = 11.992\,(2)$ Å
$c = 14.844\,(4)$ Å
$V = 1530.7\,(5)$ Å^3
$Z = 4$
$D_x = 1.697$ Mg m^{-3}
$D_m = 1.684$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections
$\theta = 7$–$11°$
$\mu = 2.641$ mm^{-1}
$T = 295\,(2)$ K
Needle
0.35 × 0.30 × 0.25 mm
Colourless

Data collection

Kuma KM-4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1990)
$T_{min} = 0.438$, $T_{max} = 0.517$
2918 measured reflections
1586 independent reflections
1187 reflections with $I > 2\sigma(I)$

$R_{int} = 0.021$
$\theta_{max} = 26.04°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -18 \rightarrow 17$
2 standard reflections every 50 reflections intensity decay: 1.04%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.062$
$S = 0.973$
1586 reflections
88 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.1980P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.328$ e Å^{-3}
$\Delta\rho_{min} = -0.415$ e Å^{-3}
Extinction correction: *SHELX*97
Extinction coefficient: 0.0064 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for (I) at 295 K*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Sb1	0.8066 (3)	3/4	0.6043 (2)	0.0440 (1)
Cl1	0.8135 (1)	0.9679 (7)	0.5959 (6)	0.0663 (2)
Cl2	1.0099 (1)	3/4	0.4932 (7)	0.0611 (3)
Cl3	0.6096 (2)	3/4	0.4828 (9)	0.0704 (3)
Cl4	1.0661 (2)	3/4	0.7262 (7)	0.0641 (3)
N1	0.8020 (4)	1.0223 (4)	0.3805 (2)	0.0800 (1)
C1	0.8256 (7)	0.9292 (5)	0.3164 (3)	0.0916 (1)
C2	0.6444 (7)	1.0626 (6)	0.3880 (4)	0.111 (2)

Table 2. *Selected geometric parameters (Å, °) for (I) at 295 K*

Sb1—Cl1	2.616 (1)	Sb1—Cl3	2.475 (1)
Sb1—Cl1^i	2.616 (1)	Sb1—Cl4	2.873 (1)
Sb1—Cl2	2.404 (1)	Sb1—Cl4^{ii}	3.257 (1)
Cl1^i—Sb1—Cl1	173.99 (4)	Cl2—Sb1—Cl4	82.37 (4)
Cl1—Sb1—Cl4	90.71 (2)	Cl2—Sb1—Cl4^{ii}	172.75 (4)
Cl1—Sb1—Cl4^{ii}	92.92 (2)	Cl3—Sb1—Cl1	88.90 (2)
Cl1^i—Sb1—Cl4	90.71 (2)	Cl3—Sb1—Cl1^i	88.90 (2)
Cl1^i—Sb1—Cl4^{ii}	92.92 (2)	Cl3—Sb1—Cl4	172.24 (4)
Cl2—Sb1—Cl1	87.20 (2)	Cl3—Sb1—Cl4^{ii}	97.38 (4)
Cl2—Sb1—Cl1^i	87.20 (2)	Cl4—Sb1—Cl4^{ii}	90.38 (2)
Cl2—Sb1—Cl3	89.87 (5)	Sb1—Cl4—Sb1^{iii}	168.44 (4)

Symmetry codes: (i) $x, \frac{3}{2} - y, z$; (ii) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (iii) $\frac{1}{2} + x, y, \frac{3}{2} - z$.

Table 3. *Hydrogen-bonding geometry (Å, °) for (I) at 295 K*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*E*···Cl1	0.88 (5)	2.46 (6)	3.266 (4)	153 (6)
N1—H1*D*···Cl4^i	0.90 (6)	2.63 (6)	3.353 (4)	138 (6)

Symmetry code: (i) $2 - x, 2 - y, 1 - z$.

Compound (I) at 85 K

Crystal data

$(C_2H_8N)_2[SbCl_5]$
$M_r = 391.19$
Orthorhombic
Pnma
$a = 8.541$ (2) Å
$b = 11.873$ (2) Å
$c = 14.830$ (3) Å
$V = 1503.9$ (5) Å^3
$Z = 4$
$D_x = 1.728$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from post-refinement on all data
$\theta = 3$–$26.5°$
$\mu = 2.688$ mm^{-1}
$T = 85$ (2) K
Needle
0.15 × 0.12 × 0.10 mm
Colourless

Data collection

DIP 2000 diffractometer
Oscillation method; 40 frames with 10° oscillation and 1° overlap
Absorption correction: none
3140 measured reflections
1622 independent reflections

1420 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\rm max} = 26.5°$
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.055$
$S = 1.069$
1622 reflections
88 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 3.8001P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.004$
$\Delta\rho_{\rm max} = 0.685$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.455$ e Å^{-3}
Extinction correction: *SHELX*97
Extinction coefficient: 0.0033 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I) at 85 K*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Sb1	0.8016 (3)	3/4	0.6002 (2)	0.0210 (1)
Cl1	0.8092 (1)	0.9699 (7)	0.5921 (5)	0.0308 (2)
Cl3	0.6044 (1)	3/4	0.4780 (8)	0.0340 (3)
Cl2	1.0089 (1)	3/4	0.4904 (7)	0.0297 (3)
Cl4	1.0658 (1)	3/4	0.72303 (7)	0.0290 (3)
N1	0.8049 (4)	1.0231 (3)	0.3780 (2)	0.0352 (7)
C1	0.8321 (5)	0.9296 (4)	0.3139 (3)	0.0410 (9)
C2	0.6395 (5)	1.0587 (4)	0.3848 (3)	0.0520 (1)

Table 5. *Selected geometric parameters (Å, °) for (I) at 85 K*

Sb1—Cl1	2.615 (1)	Sb1—Cl3	2.474 (1)
Sb1—Cl1^i	2.615 (1)	Sb1—Cl4	2.900 (1)
Sb1—Cl2	2.405 (1)	Sb1—Cl4^{ii}	3.306 (1)
Cl1^i—Sb1—Cl1	174.01 (4)	Cl2—Sb1—Cl4	81.52 (4)
Cl1—Sb1—Cl4	90.56 (2)	Cl2—Sb1—Cl4^{ii}	170.13 (4)
Cl1—Sb1—Cl4^{ii}	92.957 (2)	Cl3—Sb1—Cl1	89.03 (2)
Cl1^i—Sb1—Cl4	90.56 (2)	Cl3—Sb1—Cl1^i	89.03 (2)
Cl1^i—Sb1—Cl4^{ii}	92.96 (2)	Cl3—Sb1—Cl4	171.83 (4)
Cl2—Sb1—Cl1	87.17 (2)	Cl3—Sb1—Cl4^{ii}	99.56 (4)
Cl2—Sb1—Cl1^i	87.17 (2)	Cl4—Sb1—Cl4^{ii}	88.61 (2)
Cl2—Sb1—Cl3	90.30 (4)	Sb1—Cl4—Sb1^{iii}	166.46 (4)

Symmetry codes: (i) $x, \frac{3}{2} - y, z$; (ii) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (iii) $\frac{1}{2} + x, y, \frac{3}{2} - z$.

Table 6. *Hydrogen-bonding geometry (Å, °) for (I) at 85 K*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*E*···Cl1	0.83 (3)	2.45 (4)	3.236 (3)	159 (4)
N1—H1*D*···Cl4^i	0.85 (3)	2.48 (4)	3.275 (3)	157 (4)

Symmetry code: (i) $2 - x, 2 - y, 1 - z$.

Data collection: *Kuma Diffraction Software* (Kuma, 1997) for (I) at 295 K; *DENZO* (Otwinowski & Minor, 1997) for (I) at 85 K. Cell refinement: *Kuma Diffraction Software* for (I) at 295 K; *DENZO* for (I) at 85 K. Data reduction: *Kuma Diffraction Software* for (I) at 295 K; *DENZO* for (I) at 85 K. For both compounds, program(s) used to solve structures: *SHELX*97 (Sheldrick, 1997); program(s) used to refine structures: *SHELX*97; molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELX*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1283). Services for accessing these data are described at the back of the journal.

References

Ensinger, U., Schwarz, W. & Schmidt, A. (1982). *Z. Naturforsch. Teil B*, **37**, 1584–1589.

Knödler, F., Ensinger, U., Schwarz, W. & Schmidt, A. (1988). *Z. Anorg. Allg. Chem.* **557**, 208–218.

Kuma (1997). *Kuma Diffraction Software*. Version KM4B8. Kuma Diffraction, Wrocław, Poland.

Olivier-Fourcade, J., Ibanez, A., Jumas, J. C., Maurin, M., Lefebvre, I., Lippens, P., Lannoo, M. & Allan, G. (1990). *J. Solid State Chem.* **87**, 366–377.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. London: Academic Press.

Prassides, K., Day, P. & Cheetham, A. K. (1985). *Inorg. Chem.* **24**, 545–552.

Sheldrick, G. M. (1990). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELX97. Programs for the Solution and the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sobczyk, L., Jakubas, R. & Zaleski, J. (1997). *Pol. J. Chem.* **71**, 265–300.
Wang, X. & Liebau, F. (1996*a*). *Acta Cryst.* B**52**, 7–15.
Wang, X. & Liebau, F. (1996*b*). *Z. Kristallogr.* **211**, 437–439.
Zaleski, J. & Pietraszko, A. (1996). *Acta Cryst.* B**52**, 287–295.

Acta Cryst. (1998). C**54**, 1777–1779

(1,1′-Dimethyl-2,2′-biimidazole-N^3,$N^{3'}$)diiodoplatinum(II)

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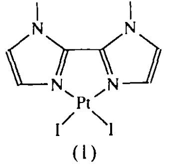
Abstract

The title compound, $[PtI_2(C_8H_{10}N_4)]$, exhibits square-planar *cis* coordination of the Pt atom to the two I atoms [mean Pt—I distance = 2.587 (6) Å] and the two unmethylated imidazole N atoms [mean Pt—N distance = 2.020 (6) Å]. Successively antiparallel near-planar $[PtI_2(C_8H_{10}N_4)]$ units form zigzag chains along the *b* axis, with Pt···Pt distances longer than the interplanar spacing.

Comment

In recent years, we have investigated the coordination chemistry of 2,2′-biimidazole derivatives, focusing on the structures and biological activities of their organotin compounds (Álvarez Boo *et al.*, 1997, and references therein). Prompted by reports (Karentzopoulos *et al.*, 1997, and references therein) that small differences between biimidazoles can be associated with significant differences in the cytotoxicity of their platinum complexes, a finding that heightens the interest of structural studies of these compounds, we have now synthesized and determined the crystal structure of (1,1′-dimethyl-2,2′-biimidazole)diiodoplatinum(II), $[Pt(Me_2bim)I_2]$, (1).



(1)

The molecular structure and atomic numbering scheme of (1) are shown in Fig. 1. The Pt atom is coordinated to the two unmethylated N atoms of the biimidazole ligand and to two I atoms in a square-planar PtN_2I_2 arrangement in which the Pt atom lies 0.0138 Å from the least-squares plane through four atoms (N_2I_2). The Pt—I and Pt—N bond distances (Table 1) are similar to those found in $[Pt(bipy)I_2]$ (bipy is bipyridyl) [Pt—I 2.589 (2) and Pt—N 2.029 (7) Å; Connick & Gray, 1994]. The N—Pt—N angle is just slightly narrower than in $[Pt(bipy)I_2]$ [79.3 (3) Å], but the I—Pt—I angle is wider than in the latter compound (87.7 Å), and is close to those found in complexes with monodentate *N*-donor ligands (Oksanen *et al.*, 1989; Raudaschl-Sieber *et al.*, 1986). The parameters of the PtN_2C_2 ring are very similar to those found in $[Pt(mimim)Cl_2].Et_4NCl$ (mimim is *N*-methyl-2,2′-biimidazole) (Karentzopoulos *et al.*, 1997); the Pt—N distances, in particular, are practically identical. The biggest difference is that the C3—C4 bond length is shorter in $[Pt(Me_2bim)I_2]$, which leads to the N—Pt—N angle being slightly narrower.

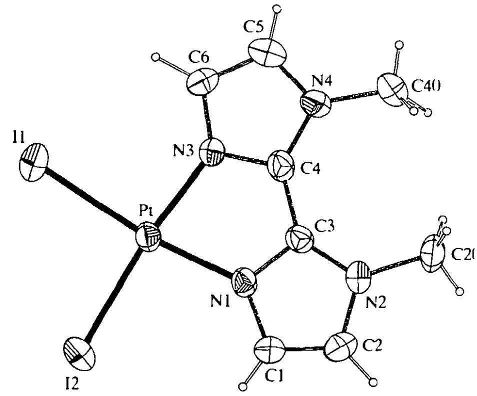


Fig. 1. The molecular structure of the title compound, showing the atom-labelling scheme. Ellipsoids are shown at the 50% probability level.

In the Me_2bim ligand, rings *A* (containing N1) and *B* (containing N3) are both planar and are almost coplanar, making angles of 2.6 (3) and 3.5 (3)°, respectively, with the PtN_2I_2 plane. This quasi-coplanarity of the two rings contrasts with the situation in $[SnMe_2Br_2(Me_2bim)]$ (23.8°; López *et al.*, 1992).

As in $[Pt(bipy)I_2]$, successively antiparallel monomer units form stacks, in this case along the *b* axis, with Pt···Pt distances [4.7388 (7) and 4.7731 (7) Å] longer than the distance between the planes of successive monomers (Fig. 2 and Table 1). The relative displacement of adjacent members of the stack gives it a zigzag structure.

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