ω scans
Absorption correction:
empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.108$, $T_{\max} = 0.123$
9321 measured reflections
9321 independent reflections

$\theta_{\max} = 27.10°$
$h = -20 \rightarrow 20$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$
104 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.159$
$S = 0.998$
9321 reflections
63 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0750P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.871$ e Å^{-3}
$\Delta\rho_{\min} = -0.973$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ge1—N1	2.112 (3)	Ge1—Br1	2.4458 (4)
N1—Ge1—Br1	90.48 (8)	C6—N1—Ge1	121.6 (3)
C6—N1—C2	119.0 (3)	C2—N1—Ge1	119.4 (3)
Br1—Ge1—N1—C2	45.543 (10)		

Three sets of 50 frames each at different values of φ and θ were used to extract 128 reflections for determination of a preliminary cell. The indexing procedure yielded an orthorhombic C-centred cell ($a = 7.34$, $b = 16.28$, $c = 37.71$ Å and $V = 4507$ Å^3) using all reflections. Thus, the collected frames were integrated using this orthorhombic cell, but after data reduction, no acceptable space group could be identified and structure solution was impossible. The reflection data showed several classes of weak reflections, but no sensible extinction conditions. However, a thorough inspection of the reciprocal space revealed that, instead of the orthorhombic cell, two monoclinic C-centred cells (related by a mirror plane perpendicular to the orthorhombic c^* axis) could be fitted to the reflection data. The reflections of the two twin components were separated sufficiently, but overlap occurred for reflections with $h = 5m$ (with m integer). After transforming the data from the orthorhombic to the monoclinic cell, using the transformation matrix $(0\bar{1}0/\bar{1}00/0,\frac{1}{5},-\frac{1}{5})$ for the direct cell parameters and the reflection indices, the resulting space group was now *C*2/*m* and the structure could be solved.

For refinement with *SHELXL*97 (Sheldrick, 1997), the twin law $(1,0,-\frac{2}{5}/010/00\bar{1})$ had to be applied to the reflection data. This means that the file containing the reflection data had to be modified by adding for every reflection with $h = 5m$ its twin counterpart (with the indices $h_{\text{twin}} = h$, $k_{\text{twin}} = k$, $l_{\text{twin}} = -0.4h - l$). The modified reflection data were read in *via HKLF*5 and an additional variable was introduced (using the *BASF* command) describing the fractional contributions of the two twin components; the ratio finally refined to 0.449 (2):0.551 (2).

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$] using a riding model with aromatic C—H = 0.95 Å or methyl C—H = 0.98 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1320). Services for accessing these data are described at the back of the journal.

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Phase transition in bis(ethyldimethylammonium) pentachloroantimonate(III)

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Abstract

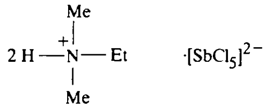
The crystal structure of a new member of the alkylammonium chloroantimonate family, namely bis(ethyldimethylammonium) pentachloroantimonate(III), $[C_2H_5NH(CH_3)_2]_2[SbCl_5]$, was determined at room temperature. The anionic sublattice consists of isolated distorted square-pyramidal $[SbCl_5]^{2-}$ units and

two crystallographically inequivalent disordered ethyldimethylammonium cations connected to anions by N—H···Cl hydrogen bonds. The disorder is realised by the presence of two positions for all C, N and H atoms, and is explained as being a result of the overall reorientation of cations along the long axis of the molecule. One second-order phase transition was found at *ca* 160 K and results in a lowering of the symmetry from orthorhombic to monoclinic or triclinic.

Comment

Alkylammonium halogenoantimonates(III) constitute a new group of salts in which a number of compounds have been found to undergo one or more phase transitions. Some are characterized by polar or non-linear optical properties. They are molecular–ionic salts with anionic sublattices composed of deformed octahedra or square pyramids isolated or connected with each other. The alkylammonium cations are located in anionic cavities. From the dielectric point of view, the most interesting compounds are those with methylammonium, dimethylammonium and trimethylammonium cations (Jakubas *et al.*, 1986). In the particular case of Sb^{III} chlorides, the following ions have been reported: $[SbCl_4]^-$, $[SbCl_5]^{2-}$, $[SbCl_6]^{3-}$ and $[Sb_2Cl_9]^{3-}$ (Knödler *et al.*, 1988; Sobczyk *et al.*, 1997). The anionic sublattices of compounds of the general formula R_2SbCl_5 (R is an organic cation) are built of either one-dimensional polyanionic zigzag chains composed of corner-sharing octahedra (Ensinger *et al.*, 1983) or isolated $[Sb_2Cl_{10}]^{4-}$ units consisting of two edge-sharing octahedra (Lipka, 1980) or isolated $[SbCl_5]^{2-}$ square pyramids (Zaleski & Pietraszko, 1995).

In the search for new compounds with interesting properties, we decided to substitute the small cations investigated earlier by similar and somewhat larger ethyldimethylammonium. By varying the ratio of $C_2H_5N(CH_3)_2$ to $SbCl_3$ from 3:2 to 10:1, we obtained only one ionic salt, of formula $[C_2H_5NH(CH_3)_2]_2[SbCl_5]$, (I). In this compound, the Sb atom is surrounded by six Cl atoms, five with Sb—Cl distances in the range 2.371 (1)–2.768 (1) Å (Table 1) and the sixth, situated further away, with an Sb···Cl distance of 3.474 (1) Å. The environment of the Sb atom may, therefore, be treated either as a considerably deformed octahedron or as a square pyramid. Taking into account the large difference between opposite axial Sb—Cl distances [2.371 (1) and 3.474 (1) Å], we will treat the Sb environment as square pyramidal with $[SbCl_5]^{2-}$ pyramids stacked one on top of the other (Fig. 1).



$$2\,H\overset{+}{\underset{\text{Me}}{\overset{\text{Me}}{N}}}\text{—Et}\quad\cdot[SbCl_5]^{2-}$$

(I)

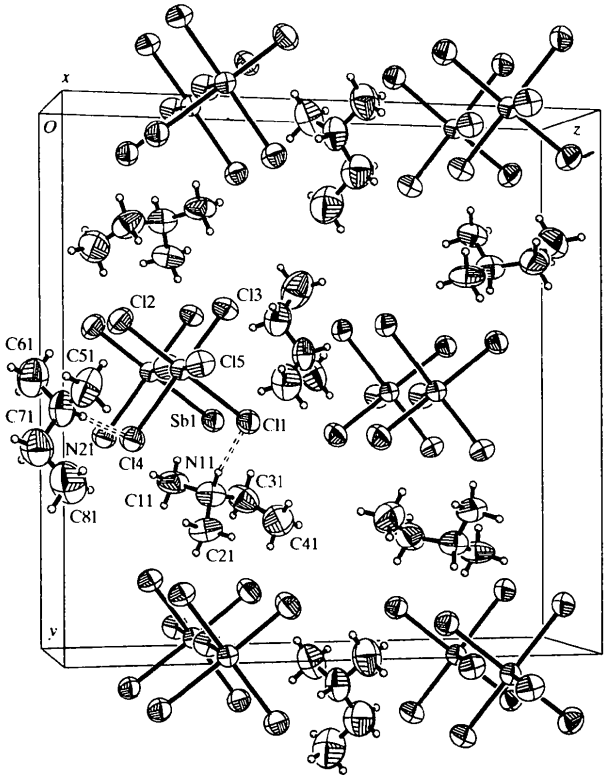


Fig. 1. Packing diagram of $[C_2H_5NH(CH_3)_2]_2[SbCl_5]$. The dashed lines denote hydrogen bonds, which tie the ethyldimethylammonium cations to the anionic sublattice (Table 2). Only one out of two disordered cation positions is shown for clarity. Displacement ellipsoids are at the 50% probability level.

In this square pyramid, the equatorial Sb—Cl bond lengths fall into the range 2.499 (1)–2.768 (1) Å. Two of them are almost identical [Sb1—Cl3 2.499 (1) Å and Sb1—Cl2 2.504 (1) Å] and involve Cl atoms *cis* to each other. The other pair of equatorial Cl atoms form much longer bonds of 2.738 (1) (Sb1—Cl1) and 2.768 (1) Å (Sb1—Cl4) [average length 2.753 (2) Å]. The axial Sb1—Cl5 bond [2.371 (1) Å] is significantly shorter. The difference between the longest (Sb1—Cl4) and shortest (Sb1—Cl3) equatorial bonds is 0.269 (2) Å. Such a large deformation of the square pyramid may be attributed to the presence of relatively strong N—H···Cl hydrogen bonds (H···Cl distance range 2.17–2.35 Å; Table 2). A shift of the electron cloud of antimony(III) in the direction of the Cl1 and Cl4 atoms, *i.e.* those involved in hydrogen bonds, results in elongation of the Sb1—Cl1 and Sb1—Cl4 bonds, and at the same time a shortening of the bonds located opposite to those that undergo elongation (Fig. 1). As a result of these interactions, the Cl1—Sb1—Cl5 and Cl4—Sb1—Cl5 angles decrease from 90° to 85.78 (4) and 88.35 (4)°, respectively (Table 1). Similar effects have been observed in other halogenoantimonates(III) (Zaleski & Pietraszko, 1996; Ciąpała *et al.*, 1996; Bujak & Zaleski, 1998).

An anionic sublattice composed of isolated $[SbCl_5]^{2-}$ anions was also observed in $[N(C_2H_5)_4]_2[SbCl_5]$ (Zaleski & Pietraszko, 1995). Here, however, the equatorial Sb—Cl bonds are almost equal, with Sb—Cl distances between 2.598 (3) and 2.605 (3) Å [average 2.602 (6) Å], whereas the axial bond is much shorter [2.346 (4) Å]. This may be connected with a shorter distance between the Sb atom belonging to one pyramid and the axial Cl atom from the other. In $[N(C_2H_5)_4]_2[SbCl_5]$, the Sb···Cl distance is equal to 8.191 (3) Å, whereas in the title compound, this distance is only 3.474 (1) Å. This suggests the presence of weak Sb···Cl interactions between the stacked pyramids in (I) which result in elongation of the axial Sb—Cl bond by 0.025 (5) Å.

In the crystal structure of (I), there are two crystallographically non-equivalent cations. Both are disordered (Fig. 2) and the disorder is realised by the presence of two positions for all C, N and H atoms, with occupancy factors of 0.5. The type of disorder suggests that the cations undergo overall reorientation around the long axis of the molecule. To check whether the disorder is dynamic in nature, we attempted to determine the crystal structure of the title compound at 90 K. On decreasing the temperature, however, we observed splitting of reflections at *ca* 160 K. This indicates that (I) undergoes structural phase transition with lowering of the symmetry to monoclinic or triclinic. The presence of the phase transition was confirmed by the temperature dependence of the lattice parameters (Fig. 3). The distinct anomaly is observed only in $c(T)$ dependence, whereas, $a(T)$ and $b(T)$ change monotonously showing no anomaly at T_c. It should be noted that we observed an increase of width of some reflections below *ca* 180 K, which may indicate that the transition takes place somewhere between 180–160 K. We did not observe any distinct anomaly in the DSC (differential scanning calorimetry) curve in the temperature range studied. This suggests that the phase transition is of second order. The postulated phase transition is probably connected with ordering of at least one of the structurally independent cations on lowering the temperature.

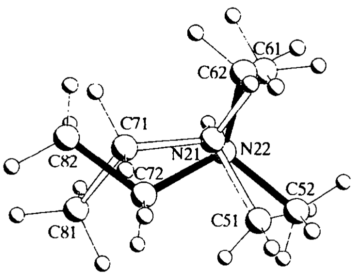


Fig. 2. View of the disordered ethyldimethylammonium cation.

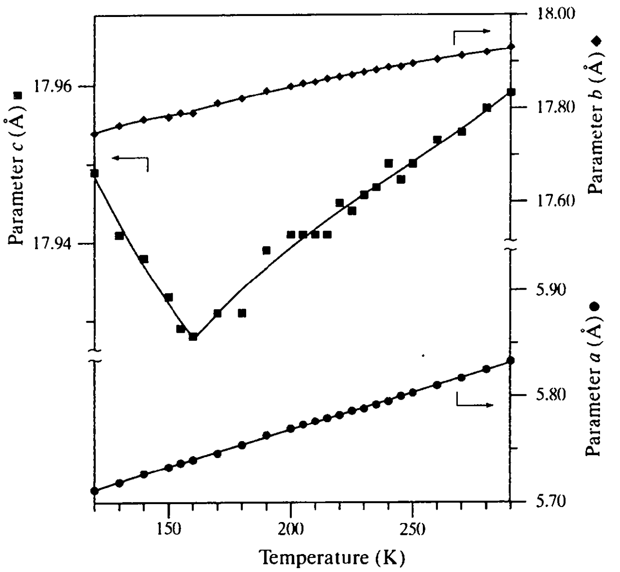


Fig. 3. Temperature dependence of the lattice parameters of bis(ethyldimethylammonium) pentachloroantimonate(III) in the vicinity of the phase transition at T_C = 160 K.

Experimental

The title compound (m.p. 424–426 K) was prepared by mixing ethyldimethylamine and antimony trichloride (molar ratio from 3:2 to 10:1) in an aqueous solution of hydrochloric acid. Crystals of suitable dimensions for X-ray structure analysis were grown by slow evaporation at room temperature from an aqueous solution of hydrochloric acid. The DSC studies were carried out on a Perkin–Elmer DSC-7 calorimeter with cooling/heating rates of 20 and 10 K min^{-1}. The measurements were performed between 100 and 500 K.

Crystal data

$(C_4H_{12}N)_2[SbCl_5]$
M_r = 447.29
Orthorhombic
$P2_12_12_1$
a = 5.826 (1) Å
b = 17.925 (4) Å
c = 17.949 (4) Å
V = 1874.4 (7) Å^3
Z = 4
D_x = 1.585 Mg m^{-3}
D_m = 1.57 (1) Mg m^{-3}
D_m measured by flotation in $CCl_4/CHCl_3$

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 31 reflections
θ = 6–13°
μ = 2.167 mm^{-1}
T = 293 (2) K
Needle
0.38 × 0.37 × 0.35 mm
Colourless

Data collection

Kuma KM-4 diffractometer
ω–θ scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1990)
T_{min} = 0.446, T_{max} = 0.486
3159 measured reflections
2166 independent reflections (plus 911 Friedel-related reflections)

2705 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 26.06°
$h = -6 \rightarrow 6$
$k = -21 \rightarrow 0$
$l = -21 \rightarrow 0$
2 standard reflections every 50 reflections intensity decay: 0.78%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.079$
$S = 1.121$
3077 reflections
239 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.3435P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.038$
$\Delta\rho_{max} = 0.439$ e Å^{-3}
$\Delta\rho_{min} = -0.518$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0948 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.03 (3)

Table 1. *Selected geometric parameters (Å, °)*

Sb1—Cl1	2.738 (1)	Sb1—Cl4	2.768 (1)
Sb1—Cl2	2.504 (1)	Sb1—Cl5	2.371 (1)
Sb1—Cl3	2.499 (1)	Sb1···Cl5^{i}	3.474 (1)
Cl1—Sb1—Cl2	174.90 (4)	Cl2—Sb1—Cl4	90.19 (4)
Cl1—Sb1—Cl3	89.60 (4)	Cl2—Sb1—Cl5	89.12 (4)
Cl1—Sb1—Cl4	89.67 (4)	Cl3—Sb1—Cl4	178.60 (4)
Cl1—Sb1—Cl5	85.78 (4)	Cl3—Sb1—Cl5	90.41 (4)
Cl2—Sb1—Cl3	90.44 (4)	Cl4—Sb1—Cl5	88.35 (4)

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*D*···Cl1	0.90	2.35	3.238 (9)	170
N12—H12*D*···Cl1	0.90	2.17	3.054 (8)	169
N21—H21*D*···Cl4	0.90	2.22	3.114 (10)	176
N22—H22*D*···Cl4	0.90	2.23	3.132 (11)	177

Data collection: *Kuma Diffraction Software* (Kuma, 1996). Cell refinement: *Kuma Diffraction Software*. Data reduction: *Kuma Diffraction Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *SHELXTL* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1330). Services for accessing these data are described at the back of the journal.

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[*N*-Acetyl-*N*′-methylureato(2–)-*N*,*N*′](η^5-pentamethylcyclopentadienyl)(triphenylphosphine-*P*)iridium(III) chloroform solvate

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Abstract

The title complex, $[Ir(C_{10}H_{15})(C_4H_6N_2O_2)(C_{18}H_{15}P)]\cdot CHCl_3$, displays a 'piano-stool'-type configuration of ligands, with the Ir atom in an Ir—N*R*—C(O)—N*R*′ ring system. This is the first structure determination of a coordinatively saturated iridaureylene complex.

Comment

Ureylene complexes containing the *M*—N*R*—C(O)—N*R*′ four-membered ring system with a coordinated urea dianion are known for the majority of transition metals (Dinger & Henderson, 1998*a*; Braunstein & Nobel, 1989; Cenini & La Monica, 1976). A variety of synthetic routes have been described for the preparation of such complexes (Dinger & Henderson, 1998*a*) and we have recently been investigating the use of silver(I) oxide as a reagent for the synthesis of transition metal ureylene complexes (Dinger & Henderson, 1998*a*,*b*; Dinger *et al.*, 1996, 1998). As part of these studies, the iridium(III) ureylene complex [Cp*Ir{NAcC(O)NAc}(PPh_3)] (Cp* is pentamethylcyclopentadienyl), derived from *N*,*N*′-diacetylurea, was reported (Dinger *et al.*, 1998). We now report the crystal structure of the analogous iridium(III) complex derived from *N*-acetyl-*N*′-methylurea, [Cp*Ir{NAcC(O)NMe}(PPh_3)]·$CHCl_3$, (I); the platinum com-

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