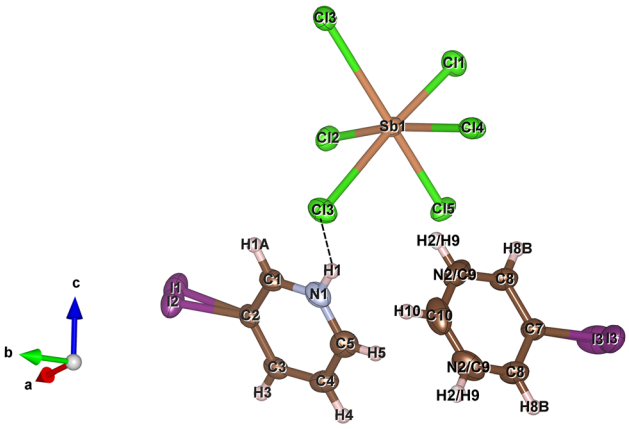
Yuxin Ma, Munan Hao, Ruijin Sun, Shifeng Jin and Changchun Zhao*

Crystal structure of tris(3-iodopyridin-1-ium) *catena*-poly[(hexachlorido-κ^1*Cl*)-(μ$_2$-trichlorido-κ^2*Cl:Cl*)diantimony(III)], $C_{15}H_{15}Cl_9I_3N_3Sb_2$



https://doi.org/10.1515/ncrs-2021-0156
Received April 24, 2021; accepted June 8, 2021;
published online June 30, 2021

Abstract

$C_{15}H_{15}Cl_9I_3N_3Sb_2$, monoclinic, *C*2/*c* (no. 15), a = 28.2633(7) Å, b = 12.4964(3) Å, c = 9.1542(3) Å, β = 99.5840(10)°, V = 3188.04(15) Å^3, Z = 4, $R_{gt}(F)$ = 0.0274, $wR_{ref}(F^2)$ = 0.0687, T = 273.15 K.

CCDC no.: 2088399

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow needles
Size:	0.23 × 0.17 × 0.06 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	5.37 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture, φ and ω
θ_{max}, completeness:	28.7°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	24,356, 4107, 0.051
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 3595
$N(param)_{refined}$:	163
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

Source of material

Dissolve antimony trioxide (2 mmol) in 10 mL hydrochloric acid (36.5 w%) to obtain an antimony trichloride solution, and then slowly add 3-iodotoluene (3 mmol). After the solution was completely clear, the yellow crystals of the title compound were obtained by evaporating the resulting solution at room temperature for 5 days.

Experimental details

The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. Hydrogen atoms were added using geometric restraints. The I atom (I1, I2) in 3-iodopyridinium cation is disordered, occupying two positions with 0.522(16) and 0.478(16) occupancy rate, respectively. C9 and N2 are mixed occupied, the occupancies are 0.5 for each.

Comment

In recent decades, organic VA group metal halides have been widely reported, and researchers have paid much attention to them because of their excellent ferroelectric properties and nonlinear optics [5–7]. The chemical formula of this materials can be summarized as $R_AM_BX_{3B+A}$ (where R = organic cations, M = VA group metal, and X = Cl,

***Corresponding author: Changchun Zhao**, School of Science, China University of Geosciences, Beijing 100083, P. R. China, E-mail: zhaocc@cugb.edu.cn
Yuxin Ma and Ruijin Sun, School of Science, China University of Geosciences, Beijing 100083, P. R. China. https://orcid.org/0000-0003-1636-5605 (Y. Ma)
Munan Hao and Shifeng Jin, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China. https://orcid.org/0000-0002-3702-0430 (M. Hao)

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sb1	0.89735 (2)	0.33505 (2)	0.65873 (2)	0.03591 (7)
Cl1	0.89849 (3)	0.19870 (6)	0.47270 (9)	0.05502 (19)
Cl2	0.80888 (3)	0.34474 (6)	0.61191 (9)	0.05179 (18)
Cl3	0.90173 (3)	0.50262 (7)	0.40647 (10)	0.0598 (2)
Cl4	1.000000	0.31148 (10)	0.750000	0.0541 (3)
Cl5	0.89046 (3)	0.20293 (7)	0.84625 (9)	0.05315 (19)
N1	0.82304 (10)	0.6197 (2)	0.5372 (3)	0.0544 (6)
H1	0.848697	0.609782	0.499939	0.065*
C1	0.78240 (12)	0.5756 (2)	0.4697 (4)	0.0502 (7)
H1A	0.782296	0.534125	0.385360	0.060*
C2	0.74078 (11)	0.5914 (2)	0.5243 (3)	0.0458 (6)
C3	0.74199 (12)	0.6539 (2)	0.6504 (3)	0.0484 (7)
H3	0.714112	0.665622	0.689562	0.058*
C4	0.78478 (14)	0.6985 (3)	0.7169 (4)	0.0572 (8)
H4	0.785872	0.741902	0.799933	0.069*
C5	0.82585 (14)	0.6782 (3)	0.6595 (4)	0.0605 (9)
H5	0.855238	0.705112	0.705717	0.073*
I1[a]	0.67553 (13)	0.5225 (3)	0.4047 (5)	0.0724 (4)
I2[b]	0.68253 (14)	0.5051 (3)	0.4498 (9)	0.0710 (8)
C7	1.000000	0.8398 (4)	0.750000	0.0501 (10)
C8	0.99062 (14)	0.7843 (3)	0.6200 (4)	0.0605 (9)
H8B[c]	0.984738	0.821002	0.530386	0.073*
H8A[c]	0.984738	0.821002	0.530386	0.073*
C10	1.000000	0.6223 (5)	0.750000	0.087 (2)
H10	1.000000	0.5480 (10)	0.750000	0.14 (3)*
C9[c]	0.98989 (15)	0.6773 (3)	0.6212 (5)	0.0779 (11)
H9[c]	0.982319	0.640183	0.532331	0.094*
I3[c]	1.01052 (9)	1.00450 (4)	0.7583 (3)	0.1088 (8)
N2[c]	0.98989 (15)	0.6773 (3)	0.6212 (5)	0.0779 (11)
H2[c]	0.982889	0.642977	0.539020	0.094*

[a]Occupancy: 0.522(16), [b]Occupancy: 0.478(16), [c]Occupancy: 0.5.

Br, I), Nevertheless, ferroelectricity is limited to few of them only, e.g., RMX_4, $R_3M_2X_9$, R_2MX_5, and $R_5M_2X_{11}$ [8], in which the $[MX_6]$ octahedron in $R_3M_2X_9$ [9–12] has a different connection pattern. The $[MX_6]$ octahedra can form either infinite one-dimensional (1D) double chains [13], two-dimensional (2D) layers [14], discrete bioctahedral (0D) [15], or four-octahedral (0D) units $[M_4X_{18}]$ [8, 16].

The asymmetric unit of the compound synthesized in this paper consists of one Sb atom, 4.5 Cl atoms, and 1.5 organic cations. Sb atom is coordinated with six surrounding Cl atoms and forms a $[SbCl_6]$ seriously distorted octahedron. Two adjacent $SbCl_6$ octahedrons are connected by sharing Cl3 atoms, and their corresponding Sb1–Cl3–Sb1 *trans*-angles are 175.46(4)°, forming a 1D chain. Two 1D chains are bridged by Cl4 atoms to form a 1D double chain Sb1–Cl4–Sb1 and the *trans*-angles are 168.33(6)°. One 3-iodopyridinium cation is located in the 1D double chain, while the other 3-iodopyridinium cations are located between two 1D chains and connect the $[SbCl_6]$ octahedron with hydrogen bonds. In the $[SbCl_6]$ octahedra, the Sb–Cl bond length range is 2.4130(6) to 3.1354(7) Å, and the Cl–Sb–Cl *cis*-angle range is 85.47(2)–96.89(2)°.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: National Natural Science Foundation of China and excellent mentor fund for fundamental research under granting numbers: No. 51772323, No. 51472224, and No. 2652019324.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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