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The crystal structure of bis(2-hydroxypyrimidinium) pentachloridobismuthate(III), $(C_4N_2H_5O)_2BiCl_5$

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.19 × 0.11 × 0.09 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	11.2 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 Venture, φ and ω
$\theta_{\max}$, completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	28978, 4209, 0.055
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3737
$N(\text{param})_{\text{refined}}$:	181
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Under the ice bath conditions, dibismuth trioxide (1 mmol) was dissolved in a heat-resistant bottle set with 5 mL concentrated hydrochloric acid (37 w%) to obtain the solution of bismuth trichloride. Then 2-hydroxypyrimidine hydrochloride (4 mmol) was added thereto. The mixture was placed on a hot plate at 353 K and refluxed for two hours to form a clear, orange solution. The title crystal could be obtained by the slow evaporation of the resulting solution for 3 days at room temperature.

Experimental details

Hydrogen atoms were added using geometric restraints.

Comment

A class of organic cationic halometalates based on the group 15 M^{III} (Sb^{III} and Bi^{III}) are defined by the general formula $R_aM_bX_a + 3b$ (where X = Cl, Br or I; M = Sb(III) or Bi(III); and R is a monovalent organic cation). Most crystals belonging to this family exhibit interesting physical properties. The aspherical distribution of the ns² lone-pair electrons in the M^{III} center often plays a key role in determining the collective performance of the material [5]. In particular, its stereochemical activity favors the formation of acentric materials with potential optical or ferroelectric properties [6].

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Abstract

$C_8N_4H_{10}O_2BiCl_5$, monoclinic, $P2_1/a$ (no. 14, non-standard setting of $P2_1/c$), $a = 9.1065(5)$ Å, $b = 14.5950(8)$ Å, $c = 12.7159(8)$ Å, $\beta = 93.557(2)^\circ$, $V = 1687.28(17)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0249$, $wR_{\text{ref}}(F^2) = 0.0612$, $T = 273$ K.

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The asymmetric unit of the title salt structure is shown in the figure. Table 1 contains crystallographic data and Table 2

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Bi1	0.19321(2)	0.87301(2)	0.24400(2)	0.02276(5)
C1	0.2254(4)	1.1828(3)	0.1084(3)	0.0273(8)
C2	0.4557(5)	1.1450(3)	0.0413(4)	0.0381(10)
H2	0.5578	1.1477	0.0494	0.046*
C3	0.3901(5)	1.1017(3)	−0.0444(4)	0.0425(10)
H3A	0.4452	1.0764	−0.0962	0.051*
C4	0.2403(5)	1.0973(3)	−0.0507(4)	0.0417(10)
H4A	0.1915	1.0669	−0.1068	0.050*
C5	0.3784(4)	1.1829(3)	0.4001(3)	0.0294(8)
C6	0.3538(6)	1.1097(3)	0.5662(4)	0.0481(12)
H6	0.3992	1.0887	0.6291	0.058*
C7	0.2056(6)	1.1018(3)	0.5488(4)	0.0447(11)
H7	0.1479	1.0756	0.5986	0.054*
C8	0.1448(5)	1.1342(3)	0.4550(4)	0.0347(9)
H8	0.0439	1.1290	0.4397	0.042*
Cl1	0.00854(10)	1.00531(6)	0.24507(9)	0.0349(2)
Cl2	0.39577(11)	0.99631(6)	0.25138(9)	0.0346(2)
Cl3	0.17869(11)	0.87935(7)	0.02931(9)	0.0364(2)
Cl4	−0.06121(12)	0.75510(7)	0.23715(10)	0.0512(3)
Cl5	0.21728(11)	0.86592(7)	0.45602(9)	0.0371(2)
N1	0.3757(3)	1.1831(2)	0.1131(3)	0.0295(7)
H1	0.4212	1.2097	0.1660	0.035*
N2	0.1636(4)	1.1363(2)	0.0230(3)	0.0360(8)
H2A	0.0693	1.1321	0.0167	0.043*
N3	0.4350(4)	1.1473(3)	0.4937(3)	0.0390(8)
H3	0.5288	1.1492	0.5066	0.047*
N4	0.2281(3)	1.1726(2)	0.3861(3)	0.0299(7)
H4	0.1856	1.1925	0.3283	0.036*
O1	0.1525(3)	1.2199(2)	0.1726(2)	0.0384(7)
O2	0.4530(3)	1.2192(2)	0.3375(2)	0.0428(7)

Single crystal X-ray diffraction reveals that the crystal structure of the title compound consisting of two substructures in an asymmetric unit: the BiCl₅^{2−} anion skeleton and a pair of C₄N₂H₅O⁺ cations, which subject to hydrogen bonding interactions. Geometrically, the anionic skeleton of the title compound is classified as a one-dimensional structure and the C₄N₂H₅O⁺ cations in the lattice separate the BiCl₅^{2−}

co-angled octahedral zigzag chains. In the crystal structure, Bi atoms are six-coordinated, and Cl4 bridges two adjacent Bi atoms to form a {BiCl₅}_n infinite chain [7, 8]. The two different Bi-Cl4 bond lengths are 2.883(1) Å and 2.920 Å, respectively, which are significantly larger than the bond lengths between other terminal chlorido ligands (from 2.5612(9) Å to 2.7274(11) Å) which is due to the repulsive force between adjacent Bi atoms [6].

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