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Crystal structure of bis(octahydrocyclopenta[c]pyrrolium)pentachlorobismuthate(III), $(C_7NH_{14})_2BiCl_5$

Table 1: Data collection and handling.

Crystal:	Colorless needle-like
Size:	0.98 × 0.35 × 0.24 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	8.84 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 Venture, φ and ω
θ_{max} , completeness:	28.4°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	35963, 5374, 0.052
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 4813
$N(param)_{refined}$:	199
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Bi1	0.60710(2)	0.64696(2)	0.18668(2)	0.02901(4)
C1	0.5353(3)	0.1174(6)	0.3293(2)	0.0687(11)
H1C	0.6002	0.1690	0.3506	0.082*
H1D	0.5427	−0.0115	0.3273	0.082*
C2	0.4542(3)	0.1660(5)	0.36393(19)	0.0550(9)
H2	0.4751	0.2694	0.3918	0.066*
C3	0.4219(4)	0.0096(7)	0.4000(2)	0.0808(13)
H3A	0.4744	−0.0813	0.4094	0.097*
H3B	0.4090	0.0509	0.4395	0.097*
C4	0.3267(3)	−0.0641(6)	0.3571(2)	0.0796(13)
H4A	0.3427	−0.1513	0.3280	0.096*
H4B	0.2847	−0.1210	0.3815	0.096*
C5	0.2745(3)	0.0932(7)	0.3223(2)	0.0734(12)
H5A	0.2359	0.1564	0.3475	0.088*
H5B	0.2288	0.0568	0.2827	0.088*
C6	0.3590(3)	0.2108(5)	0.31038(17)	0.0501(8)
H6	0.3412	0.3376	0.3121	0.060*
C7	0.3887(3)	0.1709(6)	0.24972(19)	0.0603(10)
H7A	0.3700	0.0495	0.2357	0.072*
H7B	0.3560	0.2535	0.2166	0.072*
C8	0.3790(3)	−0.1346(5)	−0.01029(18)	0.0542(9)
H8A	0.3946	−0.0079	−0.0110	0.065*
H8B	0.4386	−0.1974	0.0136	0.065*
C9	0.2901(3)	−0.1647(5)	0.01858(16)	0.0469(8)
H9	0.3038	−0.2668	0.0477	0.056*
C10	0.2582(3)	−0.0020(6)	0.05170(19)	0.0712(12)
H10A	0.2412	−0.0376	0.0906	0.085*
H10B	0.3125	0.0856	0.0617	0.085*

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Abstract

$(C_7NH_{14})_2BiCl_5$, monoclinic, $P2_1/n$ (no. 14), $a = 13.6087(3)$ Å, $b = 7.4645(2)$ Å, $c = 21.7967(6)$ Å, $\beta = 104.3220(9)^\circ$, $V = 2145.34(10)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0205$, $wR_{ref}(F^2) = 0.0528$, $T = 293(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.1662(3)	0.0748(6)	0.0052(2)	0.0681(11)
H11A	0.1228	0.1375	0.0273	0.082*
H11B	0.1864	0.1573	−0.0238	0.082*
C12	0.1125(3)	−0.0844(6)	−0.0297(2)	0.0609(9)
H12A	0.0698	−0.0494	−0.0706	0.073*
H12B	0.0709	−0.1432	−0.0054	0.073*
C13	0.1989(2)	−0.2069(5)	−0.03771(17)	0.0471(7)
H13	0.1793	−0.3331	−0.0369	0.057*
C14	0.2364(3)	−0.1680(5)	−0.09583(17)	0.0527(8)
H14A	0.2031	−0.2444	−0.1308	0.063*
H14B	0.2244	−0.0437	−0.1086	0.063*
Cl1	0.71180(6)	0.33911(10)	0.23719(4)	0.04945(19)
Cl2	0.68667(8)	0.64061(11)	0.08643(5)	0.0536(2)
Cl3	0.46583(5)	0.45268(10)	0.12149(4)	0.04471(16)
Cl4	0.50809(7)	0.63152(11)	0.28113(4)	0.0509(2)
Cl5	0.51675(6)	0.95230(9)	0.14568(4)	0.04417(16)
N1	0.4987(3)	0.1935(5)	0.26530(18)	0.0656(9)
H1A	0.5151	0.3089	0.2650	0.079*
H1B	0.5255	0.1354	0.2377	0.079*
N2	0.34627(19)	−0.2068(4)	−0.07578(13)	0.0465(6)
H2A	0.3792	−0.1528	−0.1012	0.056*
H2B	0.3576	−0.3242	−0.0762	0.056*

Source of material

Dibismuth trioxide (1 mmol) was dissolved in 9 mL hydrochloric acid (36.5 w%) to obtain a bismuth trichloride solution, then 3-azabicyclo[3.3.0]octane hydrochloride (4 mmol) was added slowly. After the solution was completely clarified, colorless crystals of the title compound were obtained by evaporating the resulting solution for 3 days at room temperature.

Experimental details

The C- and N-bound H atoms were placed geometrically and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Comment

The molecular-ionic hybrids halogenoantimonates(III) and halogenobismuthates(III) are known to exhibit extremely rich chemical compositions with general formula $\text{R}_a\text{M}_b\text{X}_{a+3b}$ (where $\text{X} = \text{Cl}, \text{Br}$ or I ; $\text{M} = \text{Sb(III)}$ or Bi(III) ; and R is a monovalent organic cation) [5]. The main structural feature of $\text{R}_a\text{M}_b\text{X}_{a+3b}$ is the presence of Jahn-Teller deformed anionic MX_6 octahedral units that can form various aggregates like anionic discrete bioctahedra, corner/edge/face-connected chains or layers [6, 7]. Accordingly, the anionic configurations of the known $\text{R}_a\text{M}_b\text{X}_{a+3b}$ compounds also cover a rich geometry from 0D to 3D [8]. Among them, the ones described by the RMX_4 , R_2MX_5 , $\text{R}_3\text{M}_2\text{X}_9$ and $\text{R}_5\text{M}_2\text{X}_{11}$ chemical compositions are the most desired due to the fact that

they frequently exhibit ferroelectric properties [9]. Here, a new R_2MX_5 compound with chemical formula $(\text{C}_7\text{NH}_{14})_2\text{BiCl}_5$ was synthesized. Single crystal X-ray diffraction reveals that the crystal structure of the title compound consists of two substructures in an asymmetric unit: the BiCl_5^{2-} anionic group and a pair of $\text{C}_7\text{NH}_{14}^+$ cations, which are connected by hydrogen bonds. Each Bi(III) cation is coordinated by six Cl anions with Bi–Cl bond distances in the range of 2.5430(7) Å to 2.9768(8) Å and Cl–Bi–Cl angles with two cis-positioned Cl anions varying from 84.553(23)° to 95.455(26)°. The BiCl_6 element maintains a typical octahedral geometry, in which the Cl1 atom acts as a bridge, connecting the adjacent Bi(III) cations with a bond angle of 152.94(3)° for Bi1–Cl1–Bi1. Thus, one-dimensional zigzag chains are formed, extending along the *c*-axis. The $\text{C}_7\text{NH}_{14}^+$ organic cations are fixed between chains by weak $\text{N–H} \cdots \text{Cl}$ hydrogen bonds, and the donor-acceptor distance ranges from 2.4056(9) Å to 2.4340(9) Å.

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