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The crystal structure of 3-butyl-1-methyl-1*H*-imidazol-3-ium *catena*-poly[tris(μ_2 -bromido- κ^2 Br:Br)lead(II)], C₈H₁₅Br₃N₂Pb

Figure 1: Showing the organic cation and a part of the polymeric PbCl₃[−] coordination polymer.

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Abstract

C₈H₁₅Br₃N₂Pb, orthorhombic, *P*₂₁₂₁₂ (no. 19), *a* = 7.7781(9) Å, *b* = 9.7129(15) Å, *c* = 19.158(2) Å, *V* = 1447.3(3) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0376, *wR*_{ref}(*F*²) = 0.0780, *T* = 100 K.

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

Source of material

In a representative experiment 1-methylimidazole (0.01 mol; 0.8210 g) and *n*-butyl bromide (0.01 mol, 1.3703 g) were dissolved in ethonal. This mixture was heated to 80 °C. Subsequently, a solution of lead bromide (0.01 mol; 3.6902 g) in *N,N*-dimethyl formamide (DMF; 50 mL) was added to the mixture. The obtained solution was filtered. Colorless

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.12 × 0.11 × 0.10 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	19.9 mm ^{−1}
Diffractometer, scan mode:	SuperNova, ω
θ _{max} , completeness:	25.0°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	9348, 2555, 0.061
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 2311
<i>N</i> (<i>param</i>) _{refined} :	129
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Diamond [4]

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}
Pb1	0.33382(5)	0.24408(6)	0.50211(2)	0.01423(17)
Br1	0.54694(15)	0.45583(17)	0.43895(8)	0.0187(4)
Br2	0.09795(17)	0.45597(16)	0.55817(8)	0.0182(3)
Br3	0.09135(16)	0.22871(16)	0.37833(7)	0.0185(3)
N1	0.6359(12)	0.7536(15)	0.5853(5)	0.020(3)
N2	0.4319(13)	0.7094(13)	0.6591(6)	0.018(3)
C1	0.5374(16)	0.6547(17)	0.6133(7)	0.020(3)
H1	0.542903	0.561707	0.602002	0.024*
C2	0.5882(18)	0.8742(17)	0.6157(8)	0.026(4)
H2	0.634296	0.960579	0.606330	0.032*
C3	0.4625(19)	0.8463(17)	0.6617(8)	0.026(4)
H3	0.406692	0.909744	0.690163	0.032*
C4	0.3096(17)	0.6299(17)	0.7024(7)	0.022(4)
H4A	0.358477	0.615889	0.748453	0.026*
H4B	0.291242	0.540174	0.681432	0.026*
C5	0.1382(17)	0.7040(18)	0.7092(8)	0.030(4)
H5A	0.154443	0.788331	0.735542	0.035*
H5B	0.096720	0.728650	0.663143	0.035*
C6	0.0050(19)	0.6155(17)	0.7455(8)	0.028(4)
H6A	0.053202	0.580519	0.788673	0.033*
H6B	−0.021973	0.537256	0.716004	0.033*
C7	−0.1607(18)	0.694(2)	0.7618(8)	0.040(5)
H7A	−0.207158	0.731123	0.719464	0.060*
H7B	−0.136433	0.766876	0.793916	0.060*
H7C	−0.242668	0.631652	0.782273	0.060*
C8	0.7672(17)	0.7352(18)	0.5319(7)	0.027(4)
H8A	0.726309	0.771364	0.488349	0.041*
H8B	0.792143	0.638949	0.526751	0.041*
H8C	0.869838	0.783220	0.545482	0.041*

Figure 2: View along the polymeric PbBr_3^- chains with a view along $[\bar{1}00]$. Cations fill the space between the almost hexagonally stacked anionic chains.

needle-shaped crystals were obtained upon slow evaporation of the solvent at room temperature after 14 days.

Experimental details

Coordinates of hydrogen atoms were refined without any constraints or restraints. All H atoms were positioned geometrically ($\text{C}-\text{H} = 0.93\text{--}0.98 \text{ \AA}$), and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ or $1.5U_{\text{eq}}(\text{methyl groups})$.

Comment

Haloplumbate materials with hybrid organic-inorganic components have received considerable research interests due to their tunable structures from the discrete mononuclear or polynuclear species to the infinite variety with higher dimensionality [5–7] and the discovery of the unprecedented photovoltaic and optoelectronic properties in APbX_3 compounds with a perovskite structure [8–10]. The octahedral building block of lead halides, PbX_3^- , has been used to construct versatile crystal structures from one-dimensional chains to three-dimensional frameworks [11, 12]. Furthermore, we tried to introduce soft organic components into haloplumbate and obtained some compounds showing novel dielectric properties [6]. This contribution is part of our continuing interest in synthesis and single-crystal characterization of hybrid compound based on PbBr_3^- units.

Figure 1 shows the asymmetric unit, which consists of one Pb^{2+} and three different Br^- (Br_1 , Br_2 and Br_3) ions together with one 1-methyl-3-butylimidazole cation (symmetric code: $a = x + 1/2, -y + 1/2, -z + 1$; $b = x + 1, y, z$;

$c = x + 3/2, -y + 1/2, -z + 1$; $d = x - 1/2, -y + 1/2, -z + 1$). The Pb^{2+} ion is coordinated with six Br^- to form the slightly distorted PbBr_6 octahedron. The similar molecular structure has been reported by Rao *et al.* [11], however, they have different cell parameters, and show a different packing of the structure. In reference [11], the Pb^{2+} ion is coordinated with four Br^- ions forming tetrahedron.

In the title structure the bond lengths and angles within the PbBr_6 octahedron are in the expected ranges. The $\text{Pb}-\text{Br}$ lengths range from $2.9055(16)$ to $3.0544(15) \text{ \AA}$ and $\text{Br}-\text{Pb}-\text{Br}$ angles fall within the range of $79.07(4)^\circ - 176.58(3)^\circ$ at 100 K. These geometric parameters within the coordination octahedron are comparable to other haloplumbates [7]. The neighboring PbBr_6 octahedra are connected *via* face-sharing to form a $[\text{PbBr}_3]^\infty$ chain (Figure 2). In imidazolium cation the imidazolium head group is planar and the *n*-butyl chain adopts an all-anti conformation. The similar conformation was observed in $[\text{C}_4\text{mim}][\text{HgBr}_3]$ [13]. The structure differences are shown in following: Compound $[\text{C}_4\text{mim}][\text{HgBr}_3]$ crystallizes in the acentric space group *Cc*; Hg^{2+} ion shows bipyramids and these bipyramids are connected by sharing edge forming linear chain.

As illustrated in Figure 2, the 1-methyl-3-butylimidazolium counterions are incorporated into the space between the inorganic chains. Each ions chain is surrounded by six cations stacks. It is noted that there is no π - π stacking interaction between the neighboring imidazole rings, and there exist only weak van der Waals faces between the inorganic and organic components besides the Coulomb attractions.

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