Crystal structure of bis(4-bromophenylaminium) tetraiodoplumbate(II), $(\text{BrC}_6\text{H}_4\text{NH}_3)_2\text{PbI}_4$

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Abstract

$\text{C}_{12}\text{H}_{14}\text{Br}_2\text{I}_4\text{N}_2\text{Pb}$, monoclinic, $P12_1/c1$ (no. 14), $a = 15.5755(2)$ Å, $b = 8.2019(1)$ Å, $c = 9.0917(1)$ Å, $\beta = 100.084(1)^\circ$, $V = 1143.5$ Å³, $Z = 2$, $R_{\text{gof}}(F) = 0.031$, $wR_{\text{ref}}(F^2) = 0.066$, $T = 293$ K.

Source of material

Crystals of the title compound were prepared by slow-cooling method similar to [1,2], with all synthetic processes being operated in dry argon atmosphere or in vacuum. 1.73 g (0.01 mol) of *p*-bromoaniline was dissolved in the mixture of concentrated (45.0 %) aqueous hydroiodic acid and anhydrous ethanol ($v/v = 3:2$) under following argon at 60 °C. The concentrated (45.0 %) aqueous HI solution of 2.30 g (5.0 mmol) of PbI_2 then dripped from the constant pressure funnel to the above solution gradually. The resulting solution was allowed to sit at 60 °C for 4 hours and then slowly (5 °C/h) cooled to room temperature. The precipitate was filtered off. After drying in vacuum, yellow plate-like crystals

(3.52 g, 66.4 %) of high quality were obtained. Elemental analysis — found: C, 12.88 %; H, 1.335 %; N, 2.606 %; calculated for $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{I}_4\text{N}_2\text{Pb}$: C, 13.59 %; H, 1.33 %; N, 2.64 %.

Experimental details

All H atoms were positioned geometrically ($d(\text{C}—\text{H}) = 0.93 - 0.98$ Å), and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{carrier})$ or $1.5 U_{\text{eq}}(\text{amino groups})$.

Discussion

The title organic-inorganic hybrid $(\text{BrC}_6\text{H}_4\text{NH}_3)_2\text{PbI}_4$ is isostructural to $(\text{ClC}_6\text{H}_4\text{NH}_3)_2\text{PbI}_4$ (figure, top) [3]. The crystal structure of the title compound contains alternate well-ordered inorganic perovskite layers and organic bimolecular layers along [100]. A corner-sharing distorted PbI_6 octahedron connects neighboring ones through four bridging iodine atoms to constitute the former, and two kinds of parallel 4-bromophenylaminium cations form the latter (figure, bottom). Hydrogens of organic cations bond to iodines in the perovskite layers through the ammonium groups and C—H groups. The perovskite sheets contain one independent Pb atom, which has a distorted octahedral iodine coordination with Pb—I bond lengths ranging from 3.1690(4) Å to 3.2255(3) Å and I—Pb—I bond angles ranging from 86.361(4)° to 93.639(4)°, and even to 180.0°. The average Pb—I bond length for the PbI_6 octahedron is 3.2095(3) Å. These values are similar to those found in $(\text{ClC}_6\text{H}_4\text{NH}_3)_2\text{PbI}_4$ and $(\text{BAESBT})\text{PbI}_4$ (BAESBT = 5,5'-bis(ammoniummethylsulfanyl)-2,2-bithiophene) [4]. The coordination type involving PbI_6 of the title compound differs from those observed in $(\text{C}_{12}\text{H}_{14}\text{NH}_2)_2\text{PbI}_6$ [5], which has three coordination types, namely, nearly ideal octahedral symmetry, distorted octahedral coordination and trigonal prismatic coordination. Face-shared PbI_6 octahedra and trigonal prisms link with one another to form chains. In $(\text{C}_{12}\text{H}_{14}\text{NH}_2)_2\text{PbI}_6$, $d(\text{Pb}—\text{I})$ are between 3.173(1) Å to 3.346(1) Å and I—Pb—I bond angles range from 82.5° to 90.0° and 166.65° to 180.0°. The organic layers comprise two kinds of parallel 4-bromo-phenylaminium cations with the dihedral angle of 37.75(2)°, whose planes are defined by Br1/C1/C2/C3/C4/C5/C6/N1. Besides electrostatic interaction, classic and non-classic hydrogen bonds between organic bimolecular layers and inorganic layers exist to maintain stability of the crystal structure.

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Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.03 × 0.07 × 0.35 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	162.67 cm ⁻¹
Diffractometer, scan mode:	Bruker APEX2 CCD, φ/ω
2 θ _{max} :	54.98°
$N(hkl)$ _{measured} , $N(hkl)$ _{unique} :	7918, 2613
Criterion for I_{obs} , $N(hkl)$ _{gt} :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2329
$N(\text{param})$ _{refined} :	99
Programs:	SHELXL-97 [6], SHELXTL [7], WinGX [8]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(2)	4e	0.5450	0.3339	0.5011	0.068
H(3)	4e	0.6857	0.3780	0.6296	0.063
H(5)	4e	0.7573	0.5293	0.2497	0.064
H(6)	4e	0.6169	0.4827	0.1223	0.062
H(1A)	4e	0.8596	0.4378	0.4977	0.088
H(1B)	4e	0.8233	0.4841	0.6283	0.088
H(1C)	4e	0.8317	0.6047	0.5147	0.088

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	4e	0.45139(5)	0.37977(8)	0.20091(7)	0.0473(5)	0.0874(4)	0.0603(3)	-0.0058(3)	-0.0008(3)	-0.0099(3)
C(1)	4e	0.5686(4)	0.4067(6)	0.3003(5)	0.033(3)	0.052(3)	0.043(2)	-0.003(2)	0.003(2)	-0.003(2)
C(2)	4e	0.5880(5)	0.3737(7)	0.4512(6)	0.052(4)	0.071(4)	0.047(2)	-0.010(3)	0.008(3)	0.010(2)
C(3)	4e	0.6715(4)	0.4001(6)	0.5279(5)	0.055(4)	0.066(4)	0.036(2)	-0.001(3)	0.007(3)	0.009(2)
C(4)	4e	0.7330(4)	0.4593(6)	0.4517(5)	0.046(4)	0.053(3)	0.039(2)	0.004(3)	0.003(3)	-0.005(2)
C(5)	4e	0.7143(5)	0.4905(6)	0.2999(6)	0.053(5)	0.072(4)	0.035(2)	-0.008(3)	0.010(3)	-0.000(2)
C(6)	4e	0.6307(5)	0.4629(7)	0.2244(5)	0.056(5)	0.064(3)	0.033(2)	0.000(3)	0.004(3)	-0.003(2)
I(1)	4e	-0.03871(3)	0.17976(4)	0.79710(3)	0.0604(3)	0.0442(2)	0.0388(2)	-0.0053(2)	0.0128(2)	-0.0149(1)
I(2)	4e	0.20191(3)	0.42119(5)	1.08206(3)	0.0369(3)	0.0830(3)	0.0404(2)	0.0067(2)	0.0024(2)	-0.0054(1)
N(1)	4e	0.8205(4)	0.5005(6)	0.5309(5)	0.042(4)	0.090(4)	0.043(2)	-0.002(2)	0.004(2)	-0.010(2)
Pb(1)	2c	0	½	0	0.0407(2)	0.0381(2)	0.0273(1)	-0.0009(1)	0.0024(1)	-0.00019(7)

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