Crystal structure of bis(4-bromophenylaminium) tetraiodoplumbate(II), (BrC₆H₄NH₃)₂PbI₄

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Abstract
C₁₂H₁₄Br₂UN₂Pb, monoclinic, P2₁/c1 (no. 14), a = 15.5755(2) Å, b = 8.2019(1) Å, c = 9.0917(1) Å, β = 100.084(1)°, V = 1143.5 Å³, Z = 2, R启(F) = 0.031, wR启(F²) = 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 PbI₂ 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 C₁₂H₁₄C₂H₄N₃Pb: C, 13.59 %; H, 1.33 %; N, 2.64 %.

Experimental details
All H atoms were positioned geometrically (d(C—H) = 0.93 - 0.98 Å), and refined as riding with \( \frac{1}{2} \)iso(H) = 1.2 \( \frac{1}{2} \)eq(carrier) or 1.5\( \frac{1}{2} \)eq(amine groups).

Discussion
The title organic-inorganic hybrid (BrC₆H₄NH₃)₂PbI₄ is isostructural to (ClC₆H₄NH₃)₂PbI₄ (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 PbI₆ octahedron connects neighboring ones through four bridging iodine atoms to constitute the former, and two kinds of parallel 4-bromo-phenylammonium 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 PbI₆ octahedron is 3.2095(3) Å. These values are similar to those found in (ClC₆H₄NH₂)₂PbI₆ [4]. The coordination type involving PbI₆ of the title compound differs from those observed in (ClC₆H₄NH₂)₂PbI₆ [5], which has three coordination types, namely, nearly ideal octahedral symmetry, distorted octahedral coordination and trigonal prismatic coordination. Face-shared PbI₆ octahedra and trigonal prisms link with one another to form chains. In (C₁₂H₁₄NH₂)₂PbI₆, d(Pb—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-phenylammonium 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.
Table 1. Data collection and handling.

<table>
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<th>Crystal:</th>
<th>yellow plate, size 0.03  \times 0.07  \times 0.35 mm</th>
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<tr>
<td>Wavelength:</td>
<td>Mo Kα radiation (0.71073 Å)</td>
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<td>μ:</td>
<td>162.67 cm⁻¹</td>
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<td>Diffractometer, scan mode:</td>
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<td>2θmax:</td>
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<tr>
<td>N(hkl) measured, N(hkl) Unique:</td>
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<tr>
<td>Criterion for lobs, N(hkl)ip:</td>
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<tr>
<td>Programs:</td>
<td>SHELXL-97 [6], SHELXTL [7], WinGX [8]</td>
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Table 2. Atomic coordinates and displacement parameters (in Å²).

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<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<th>U22</th>
<th>U33</th>
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<th>U23</th>
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<td>-0.003(2)</td>
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<td>0.0024(1)</td>
<td>-0.00019(7)</td>
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References