Crystal structure of bis(4-bromoanilinium) tetrachloroplumbate(II), $(\text{BrC}_6\text{H}_4\text{NH}_3)_2\text{PbCl}_4$

Z. Liu*, W.-T. Yu, X.-T. Tao and M.-H. Jiang

Shandong University, State Key Laboratory of Crystal Materials, Jinan, Shandong, 250100 P. R. China

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Abstract

$\text{C}_{12}\text{H}_{14}\text{Br}_2\text{Cl}_4\text{N}_2\text{Pb}$, monoclinic, $P12_1/c1$ (no. 14), $a = 17.373(2)$ Å, $b = 7.763(1)$ Å, $c = 22.242(2)$ Å, $\beta = 104.774(7)^\circ$, $V = 2900.5$ Å³, $Z = 6$, $R_{\text{gt}}(F) = 0.057$, $wR_{\text{ref}}(F^2) = 0.145$, $T = 293$ K.

Source of material

In a three-neck flask, 0.918 g of *p*-bromoaniline was dissolved in 20.0 ml of concentrated (37 %) hydrochloric acid under argon at 60 °C. The metal halide solution of 0.730 g of PbCl_2 in 20.0 ml of concentrated (37 %) aqueous HCl was then added to the three-neck flask gradually with stirring. The resulting solution was allowed to stand at 80 °C for 4 hours and then slowly (5 K/h) cooled to room temperature without stirring. Slow evaporation over a period of 3 days under following argon yielded long rod-like white crystals (0.363 g, 20 %) suitable for X-ray single-crystal investigation. C, H and N elemental analyses were performed on a Perkin-Elmer elemental analyzer. Elemental analysis: found – C, 20.72 %; H, 1.84 %; N, 4.04 %; calc. for $\text{C}_{12}\text{H}_{14}\text{Br}_2\text{Cl}_4\text{N}_2\text{Pb}$ – C, 20.74 %; H, 2.03 %; N, 4.03 %.

Discussion

The $(p\text{-BrC}_6\text{H}_4\text{NH}_3)_2\text{PbCl}_4$ structure consists of alternated well-ordered inorganic perovskite layers and organic layers stacked along the *a*-axis (figure, bottom). The linkage of corner-sharing distorted PbCl_6 octahedra and PbCl_5 square pyramids, each of which contains four and two bridging chlorine atoms, respectively, constitutes the former, and bilayers of *p*-bromo-anilinium (4-bromophenyl-1-ammonium) cations connected by Br–Br interaction constitute the latter. Hydrogens of organic cations bond to halogens in the perovskite layer through the –NH_3^+ group on each molecule. The perovskite sheets contain two independent Pb atoms. One has a distorted octahedral chloride coordination and the other has a distorted square pyramid chloride coordination, with Pb–Cl bond lengths ranging from 2.770(4) Å to 3.022(4) Å and Cl–Pb–Cl bond angles ranging from 77.6(1)° to 96.8(1)° as well as 158.9(2)° to 180.0°. The average Pb–Cl bond lengths for the PbCl_6 octahedra and PbCl_5 square pyramids are 2.836 Å and 2.895 Å, respectively. Note, that the bridging Pb1–Cl–Pb2 bond angles are substantially different from 180° (i.e., 158.9(2)° and 170.0(2)°), indicating that adjacent PbCl_5 square pyramids are substantially rotated and tilted relative to the PbCl_6 octahedra.

The Pb coordination differs from that in $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4$, which has two similarly distorted chloride octahedra with Pb–Cl bond lengths between 2.752(2) Å to 3.033(2) Å and Cl–Pb–Cl bond angles, which range from 83.11(4)° to 97.26(4)° and 171.01(4)° to 179.08(4)° [1]. It is also different from the Cd coordination in $(p\text{-BrC}_6\text{H}_4\text{NH}_3)_3\text{CdCl}_5$, which has chain structure formed by corner-sharing CdCl_6 octahedra [2]. The organic layers in the title compound comprise three independent *p*-bromo-anilinium cations, each of which has good planarity (figure, top). The plane defined by Br1–C1–C2–C3–C4–C5–C6–N1 is almost coplanar to that of Br3–C13–C14–C15–C16–C17–C18–N3 with a small dihedral angle of 22.0°. In contrast, the plane defined by Br2–C7–C8–C9–C10–C11–C12–N2 is nearly perpendicular to the former two planes with angles of 111.2° and 114.6°, respectively.

* Correspondence author (e-mail: namezhi@hotmail.com)

Table 1. Data collection and handling.

Crystal:	white prism, size 0.12 × 0.19 × 0.23 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	134.04 cm ⁻¹
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{\max}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6570, 5120
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2741
$N(\text{param})_{\text{refined}}$:	287
Programs:	SHELXTL [3], WinGX [4]

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

Atom	Site	x	y	z	U_{iso}
H(2D)	4e	0.7017	1.1016	0.0161	0.081
H(3D)	4e	0.5689	1.1390	0.0137	0.087
H(5A)	4e	0.6131	0.9926	0.1898	0.084

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(6A)	4e	0.7480	0.9450	0.1929	0.060
H(8A)	4e	0.7467	0.7257	0.3450	0.089
H(9A)	4e	0.6175	0.7949	0.3007	0.091
H(11A)	4e	0.5955	0.3742	0.1894	0.074
H(12A)	4e	0.7250	0.3026	0.2361	0.080
H(14A)	4e	0.7250	-0.0069	0.4188	0.086
H(15A)	4e	0.6100	-0.0516	0.4501	0.077
H(17A)	4e	0.7353	-0.0502	0.6204	0.089
H(18A)	4e	0.8510	-0.0143	0.5916	0.085
H(1A)	4e	0.8463	0.9541	0.1411	0.092
H(1B)	4e	0.8397	1.0944	0.0968	0.092
H(1C)	4e	0.8226	0.9188	0.0748	0.092
H(2A)	4e	0.8571	0.5528	0.3489	0.118
H(2B)	4e	0.8608	0.4649	0.2920	0.118
H(2C)	4e	0.8381	0.3705	0.3412	0.118
H(3A)	4e	0.8610	0.0384	0.4392	0.114
H(3B)	4e	0.9052	-0.0611	0.4921	0.114
H(3C)	4e	0.8965	0.1240	0.4978	0.114

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}
C(1)	4e	0.734(1)	1.018(2)	0.1043(7)	0.06(1)	0.05(1)	0.048(8)	0.01(1)	0.013(8)	-0.022(9)
C(2)	4e	0.683(1)	1.078(3)	0.0510(8)	0.07(1)	0.09(1)	0.047(9)	0.02(1)	0.010(9)	0.02(1)
C(3)	4e	0.605(1)	1.102(3)	0.0499(7)	0.07(1)	0.10(2)	0.038(9)	0.01(1)	0.001(9)	0.01(1)
C(4)	4e	0.580(1)	1.072(3)	0.1012(9)	0.06(1)	0.07(1)	0.07(1)	-0.00(1)	0.02(1)	-0.01(1)
C(5)	4e	0.632(1)	1.014(3)	0.1548(9)	0.07(1)	0.07(1)	0.07(1)	-0.02(1)	0.03(1)	-0.03(1)
C(6)	4e	0.712(1)	0.985(2)	0.1571(7)	0.05(1)	0.05(1)	0.045(8)	0.01(1)	0.004(7)	0.003(9)
C(7)	4e	0.751(1)	0.514(3)	0.2939(8)	0.07(1)	0.05(1)	0.06(1)	-0.02(1)	0.016(9)	0.01(1)
C(8)	4e	0.717(1)	0.657(3)	0.3135(9)	0.07(1)	0.07(2)	0.09(1)	-0.02(1)	0.03(1)	-0.04(1)
C(9)	4e	0.640(2)	0.698(2)	0.2876(9)	0.12(2)	0.04(1)	0.08(1)	-0.00(1)	0.05(1)	-0.01(1)
C(10)	4e	0.593(1)	0.591(3)	0.2400(8)	0.08(1)	0.08(1)	0.07(1)	-0.01(1)	0.05(1)	0.00(1)
C(11)	4e	0.626(1)	0.444(2)	0.2205(8)	0.05(1)	0.06(1)	0.07(1)	0.001(9)	0.00(1)	-0.023(9)
C(12)	4e	0.703(1)	0.403(2)	0.2476(8)	0.09(2)	0.06(1)	0.06(1)	0.02(1)	0.02(1)	0.00(1)
C(13)	4e	0.799(1)	0.000(3)	0.5004(7)	0.05(1)	0.07(1)	0.057(9)	0.00(1)	0.014(8)	-0.01(1)
C(14)	4e	0.728(1)	-0.015(3)	0.4611(7)	0.09(2)	0.09(2)	0.036(8)	-0.01(2)	0.021(9)	-0.01(1)
C(15)	4e	0.659(1)	-0.044(2)	0.4797(8)	0.07(1)	0.06(1)	0.06(1)	-0.00(1)	0.009(9)	0.005(9)
C(16)	4e	0.662(1)	-0.061(2)	0.5386(8)	0.06(1)	0.07(1)	0.05(1)	-0.01(1)	0.015(9)	0.000(9)
C(17)	4e	0.733(1)	-0.044(2)	0.5782(9)	0.11(2)	0.07(2)	0.06(1)	0.01(1)	0.05(1)	-0.00(1)
C(18)	4e	0.803(1)	-0.019(3)	0.5618(8)	0.05(1)	0.10(2)	0.052(9)	0.02(1)	0.007(8)	0.01(1)
N(1)	4e	0.8193(8)	0.994(2)	0.1042(6)	0.067(9)	0.067(9)	0.050(7)	-0.01(1)	0.016(7)	-0.009(8)
N(2)	4e	0.835(1)	0.471(2)	0.3217(7)	0.08(1)	0.09(2)	0.061(9)	-0.00(1)	0.018(9)	-0.004(9)
N(3)	4e	0.8727(9)	0.028(2)	0.4804(7)	0.07(1)	0.08(1)	0.075(9)	0.00(1)	0.027(9)	-0.002(9)
Cl(1)	4e	0.8954(3)	1.2593(6)	0.2108(2)	0.058(3)	0.052(3)	0.054(2)	-0.001(2)	0.015(2)	0.010(2)
Cl(2)	4e	0.8209(3)	1.0557(6)	0.3322(2)	0.062(3)	0.074(3)	0.057(2)	-0.004(2)	0.026(2)	0.002(2)
Cl(3)	4e	0.8898(3)	0.7366(6)	0.2241(2)	0.054(3)	0.051(3)	0.056(2)	-0.001(2)	0.012(2)	-0.003(2)
Cl(4)	4e	0.8313(3)	0.4639(8)	0.4644(2)	0.059(3)	0.151(6)	0.051(2)	-0.011(4)	0.018(2)	-0.006(3)
Cl(5)	4e	1.0145(3)	0.2511(7)	0.4111(2)	0.076(3)	0.076(3)	0.073(3)	-0.008(3)	0.027(3)	-0.030(3)
Cl(6)	4e	0.9875(4)	0.7698(7)	0.4120(2)	0.119(5)	0.070(3)	0.062(3)	0.005(3)	0.028(3)	0.026(3)
Br(1)	4e	0.4737(1)	1.0993(3)	0.1055(1)	0.063(1)	0.107(2)	0.083(1)	0.010(1)	0.022(1)	-0.004(1)
Br(2)	4e	0.4849(1)	0.6424(3)	0.2043(1)	0.075(2)	0.092(2)	0.099(2)	0.018(1)	0.036(1)	0.012(1)
Br(3)	4e	0.5731(1)	-0.1091(3)	0.56797(9)	0.069(1)	0.092(2)	0.078(1)	-0.002(1)	0.031(1)	0.012(1)
Pb(1)	4e	0.96485(4)	1.0059(1)	0.30258(2)	0.0550(4)	0.0471(4)	0.0424(3)	0.0009(4)	0.0153(3)	-0.0005(4)
Pb(2)	2a	0	½	½	0.0578(6)	0.0429(5)	0.0415(4)	-0.0014(6)	0.0157(4)	0.0000(5)

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References

- Mitzi, D. B.: A Layered Solution Crystal Growth Technique and the Crystal Structure of (C₆H₅C₂H₄NH₃)₂PbCl₄. *J. Sol. State Chem.* **145** (1999) 694-704.
- Li, D.-G.; Liu, C.-M.; You, X.-Z.; Fu, W.-Q.; Chen, W.; Lo, K.-M.: A Novel Organic-inorganic Complex With a One-dimensional Helical Anion Chain: Crystal Structure and Thermal Study of Tris(4-Bromo-Benzen-ammonium) Pentachlorocadmate [(Br-C₆H₄NH₃)₃CdCl₅]. *J. Coord. Chem.* **46** (1998) 33-41.
- Sheldrick, G. M.: SHELXTL-97, v. 5.10. Programs for the Analysis of Crystal Structures. Bruker Analytical X-ray Instruments Inc., Madison, WI-53719, USA 1997.
- Farrugia, L. J.: WinGX – Version 1.63.05. An integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystals X-Ray Diffraction Data. *J. Appl. Crystallogr.* **32** (1999) 837-838.