Supporting information for the article

Crystal Structure and Properties of Acetamidinium Lead Bromide: A New Member of the A_3PbBr_5 Halide Family

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Table S1. Crystal data and structure refinement for Aca_3PbBr_5 at 100 K and 298 K.

Empirical formula	$C_6H_{21}Br_5N_6Pb$	$C_6H_{21}Br_5N_6Pb$
Formula weight	784.03	784.03
Temperature/K	**100**	**298**
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	18.9112(13)	18.550(3)
b/Å	9.0412(6)	9.2337(15)
c/Å	11.7688(8)	11.9729(18)
α/°	90	90
β/°	100.974(3)	100.272(6)
γ/°	90	90
Volume/Å^3	1975.4(2)	2017.9(6)
Z	4	4
ρ_{calc}/g·cm^3	2.636	2.581
μ/mm^{-1}	18.649	18.256
F(000)	1424.0	1424.0
Crystal size/mm^3	0.38 × 0.32 × 0.29	0.26 × 0.24 × 0.19
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.388 to 54.968	5.606 to 60.976
Index ranges	-24 ≤ h ≤ 24, -11 ≤ k ≤ 11, -13 ≤ l ≤ 15	-26 ≤ h ≤ 26, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	40772	76176
Independent reflections	4527 [Rint = 0.0779, Rsigma = 0.0423]	6140 [R_{int} = 0.0823, R_{sigma} = 0.0376]
Data/restraints/parameters	4527/0/167	6140/0/167
Goodness-of-fit on F^2	1.053	1.069
Final R indexes [I>=2σ (I)]	R1 = 0.0368, wR2 = 0.0963	R_1 = 0.0424, wR_2 = 0.1116
Final R indexes [all data]	R1 = 0.0428, wR2 = 0.0997	R_1 = 0.0648, wR_2 = 0.1222
Largest diff. peak/hole / e Å^{-3}	3.45/-2.59	2.60/-2.22

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Aca_3PbBr_5 (298 K). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pb1	2289.1(2)	2316.5(3)	3068.4(2)	31.84(10)
Br1	2199.7(5)	2017.7(10)	538.0(6)	49.6(2)
Br2	1258.0(5)	-143.0(11)	3029.7(8)	60.0(2)
Br3	3646.5(5)	394.0(11)	3644.1(9)	62.4(3)
Br4	1139.8(5)	4515.4(10)	2479.3(8)	55.8(2)
Br5	3396.7(6)	4710.2(11)	3107.4(9)	63.8(3)
N2	864(4)	5851(8)	5171(6)	52.2(17)
N4	2324(5)	8919(9)	5614(6)	69(2)
N6	4105(5)	2397(13)	6073(10)	98(4)
N1	119(4)	6906(8)	3669(6)	51.4(17)
C1	358(4)	6792(8)	4774(6)	39.1(15)
N3	2382(5)	7209(8)	4256(7)	62(2)
C3	2572(5)	7702(9)	5300(7)	48.7(19)
C4	3099(7)	6831(13)	6134(10)	84(3)
C5	4718(5)	3077(12)	6155(8)	59(2)
N5	4943(5)	3957(12)	7010(8)	88(3)
C2	39(6)	7737(11)	5539(9)	64(3)
C6	5172(6)	2865(11)	5299(9)	63(2)

Table S3. Bond Lengths for Aca_3PbBr_5 (298 K).

Atom(1)	Atom(2)	Length/Å		Atom(1)	Atom(2)	Length/Å
Pb1	Br1[1]	3.0533(9)		N6	C5	1.287(13)
Pb1	Br1	3.0172(8)		N1	C1	1.322(10)
Pb1	Br2	2.9642(10)		C1	C2	1.465(12)
Pb1	Br3	3.0573(10)		N3	C3	1.318(11)
Pb1	Br4	2.9375(10)		C3	C4	1.499(14)
Pb1	Br5	3.0123(10)		C5	N5	1.314(14)
N2	C1	1.305(10)		C5	C6	1.451(14)
N4	C3	1.296(11)				

[1]+X,1/2-Y,1/2+Z

Table S4. Bond Angles for Aca_3PbBr_5 (298 K).

Atom(1)	Atom(2)	Atom(3)	Angle/˚	Atom(1)	Atom(2)	Atom(3)	Angle/˚
Br1	Pb1	Br1[1]	171.13(3)	Br5	Pb1	Br1[1]	89.54(3)
Br1	Pb1	Br3	93.95(3)	Br5	Pb1	Br3	83.71(3)
Br1[1]	Pb1	Br3	94.78(3)	Pb1	Br1	Pb1[2]	162.03(4)
Br2	Pb1	Br1	89.68(3)	N2	C1	N1	120.6(8)
Br2	Pb1	Br1[1]	91.32(3)	N2	C1	C2	120.9(8)
Br2	Pb1	Br3	93.55(3)	N1	C1	C2	118.5(8)
Br2	Pb1	Br5	177.19(3)	N4	C3	N3	121.7(9)
Br4	Pb1	Br1	85.09(3)	N4	C3	C4	119.7(9)
Br4	Pb1	Br1[1]	86.04(3)	N3	C3	C4	118.6(9)
Br4	Pb1	Br2	95.00(3)	N6	C5	N5	120.9(11)
Br4	Pb1	Br3	171.39(3)	N6	C5	C6	119.7(11)
Br4	Pb1	Br5	87.73(3)	N5	C5	C6	119.4(9)
Br5	Pb1	Br1	89.88(3)				

[1]+X,1/2-Y,1/2+Z; [2]+X,1/2-Y,-1/2+Z

Table S5. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Aca_3PbBr_5 (100 K). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pb1	2280.4(2)	2779.7(2)	3145.3(2)	12.96(10)
Br1	1171.5(3)	487.8(6)	2452.2(5)	17.01(15)
Br2	3402.8(3)	356.3(6)	3139.7(5)	16.88(15)
Br3	3648.6(3)	4680.9(7)	3780.5(5)	20.00(15)
Br4	1207.6(3)	5182.1(6)	3131.3(5)	18.07(15)
Br5	2217.3(3)	3171.6(7)	644.7(5)	18.86(15)
N2	94(3)	-1844(6)	3642(4)	19.6(11)
N4	867(3)	-884(6)	5177(5)	20.4(11)
N6	-12(4)	-2656(7)	5556(6)	22.0(14)
N1	336(3)	-1744(6)	4757(5)	17.4(12)
C1	4058(3)	2415(7)	6143(5)	29.6(14)
N3	4924(3)	892(6)	7118(5)	28.8(13)
C3	5111(4)	2023(7)	5332(6)	22.9(14)
C4	4680(3)	1771(7)	6239(6)	19.4(13)
C5	2370(3)	7856(6)	4294(5)	21.7(12)
N5	2334(3)	6127(6)	5688(4)	23.2(12)
C2	3250(4)	8014(7)	6046(6)	29.5(16)
C6	2623(4)	7303(6)	5309(6)	18.7(13)

Table S6. Bond Lengths for Aca_3PbBr_5 (100 K).

Atom(1)	Atom(2)	Length/Å		Atom(1)	Atom(2)	Length/Å
Pb1	Br1	2.9506(6)		C1	C2	1.494(8)
Pb1	Br2	3.0514(6)		N3	C4	1.299(8)
Pb1	Br3	3.0776(7)		N4	C4	1.317(8)
Pb1	Br4	2.9702(6)		C3	C4	1.479(9)
Pb1	Br5^1	3.0888(6)		N5	C6	1.300(8)
Pb1	Br5	2.9439(6)		N6	C6	1.313(8)
N1	C2	1.308(8)		C5	C6	1.477(9)
N2	C2	1.292(8)				

^{1}+X,1/2-Y,1/2+Z

Table S7. Bond Angles for Aca_3PbBr_5 (100 K).

Atom(1)	Atom(2)	Atom(3)	Angle/˚	Atom(1)	Atom(2)	Atom(3)	Angle/˚
Br1	Pb1	Br2	87.320(18)	Br5	Pb1	Br4	90.503(18)
Br1	Pb1	Br3	168.474(19)	Br5	Pb1	$Br5^1$	169.724(14)
Br1	Pb1	Br4	93.626(18)	Pb1	Br5	$Pb1^2$	156.48(2)
Br1	Pb1	$Br5^1$	85.033(17)	N1	C2	C1	118.8(6)
Br2	Pb1	Br3	81.291(17)	N2	C2	N1	121.6(6)
Br2	Pb1	$Br5^1$	87.428(17)	N2	C2	C1	119.7(6)
Br3	Pb1	$Br5^1$	96.160(18)	N3	C4	N4	121.0(6)
Br4	Pb1	Br2	178.815(18)	N3	C4	C3	118.9(6)
Br4	Pb1	Br3	97.741(18)	N4	C4	C3	120.1(6)
Br4	Pb1	$Br5^1$	93.364(18)	N5	C6	N6	121.3(6)
Br5	Pb1	Br1	85.224(18)	N5	C6	C5	119.1(6)
Br5	Pb1	Br2	88.863(18)	N6	C6	C5	119.6(6)
Br5	Pb1	Br3	92.743(18)				

^{1}+X,1/2-Y,1/2+Z; ^{2}+X,1/2-Y,-1/2+Z

Definitions of intrinsic descriptors of molecular cations

A_{2D} steric footprint (Å^2): convex-hull area of the full idealized cation (all atoms) projected onto the best-fit molecular plane.

L_{max} (Å): maximum pairwise atomic separation within the projected full cation.

W_{min} (Å): Minimum width of the projected full cation, obtained from the convex hull.

Aspect ratio, AR (dimensionless): **L_{max} / W_{min}**.

Radius of gyration, R_g (Å): Root-mean-square distance of all projected cation atoms from their geometric centroid.

Effective radius, R_{eff} (Å): **$R_{eff} = (A_{2D} / \pi)^{(1/2)}$**, i.e., the radius of a circle with the same projected area.

Donor density, ρD, H donor per Å^2. $D_{HBD} = N_{HBD} / A_{2D}$, where **$N_{HBD}$** is the number of chemically relevant donor hydrogens.

Donor-field asymmetry, P_1: Magnitude of the mean unit-vector sum of all relevant D–H bond vectors (D = N or polar C), taken from the geometric centroid of the full non-H cation scaffold: $P_1 = |(1 / N\_HBD) \Sigma_i u_i|$. Small P_1 indicates a nearly isotropic donor field; larger P_1 indicates a more one-sided donor-field distribution.

Donor-field axial anisotropy, P_2: Second angular moment of the donor-field distribution in the molecular plane: $P_2 = |(1 / N\_HBD) \Sigma_i \exp(2i\theta_i)|$. Small P_2 indicates a nearly azimuthally uniform donor field; larger P_2 indicates stronger axial or lobed anisotropy.

Donor-field eccentricity, E_{DF}. Distance between the geometric centroid of all relevant donor hydrogens and the geometric centroid of the full non-H cation scaffold, normalized by **R_g** of the non-H scaffold:

$E_{DF} = |r_{H,cent} - r_o| / R_g$(non-H).

Intrinsic descriptors were computed for idealized cations from MMFF-optimized planar geometries of the isolated protonated species. For P_1, P_2, and E_{DF}, the reference point was the geometric centroid of all non-H atoms of the full cation. Size descriptors (A_{2D}, L_{max}, W_{min}, AR, R_g, R_{eff}, and D_{HBD}) were derived from the all-atom 2D footprint projected onto the best-fit molecular plane. Relevant donor H atoms were defined as follows: AcA^+, 4 N–H; FA^+, 4 × N–H + amidinium C–H; Im^+, 2 × N–H + 3 × ring C–H.

Table S8. Intrinsic organic cation descriptors.

Descriptor	Acetamidinium (Aca^+)	Formamidinium (Aca^+)	Imidazolium (Im^+)
Intrinsic cation archetype	ordered asymmetric amidinium	symmetric amidinium template	rigid imidazolium ring
Relevant HBD count, $\mathbf{N_{HBD}}$	4	5	5
N–H donors count	4	4	2
Activated C–H donors count	0	1	3
Steric footprint $\mathbf{A_{2D}}$, Å²	10.752	7.405	11.562
$\mathbf{L_{max}}$, Å	4.096	4.055	4.232
$\mathbf{W_{min}}$, Å	3.511	2.707	3.949
Aspect ratio, **AR**	1.166	1.498	1.072
Radius of gyration, Rg, Å	1.753	1.567	1.763
Effective radius, $\mathbf{R_{eff}}$, Å	1.850	1.535	1.918
HBD density, $\mathbf{D_{HBD}}$, H-donor per Å²	0.372	0.675	0.432
HBD-field asymmetry, $\mathbf{P_1}$	0.446	0.016	0.024
HBD-field axial anisotropy, $\mathbf{P_2}$	0.337	0.189	0.045
HBD-field eccentricity, $\mathbf{E_{DF}}$	0.784	0.057	0.037

Table S9. Parameters of cation-framework coupling.

Descriptor	Aca_3PbBr_5 (100K)	FA_3PbBr_5	Im_3PbBr_5
Ordered/disordered cation state	ordered	disorder-resolved	ordered
Mean plane–chain angle, deg (range)	22.8 (10.5–31.9)	15.3 (5.1–31.4)	27.4 (21.1–30.7)
Overall shortest donor···Br, Å	3.377	2.837	3.285
Overall shortest N···Br, Å	3.377	2.837	3.285
Overall shortest relevant C···Br, Å	NA	3.399	3.545
Shortest bridging donor···Br, Å	3.459	3.593	3.445
Shortest interchain Br···Br, Å [alignment, deg]	4.429 [164.6]	4.179 [146.4 / 122.5]	4.392 [177.9]

Table 10. Inorganic structure distortions.

Descriptor	Aca_3PbBr_5 (100K)	FA_3PbBr_5	Im_3PbBr_5
Baur distortion index, D	0.01954	0.00361	0.00931
Bond-angle variance, σ^2_{oct}, deg²	24.41657	4.09000	10.71000
Chain deviation from linearity, D_{chain}, deg	23.51854	17.29200	9.86100
Pb off-centering, δ_{Pb}, Å	0.15908	0.00000	0.08400
Transverse Pb off-centering, $\delta_{Pb,\perp}$, Å	0.09500	0.00000	0.08000

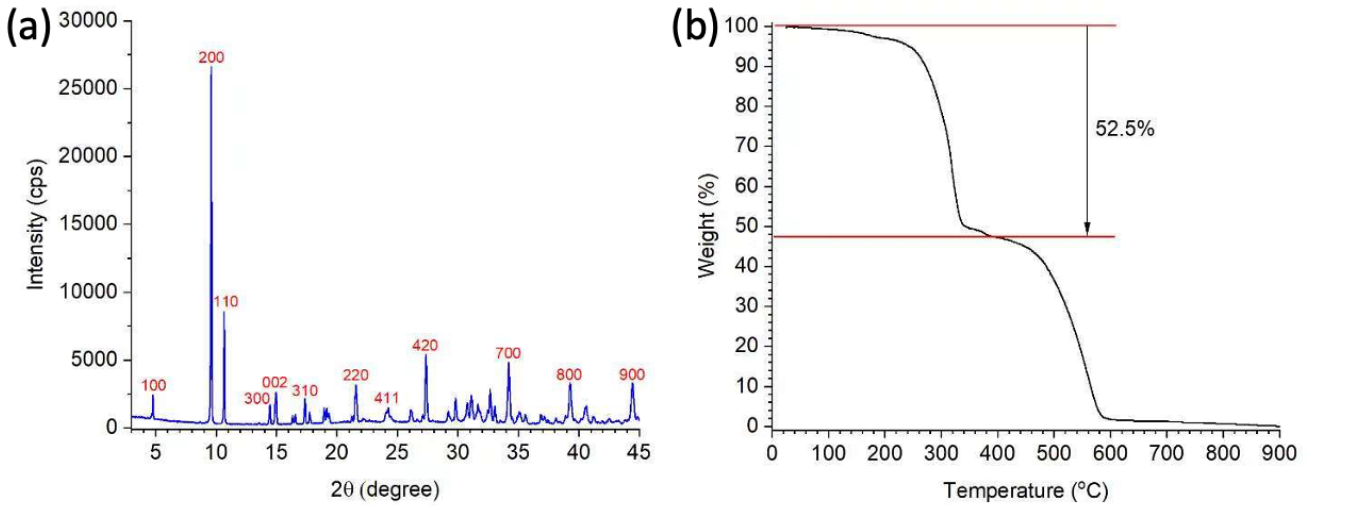

Figure S1. (a) X-ray diffraction pattern of Aca_3PbBr_5, (b) thermogravimetric analysis (TGA) curve showing thermal decomposition behavior.

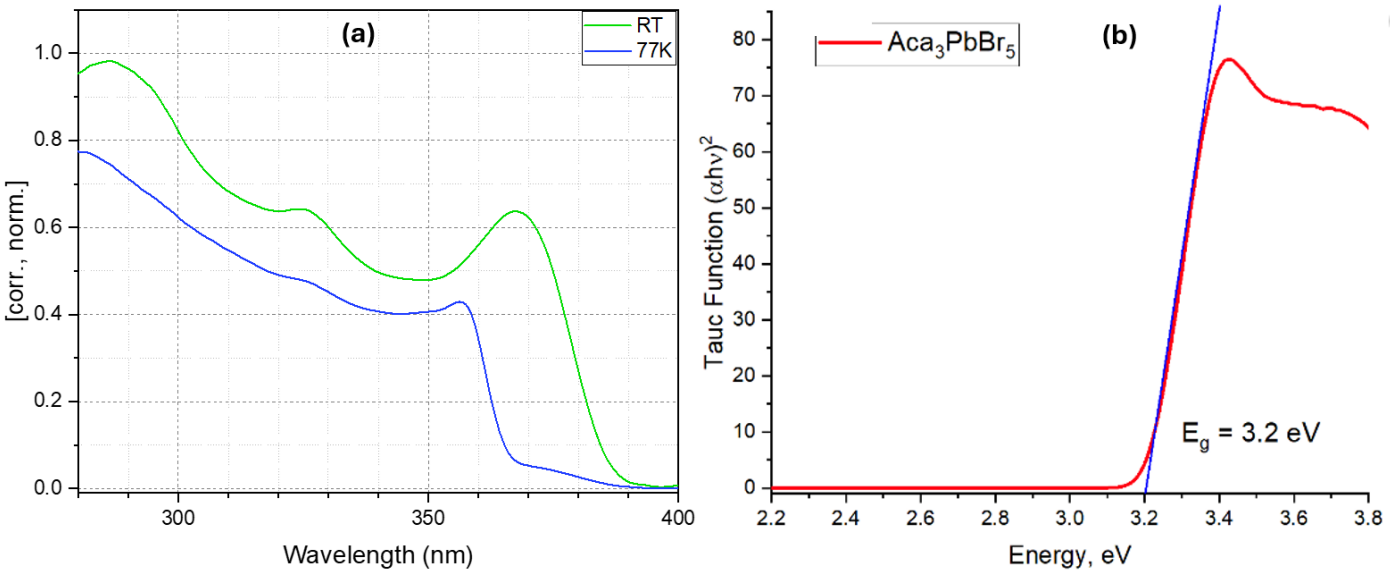

Figure S2. (a) PLE spectra of Aca_3PbBr_5 at room temperature and at liquid nitrogen temperature, (b) Diffuse reflectance spectrum plotted in Tauc coordinates with estimated optical band gap of 3.2 eV.