Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Lead-Free 3D Hybrid Perovskites based on Aziridinium Cation

Olesia I. Kucheriv,[a] Valerii Y. Sirenko,[a] Hanna R. Petrosova,[a] Vadim A. Pavlenko,[a]

Sergiu Shova*[b] and Il'ya A. Gural'skiy*[a]

[a.]Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska St. 64, Kyiv 01601, Ukraine

E-mail: illia.guralskyi@univ.kiev.ua

[b.]Department of Inorganic Polymers, Petru Poni Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41-A, Iasi 700487, Romania

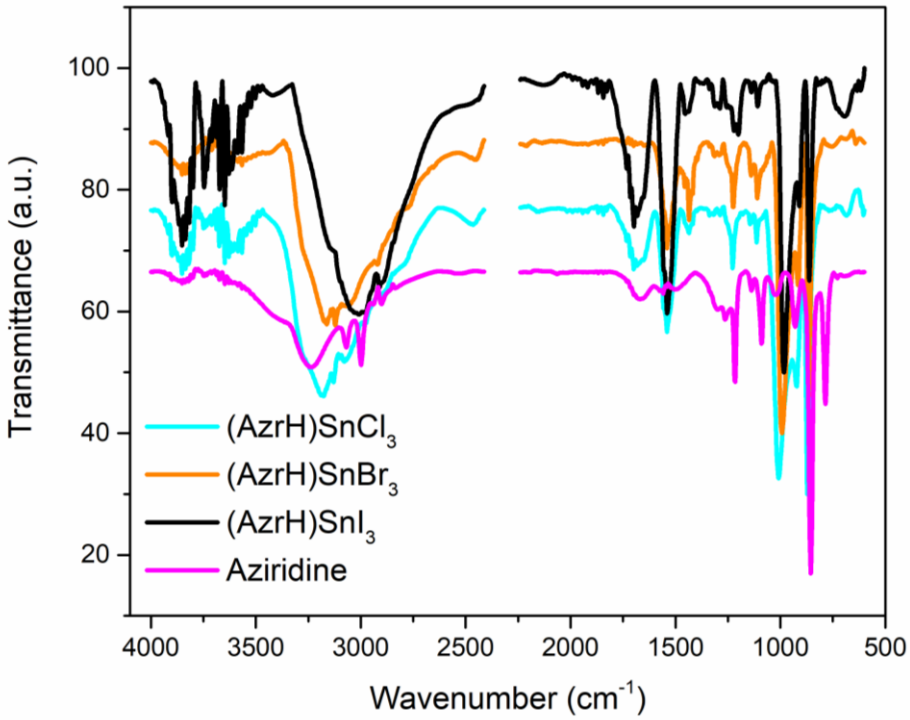

Figure S1. IR spectra of $(AzrH)SnHal_3$ and aziridine (4000 – 600 cm^{-1} region).

Table S1. Interpretation of IR bands of $(AzrH)SnHal_3$ and aziridine.[1,2]

Aziridine	**SnCl**	**SnBr**	**SnI**	Bands assignment
3234	3180	3158	3017	$NH_{str.}$ / $NH_{2str.}$
3067	3127	3121		$CH_{2str.\ asym.}$
2996	2997	2919	2905	$CH_{2str.\ sym.}$
	1537	1537	1537	$NH_{2bending\ (scissoring)}$
	1431	1431	1431	$NH_{2wagging}$
1218	1228	1224	1220	Ring stretch
1136	1145	1140	1138	$CH_{2wagging}$
1089	1114	1140	1138	$CH_{2twisting}$
	1009	995	985	$NH_{2rocking}$
929	924	914	909	Asymmetric ring deformation
858	868	863	858	Symmetric ring deformation

Table S2. Bond valance sums[3] ($s = \Sigma[(R_0-R)/0.37]$), where R is the bond length and R_0 is bond-valence parameter according to O'Keeffe[4]) of $(AzrH)SnHal_3$

	T (K)	s	Ro	Contribution of longer bonds (%)
$(AzrH)SnCl_3$	270	2.13	2.36	11.3
	180	2.07	2.36	11.8
	120	2.07	2.36	12.1
$(AzrH)SnBr_3$	180	2.13	2.55	23.6
	120	2.23	2.55	19.8
$(AzrH)SnI_3$	180	2.14	2.76	–
	108	2.27	2.76	31.5

Table S3. Goldschmidt tolerance factors of $(AzrH)SnX_3$ perovskites and their closest analogues ABX_3 where A = MA, FA, AzrH, B = Sn, Pb, X = Cl, Br, I.

Compound	Tolerance factor	Compound	Tolerance factor	Compound	Tolerance factor
Sn series					
$AzrSnCl_3$	0.978	$MASnCl_3$	0.945	$FASnCl_3$	1.032
$AzrSnBr_3$	0.969	$MASnBr_3$	0.937	$FASnBr_3$	1.021
$AzrSnI_3$	0.950	$MASnI_3$	0.920	$FASnI_3$	0.998
Pb series					
$AzrPbCl_3$	0.965	$MAPbCl_3$	0.933	$FAPbCl_3$	1.019
$AzrPbBr_3$	0.956	$MAPbBr_3$	0.925	$FAPbBr_3$	1.008
$AzrPbI_3$	0.939	$MAPbI_3$	0.909	$FAPbI_3$	0.987

Ionic radii (Å) used for calculations[5]:

Cation	Radius	Cation	Radius	Anion	Radius
AZR^+	2.30	Sn^{2+}	1.15	Cl^-	1.85
MA^+	2.16	Pb^{2+}	1.19	Br^-	1.96
FA^+	2.53			I^-	2.20

Goldschmidt tolerance factors for ABX_3 were calculated as

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

Crystallographic tables for SnI (180 K)

Table S1.1 Crystal data and structure refinement for SnI (180 K).

Empirical formula	C_2I_3NSn
Formula weight	537.42
Temperature/K	180
Crystal system	cubic
Space group	$Pm\bar{3}m$
a/Å	6.2847(3)
Volume/Å^3	248.23(4)
Z	1
ρ_{calc}g/cm^3	3.595
μ/mm^{-1}	11.821
Crystal size/mm^3	0.17 × 0.05 × 0.04
2Θ range for data collection/°	6.484 to 58.21
Reflections collected	269
Independent reflections	88 [R_{int} = 0.0379, R_{sigma} = 0.0361]
Data/restraints/parameters	88/0/8
Goodness-of-fit on F^2	0.808
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0307, wR_2 = 0.0837
Final *R* indexes [all data]	R_1 = 0.0500, wR_2 = 0.1166
Largest diff. peak/hole / e Å^{-3}	0.78/-0.80

Table S1.2 Bond Lengths for SnI (180 K).

	Bond length/Å
Sn1–I1^1	3.14233(17)
C1–C1^2	1.46(5)

^{1}+ *x*,1 – *z*,1 + *y*; ^{2}1 + *y*,1 – *x*,–*z*;

Table S1.3 Bond Angles for SnI (180 K).

	Angle/°
I1^1–Sn1–I1	90
I1–Sn1–I1^2	180
C1^3–C1–C1^4	60

^{1} + *x*, 1 – *z*, 1 + *y*; ^{2}+ *x*, 1 + y, + *z*; ^{3}+ *x*, + *z*, – *y*; ^{4}2 – *x*, – *y*, – *z*.

Crystallographic tables for SnI (105 K)

Table S2.1 Crystal data and structure refinement for SnI (105 K).

Empirical formula	$C_2H_6I_3NSn$
Formula weight	543.47
Temperature/K	105
Crystal system	orthorhombic
Space group	*Pbca*
a/Å	9.0636(8)
b/Å	12.5283(13)
c/Å	17.1804(16)
Volume/Å^3	1950.9(3)
Z	8
ρ_{calc}g/cm^3	3.701
μ/mm^{-1}	12.034
Crystal size/mm^3	0.16 × 0.05 × 0.03
2Θ range for data collection/°	4.742 to 51.35
Reflections collected	4656
Independent reflections	4656 [R_{int} = ?, R_{sigma} = 0.1990]
Data/restraints/parameters	4656/0/65
Goodness-of-fit on F^2	0.749
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.0978
Final *R* indexes [all data]	R_1 = 0.1370, wR_2 = 0.1108
Largest diff. peak/hole / e Å^{-3}	2.33/-1.41

Table S2.2 Bond Lengths for SnI (105 K).

	Bond length/Å
Sn1–I1	2.990(2)
Sn1–I1^1	3.3209(18)
Sn1–I2^2	3.256(3)
Sn1–I2	3.036(3)
Sn1–I3	2.9850(19)
Sn1–I3^3	3.2960(19)
C1–N1	1.46(3)
C1–C2	1.48(3)
N1–C2	1.49(3)

^{1}1/2+ *x*,+ *y*,1/2 – *z*; ^{2}1/2 – *x*, – 1/2 + *y*,+ *z*; ^{3}1/2 + *x*, 1/2 – *y*, – *z*.

Table S2.3 Bond Angles for SnI (105 K).

	Angle/°
I1–Sn1–I1[1]	92.35(4)
I1–Sn1–I[2]	93.34(7)
I1–Sn1–I2[2]	89.84(7)
I1–Sn1–I3[3]	170.46(7)
I2–Sn1–I1[1]	86.26(6)
I2[2]–Sn1–I1[1]	96.61(6)
I2–Sn1–I2[2]	175.63(8)
I2–Sn1–I3[3]	91.28(6)
I2[2]–Sn1–I3[3]	86.02(5)
I3–Sn1–I1[1]	171.61(7)
I3[3]–Sn1–I1[1]	79.62(5)
I3–Sn1–I1	95.23(6)
I3–Sn1–I2	89.72(6)
I3–Sn1–I2[2]	87.01(6)
I3–Sn1–I3[3]	93.14(4)
N1–C1–C2	61.1(15)
C1–N1–C2	60.2(15)
C1–C2–N1	58.7(15)

[1] 1/2 + *x*, + *y*, 1/2 – *z*; [2] 1/2 – *x*, – 1/2 + *y*, + *z*; [3] 1/2 + *x*, 1/2 – *y*, –*z*.

Crystallographic tables for SnBr (180 K)

Table S3.1 Crystal data and structure refinement for SnBr (180 K).

Empirical formula	Br_3C_2NSn
Formula weight	396.45
Temperature/K	180(2)
Crystal system	cubic
Space group	$Pm\bar{3}m$
a/Å	5.9849(3)
Volume/Å^3	214.37(3)
Z	1
ρ_{calc}g/cm^3	3.071
μ/mm^{-1}	16.864
Crystal size/mm^3	0.1 × 0.03 × 0.03
2Θ range for data collection/°	6.808 to 58.158
Reflections collected	257
Independent reflections	78 [R_{int} = 0.0388, R_{sigma} = 0.0416]
Data/restraints/parameters	78/0/9
Goodness-of-fit on F^2	0.825
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0307, wR_2 = 0.0682
Final *R* indexes [all data]	R_1 = 0.0321, wR_2 = 0.0711
Largest diff. peak/hole / e Å^{-3}	0.44/-0.48

Table S3.2 Bond Lengths for SnBr (180 K).

	Bond length/Å
Sn1–Br1[1]	2.775(4)
C1–C1[2]	1.39(5)

[1]1 – *y*,1 – *z*, 1 – *x*; [2] – *z*, – *x*, – *y*.

Table S3.3 Bond Angles for SnBr (180 K).

	Angle/°
Br1[1]–Sn1–Br1[2]	180
Br1[1]–Sn1–Br1	90
C1[2]–C1–C1[3]	60.002(1)

[1] 1 – *y*, 1 – *z*, 1 – *x*; [2] + *y*, + *z*, + *x*; [3] – *x*, – *y*, – *z*.

Crystallographic tables for SnBr (120 K)

Table S4.1 Crystal data and structure refinement for SnBr (120 K).

Empirical formula	$C_2H_6Br_3NSn$
Formula weight	402.50
Temperature/K	120.00(10)
Crystal system	orthorhombic
Space group	*Pbca*
a/Å	8.6989(16)
b/Å	11.969(3)
c/Å	16.144(4)
Volume/Å^3	1680.8(7)
Z	8
ρ_{calc}g/cm^3	3.181
μ/mm^{-1}	17.210
Crystal size/mm^3	0.09 × 0.076 × 0.053
2Θ range for data collection/°	5.046 to 58.694
Reflections collected	8045
Independent reflections	8045 [R_{int} = ?, R_{sigma} = 0.2096]
Data/restraints/parameters	8045/15/67
Goodness-of-fit on F^2	0.942
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0786, wR_2 = 0.1890
Final *R* indexes [all data]	R_1 = 0.1577, wR_2 = 0.2138
Largest diff. peak/hole / e Å^{-3}	4.01/-2.67

Table S4.2 Bond Lengths for SnBr (120 K).

	Bond length/Å
Sn1–Br3	2.745(3)
Sn1–Br2	2.733(3)
Sn1–Br1	2.746(3)
N1–C2	1.460(2)
N1–C1	1.460(2)
C2–C1	1.460(2)

Table S4.3 Bond Angles for SnBr (120 K).

	Angle/°
Br3–Sn1–Br1	92.30(10)
Br2–Sn1–Br3	94.04(9)
Br2–Sn1–Br1	89.71(10)
C1–N1–C2	60.00(12)
C1–C2–N1	60.00(12)
C2–C1–N1	60.00(12)

Crystallographic tables for SnCl (270 K)

Table S5.1 Crystal data and structure refinement for SnCl (270 K).

Empirical formula	C_2Cl_3NSn
Formula weight	263.07
Temperature/K	270.00(14)
Crystal system	orthorhombic
Space group	*Pnma*
a/Å	11.6343(11)
b/Å	8.3830(6)
c/Å	8.0626(6)
Volume/Å^3	786.34(11)
Z	4
ρ_{calc}g/cm^3	2.222
μ/mm^{-1}	4.164
Crystal size/mm^3	0.13 × 0.11 × 0.07
2Θ range for data collection/°	6.148 to 58.262
Reflections collected	3120
Independent reflections	981 [R_{int} = 0.0314, R_{sigma} = 0.0403]
Data/restraints/parameters	981/6/38
Goodness-of-fit on F^2	1.072
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0430, wR_2 = 0.0869
Final *R* indexes [all data]	R_1 = 0.0735, wR_2 = 0.1028
Largest diff. peak/hole / e Å^{-3}	0.95/-0.94

Table S5.2 Bond Lengths for SnCl (270 K).

	Bond length/Å
Sn1–Cl2[1]	3.291(2)
Sn1–Cl2	2.530(2)
Sn1–Cl1	2.531(3)
C2A–N1A	1.464(19)
C2A–C1A	1.406(19)
N1A–C1A	1.456(19)
C2B–N1B	1.50(2)
C2B–C1B	1.431(19)
N1B–C1B	1.444(19)

[1] 3/2 – *x*, – 1/2 + *y*, – 1/2 + *z*.

Table S5.3 Bond Angles for SnCl (270 K).

	Angle/°
Cl2[1]–Sn1–Cl[2]	90.38(9)
Cl2[1]–Sn1–Cl2[2]	88.003(13)
Cl2–Sn1–Cl2[2]	176.76(5)
Cl2–Sn1–Cl1	91.33(5)
Cl1–Sn1–Cl2[2]	85.90(5)
Sn1–Cl2–Sn1[3]	176.09(7)
Sn1–Cl1–Sn1[4]	175.96(9)
C1A–C2A–N1A	60.9(10)
C1A–N1A–C2A	57.6(10)
C2A–C1A–N1A	61.5(11)
C1B–C2B–N1B	59.1(10)
C1B–N1B–C2B	58.2(10)
C2B–C1B–N1B	62.7(11)

[1] + x, 1/2 – y, + z; [2]3/2 – x, – 1/2 + y, – 1/2 + z; [3]3/2 – x, 1 – y, 1/2 + z;
[4]– 1/2 + x, 1/2 – y, 1/2 –z.

Crystallographic tables for SnCl (180 K)

Table S6.1 Crystal data and structure refinement for SnCl (180 K).

Empirical formula	$C_2H_6Cl_3NSn$
Formula weight	269.12
Temperature/K	179(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.1182(6)
b/Å	11.5499(6)
c/Å	8.1286(5)
β/°	90.283(6)
Volume/Å^3	762.16(8)
Z	4
ρ_{calc}g/cm^3	2.345
μ/mm^{-1}	4.298
Crystal size/mm^3	0.07 × 0.05 × 0.05
2Θ range for data collection/°	6.128 to 52.74
Reflections collected	1516
Independent reflections	1516 [R_{int} = ?, R_{sigma} = 0.0322]
Data/restraints/parameters	1516/0/65
Goodness-of-fit on F^2	1.157
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0688
Final *R* indexes [all data]	R_1 = 0.0415, wR_2 = 0.0708
Largest diff. peak/hole / e Å^{-3}	1.11/-1.16

Table S6.2 Bond Lengths for SnCl (180 K).

	Bond length/Å
Sn1–Cl2	2.5283(15)
Sn1–Cl1	2.559(2)
Sn1–Cl3	2.546(2)
N1–C1	1.433(10)
N1–C2	1.449(12)
C1–C2	1.460(13)

Table S6.3 Bond Angles for SnCl (180 K).

	Angle/°
Cl2–Sn1–Cl1	90.52(7)
Cl2–Sn1–Cl3	91.43(7)
Cl3–Sn1–Cl1	90.29(7)
C1–N1–C2	60.9(6)
N1–C1–C2	60.1(6)
N1–C2–C1	59.0(6)

Crystallographic tables for SnCl (120 K)

Table S7.1 Crystal data and structure refinement for SnCl (120 K).

Empirical formula	$C_2H_6Cl_3NSn$
Formula weight	269.12
Temperature/K	120.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.0784(12)
b/Å	8.1003(10)
c/Å	11.5627(14)
β/°	96.128(13)
Volume/Å^3	752.31(17)
Z	4
ρ_{calc}g/cm^3	2.376
μ/mm^{-1}	4.355
Crystal size/mm^3	0.13 × 0.11 × 0.09
2Θ range for data collection/°	5.072 to 57.38
Reflections collected	2534
Independent reflections	2534 [R_{int} = ?, R_{sigma} = 0.0732]
Data/restraints/parameters	2534/0/65
Goodness-of-fit on F^2	0.943
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.0887
Final *R* indexes [all data]	R_1 = 0.0600, wR_2 = 0.0921
Largest diff. peak/hole / e Å^{-3}	3.59/-0.90

Table S7.2 Bond Lengths for SnCl (120 K).

	Bond length/Å
Sn1–Cl2	2.557(2)
Sn1–Cl3	2.544(2)
Sn1–Cl1	2.5338(17)
N1–C2	1.452(10)
N1–C1	1.468(10)
C2–C1	1.453(11)

Table S7.3 Bond Angles for SnCl (120 K).

	Angle/°
Cl3–Sn1–Cl2	90.70(6)
Cl1–Sn1–Cl2	92.19(7)
Cl1–Sn1–Cl3	88.74(7)
C2–N1–C1	59.7(5)
N1–C2–C1	60.7(5)
C2–C1–N1	59.6(5)

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