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Unprecedented tin iodide perovskite structures featuring ordering of organic moieties

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Supplementary Information

Synthesis

Tin powder (~325 mesh, 99.8% metals basis), hydroiodic acid (HI, 57%, w/w aqueous solution stabilised with 1.5% HPA), hypophosphorous acid (H_3PO_2 (HPA), 50% w/w aqueous solution), 1,2,4-triazole ($C_2H_3N_3$, 99%) and 1-methyl imidazole ($C_4N_2H_7$, 99%) were purchased from Alfa Aesar. Guanidinium carbonate ($C_2H_{10}N_6H_2CO_3$, 99%) and diethyl ether ($(C_2H_5)_2O$, 99.5%) were purchased from Sigma Aldrich. All chemicals were directly used without further purification.

Both $(GuH)_{1.5}(Me\text{-}ImH)_{0.5}SnI_4$ and $(GuH)_{0.5}(TzH)_{0.5}SnI_3$ were crystallised by a slow evaporation method.

For $(GuH)_{1.5}(Me\text{-}ImH)_{0.5}SnI_4$ ($[C(NH_2)_3]_{1.5}[C_4N_2H_7]_{0.5}SnI_4$: Tin powder (237 mg, 2 mmol) was dissolved in conc. HI (5 ml) and HPA (5 ml) with moderate heating. Once fully dissolved, guanidinium carbonate (180 mg, 2 mmol) and 1-methyl imidazole (164 mg, 2 mmol) were added and the solution allowed to cool for several days. A mixture of red crystals was obtained. These were filtered and washed with diethyl ether. Elemental analysis: (Anal. Calc. (%) for $(GuH)_{1.5}(Me\text{-}ImH)_{0.5}SnI_4$: C 5.55; N 10.16; H 1.66. Found: C 6.36; N 8.79; H 1.68). The excess of C found in the sample and lower than expected N suggests a mixture of phases present consistent with the mixture of crystals obtained.

For $G_{0.5}T_{0.5}SnI_3$ ($[C(NH_2)_3]_{0.5}[C_2N_3H_4]_{0.5}SnI_3$: Tin powder (237 mg, 2 mmol) was dissolved in conc. HI (5 ml) and HPA (5 ml) with moderate heating. Once fully dissolved, guanidinium carbonate (180 mg, 2 mmol) and 1,2,4-triazole (138 mg, 2 mmol) were added and the solution allowed to cool. Within days, small red crystals formed, these were left to grow in solution for several months before being filtered and washed with diethyl ether. Elemental analysis: (Anal. Calc. (%) for $G_{0.5}T_{0.5}SnI_3$: C 3.19; N 7.44; H 0.89. Found: C 3.31; N 7.57; H 0.88).

The synthesis of both $(GuH)_{1.5}(Me\text{-}ImH)_{0.5}SnI_4$ and $(GuH)_{0.5}(TzH)_{0.5}$ was carried out in air. HPA was used in the reaction to prevent oxidation of Sn^{2+} to Sn^{4+} while the crystals remained in solution. After filtration the crystals were stored under argon. In air $(GuH)_{1.5}(Me\text{-}ImH)_{0.5}SnI_4$ oxidises within seconds with a clear colour change and evolution of I_2. In $(GuH)_{0.5}(TzH)_{0.5}SnI_3$ however, there is no evidence of an immediate colour change or evolution of I_2. There does appear to be some decomposition after 30 minutes suggesting that $(GuH)_{0.5}(TzH)_{0.5}SnI_3$ is more stable than the 3D perovskites $CsSnI_3$[1] and $MASnI_3$[2] but not as stable as $FASnI_3$,[3] which is air stable for approximately 2h before total decomposition after 1 day.

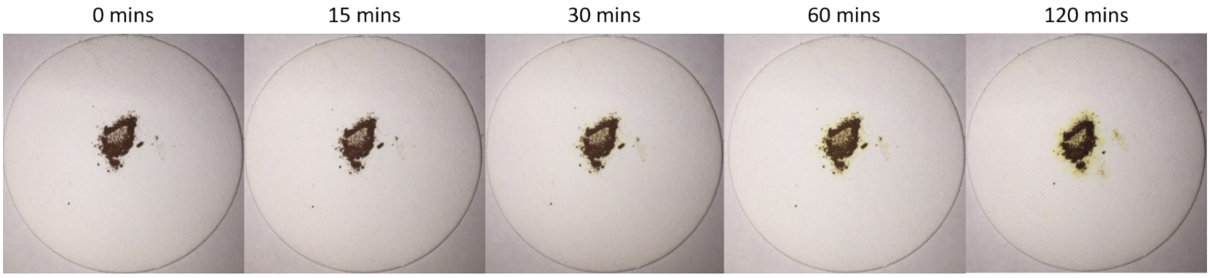

Figure S1 Powdered $(GuH)_{0.5}(TzH)_{0.5}SnI_3$ at different exposure times to air.

Characterisation

Single Crystal data were collected at 173 K on a Rigaku SCX Mini diffractometer using Mo-Kα radiation. Data were collected using CrystalClear (Rigaku).[4] Structures were solved by direct methods and refined using SHELX-2014[5] incorporated in the WINGX program.[6] Absorption corrections were performed semi-empirically from equivalent reflections on the basis of multi scans. Non-H atoms were refined anisotropically and hydrogen atoms were treated as riding atoms.

The bond length distortion of the SnI_6 octahedra in each composition at 173 K was calculated using eq. 1,[7] where d is the average Sn-I bond distance and d_n are the six individual bond distances. The bond angle variance of each octahedron from the ideal 90° of an undistorted structure was calculated using eq. 2,[8] where θ_i is the individual I-Sn-I angle.

$$\Delta d = \left(\frac{1}{6}\right)\sum\left[\frac{d_n - d}{d}\right]^2 \tag{1}$$

$$\sigma^2 = \sum_{i=1}^{12}\frac{(\theta_i - 90)^2}{11} \tag{2}$$

Table S1 Selected bond lengths (Å) and angles (°) derived from single crystal data collected at 173 K.

	$(GuH)_{1.5}(Me\text{-}ImH)_{0.5}SnI_4$				**$(GuH)_{0.5}(TzH)_{0.5}SnI_3$**	
Sn-I	Sn1-I1	3.585(3)	Sn2-I2	3.502(2)	Sn-I3	3.562(1)
	Sn1-I6	3.269(5)	Sn2-I3	3.462(9)	Sn-I2	3.544(1)
	Sn1-I3	3.217(6)	Sn2-I6	3.325(5)	Sn-I1	3.442(1)
	Sn1-I5	3.147(6)	Sn2-I7	3.050(4)	Sn-I1	2.944(1)
	Sn1-I4	3.104(4)	Sn2-I1	2.994(2)	Sn-I2	2.937(1)
	Sn1-I2	2.978(2)	Sn2-I8	2.985(7)	Sn-I3	2.936(1)
BVS	Sn1	1.91	Sn2	1.99	Sn	2.19
	I1	0.63	I2	0.67	I1	0.75
	I3	0.43	I6	0.46	I2	0.72
					I3	0.72
I-Sn-I	84.501(2)		81.549(2)		78.91(2)	
	84.525(2)		84.237(2)		79.00(2)	
	86.708(2)		87.948(2)		86.77(2)	
	88.362(2)		88.822(2)		88.24(2)	
	89.378(2)		89.108(2)		89.20(2)	
	90.763(2)		89.916(2)		89.48(2)	
	91.163(2)		91.222(2)		89.61(2)	
	91.823(1)		92.451(2)		90.42(2)	
	92.307(2)		92.594(2)		91.64(2)	
	93.366(2)		93.347(2)		91.89(2)	
	93.593(2)		93.687(2)		94.11(2)	
	93.807(2)		94.337(2)		112.45(2)	
Sn-I-Sn	159.205(2)		164.832(2)			
	159.809(2)		169.057(2)			
			172.886(2)			

Table S2 Hydrogen bond lengths (Å) and angles (°) for $(GuH)_{1.5}(Me\text{-}ImH)_{0.5}SnI_4$ at 173 K.

D-H…A	**d(D-H)**	**d(H…A)**	**d(D…A)**	**<(DHA)**
N(1)-H(1A)...I(1) #3	0.86	3.30	3.704(5)	111.5
N(1)-H(1A)...I(6) #3	0.86	3.01	3.776(6)	148.9
N(1)-H(1B)...I(5) #4	0.86	3.11	3.801(6)	139.4
N(1)-H(1B)...I(6) #4	0.86	3.29	3.880(6)	127.8
N(2)-H(2A)...I(6) #3	0.86	3.04	3.796(6)	148.1
N(2)-H(2B)...I(1) #5	0.86	3.04	3.853(6)	158.9
N(3)-H(3A)...I(5) #4	0.86	3.11	3.814(6)	141
N(3)-H(3B)...I(1) #5	0.86	3.10	3.899(6)	156
N(4)-H(4A)...I(4) #6	0.86	2.97	3.761(6)	154.7
N(4)-H(4B)...I(8) #5	0.86	2.90	3.734(5)	164.1
N(5)-H(5A)...I(4) #2	0.86	3.25	3.969(6)	142.5
N(5)-H(5A)...I(5) #2	0.86	3.32	3.711(5)	110.8
N(5)-H(5B)...I(4) #6	0.86	2.90	3.708(6)	158
N(6)-H(6A)...I(2) #2	0.86	3.22	3.863(7)	133.5
N(6)-H(6B)...I(7)	0.86	3.16	3.558(6)	111.2
N(7)-H(7A)...I(6)	0.86	3.01	3.678(5)	136.2
N(7)-H(7A)...I(8)	0.86	3.30	3.770(5)	116.8
N(7)-H(7B)...I(7) #7	0.86	2.85	3.660(6)	158.7
N(8)-H(8A)...I(7) #7	0.86	3.02	3.788(6)	150.5
N(8)-H(8B)...I(3) #1	0.86	2.92	3.732(5)	158.2
N(9)-H(9A)...I(2) #2	0.86	3.32	3.968(7)	134.3
N(9)-H(9B)...I(3) #1	0.86	3.10	3.878(7)	151.3
N(9)-H(9B)...I(6) #2	0.86	3.22	3.620(6)	111.2
N(11)-H(12)...I(4) #1	0.86	3.14	3.694(6)	124
N(11)-H(12)...I(5) #2	0.86	3.04	3.643(6)	129.3

Symmetry transformations used to generate equivalent atoms:

#1 $-x + 2, -y + 1, -z$

#2 $-x + 1, -y + 1, -z$

#3 $-x + 2, -y + 2, -z + 1$

#4 $x + 1, y, z + 1$

#5 $-x + 1, -y + 2, -z + 1$

#6 $x, y, z + 1$

#7 $x + 1, y, z$

Table S3 Hydrogen bond lengths (Å) and angles (°) for $(GuH)_{0.5}(TzH)_{0.5}SnI_3$ at 173 K.

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N(1a)-H(1Aa)...I(2) #2	0.86	3.31	3.958(5)	133.9
N(1a)-H(1Aa)...I(3) #2	0.86	3.10	3.818(5)	142.9
N(1a)-H(1Ba)...I(2) #5	0.86	3.31	3.958(5)	133.9
N(1a)-H(1Ba)...I(3) #5	0.86	3.10	3.818(5)	142.9
N(1'b)-H(1'1b)...I(1) #6	0.86	3.28	3.958(18)	138
N(1'b)-H(1'1b)...I(2) #3	0.86	2.82	3.45(2)	131.5
N(1'b)-H(1'2b)...I(1) #3	0.86	3.28	3.958(18)	138
N(1'b)-H(1'2b)...I(2) #6	0.86	2.82	3.45(2)	131.5
N(2a)-H(2Aa)...I(1)	0.86	3.12	3.863(9)	146.3
N(2a)-H(2Ba)...I(2) #6	0.86	3.17	3.810(10)	132.9
N(2'b)-H(2'1b)...I(2) #2	0.86	3.00	3.62(3)	130.8
N(2'b)-H(2'1b)...I(3) #2	0.86	2.98	3.55(3)	125.4
N(2'b)-H(2'2b)...I(1)	0.86	3.12	3.79(3)	136.7
N(4)-H(4A)...I(1)	0.93	3.13	3.927(9)	144.8
N(4)-H(4A)...I(2) #1	0.93	3.01	3.664(9)	128.7
N(5)-H(5A)...I(2) #7	0.93	3.28	3.833(14)	120.2
N(5)-H(5A)...I(3) #2	0.93	3.07	3.823(14)	139.6
N(5)-H(5A)...I(3) #7	0.93	3.25	3.822(13)	121.8

Symmetry transformations used to generate equivalent atoms:

#1 *y*, *x*, -*z*

#2 *x* - ½, -*y* + ½, -*z* + ¼

#3 *x* + ½, -*y* + ½, -*z* + ¼

#4 -*y* + 1, -*x* + 1, -*z* + ½

#5 *y* + ½, -*x* + 3/2, *z* + ¼

#6 *y* + ½, -*x* + ½, *z* + ¼

#7 *x*, *y* + 1, *z*

Table S4 Distortion mode amplitudes for the SnI_6 octahedra in $(GuH)_{0.5}(TzH)_{0.5}SnI_3$ obtained from the ISODISTORT software suite[9] compared to the aristotype $CsSnI_3$ structure.[10]

Mode	Amplitude (Å)	Origin	S, i	*k*-active
Δ_5^a	1.704	(0, 0, 3/2)	4, 24	(0, 0, ¼)
R_3^+	0.034	(-½, -½, 0)	2, 6	(½, ½, ½)
X_4^-	0.299	(0, 0, ½)	2, 6	(0, 0, ½)
M_3^+	0.077	(0, 0, 0)	2, 6	(½, ½, 0)
M_3^-	0.370	(-½, 0, 0)	2, 6	(½, ½, 0)
T_5	0.459	(-½, 0, -½)	4, 24	(½, ½, ¼)

$^a\Delta_5$ is clearly the dominant distortion mode and is responsible for displacement of the iodide ligands leading to the extreme octahedral distortion observed.

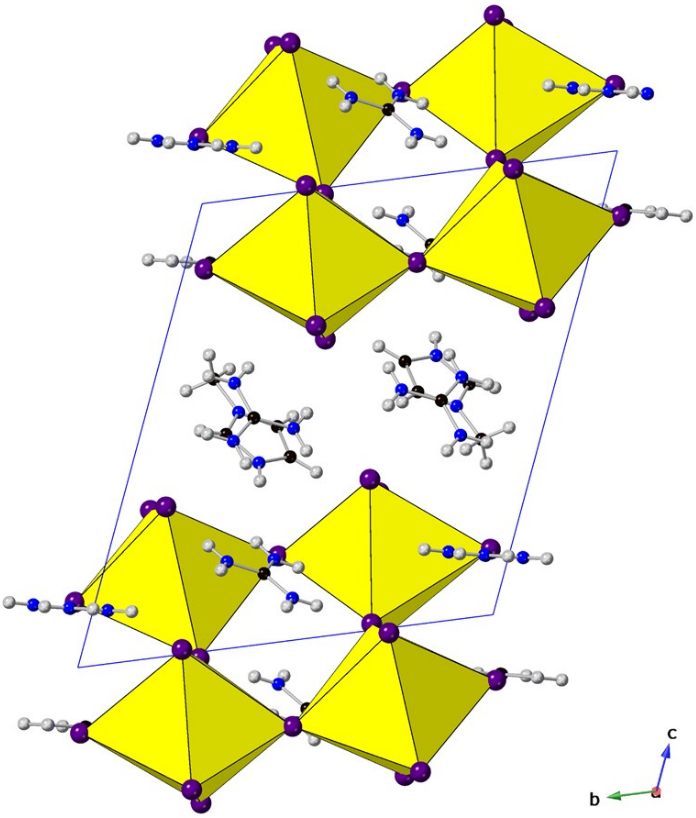

Figure S2 Crystal structure of $(GuH)_{1.5}(Me\text{-}ImH)_{0.5}SnI_4$ viewed along the *b*-axis highlighting the observed staggering of amines.

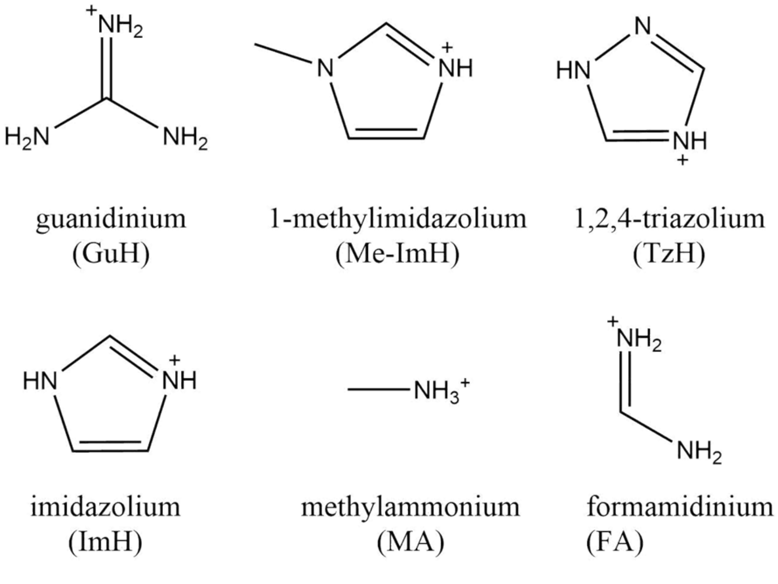

Figure S3 Structures of organic moieties used in this work (top) and previously in literature (bottom).

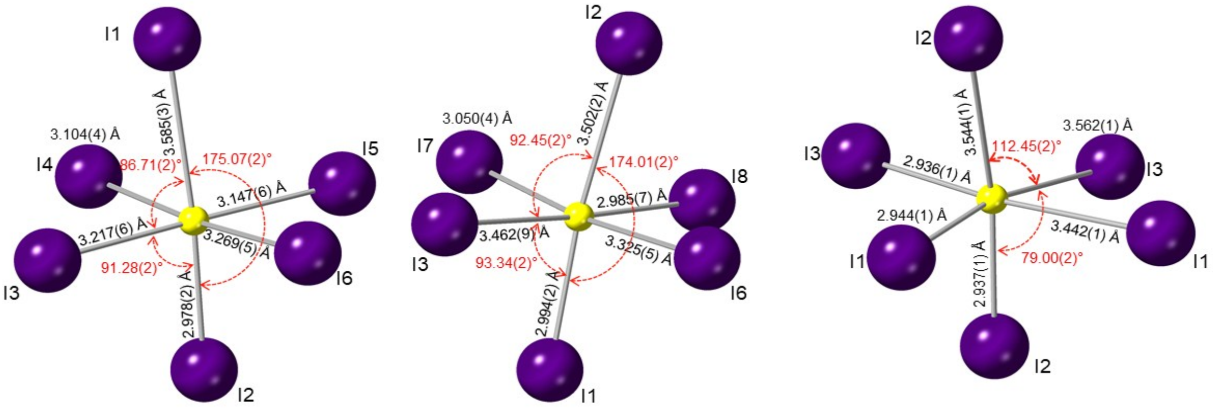

Figure S4 Ball and stick representations of the octahedra present in (left and middle) **1** and (right) **2** highlighting the significant distortion in both bond lengths and bond angles. Note the considerably distorted I2-Sn-I3 bond angle present in **2**.

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