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## Structural diversity in hybrid organic-inorganic lead iodide materials

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**Abstract** The structural chemistry of hybrid organic-inorganic lead iodide materials has become of increasing significance for energy applications since the discovery and development of perovskite solar cells based on methylammonium lead iodide. Seven new hybrid lead iodide compounds have been synthesised and structurally characterised using single crystal X-ray diffraction. The lead iodide units in materials templated with bipyridyl, 1,2-bis(4-pyridyl)ethane, 1,2-di(4-pyridyl)ethylene and imidazole adopt one-dimensional chain structures, while crystallization from solutions containing piperazinium cations generates a salt containing isolated  $[\text{PbI}_6]^+$  octahedral anions. Templating with 4-chlorobenzylammonium lead iodide adopts the well-known 2D layered perovskite structure with vertex shared sheets of composition  $[\text{PbI}_4]^{2-}$  separated by double layers of organic cations. The relationships between the various structures determined, their compositions, stability and hydrogen bonding between the protonated amine and the iodide ions of the  $\text{PbI}_6$  octahedra are described.

**Keywords:** Organic / inorganic hybrid, lead iodide, photovoltaic

### 1. Introduction

Hybrid lead iodide compounds comprised of isolated and linked  $\text{PbI}_6$  octahedral units and organic cations form the basis for a wide range of structures of varying dimensionality, from isolated  $[\text{PbI}_6]^+$  octahedra in simple salt-like materials through to three-dimensional (3D) halide perovskites formed from fully connected  $\text{PbI}_6$  octahedral units. The structural diversity of iodoplumbate and iodobismuthate hybrid compounds has been recently reviewed (Teo, 2009 & Fan, 2006). These compounds have become of increasing technological importance since the discovery of high efficiency photovoltaic cells based on the 3D hybrid perovskite methylammonium lead iodide (Lee, 2012). These compounds self-assemble from solution (Mitzi, 2001) making them extremely attractive functional materials from a processing perspective. A wide range of important physical properties including photoluminescence, (Dammak, 2013), ferroelectricity (Liao, 2015), non-linear optical

activity (Innocenzi & Lebeau, 2005), and conductivity from wide band gap semiconductivity to metallic (Mitzi, 1994) can be induced as a result of the structure-directing and functional effects of different organic moieties.

The 2D layered perovskite structure, of the general composition  $A_2BX_4$ ,  $[A^+]_2[PbI_4^{2-}]$ , is adopted in combination with a wide range of mono- and di-alkylammonium cations, such as hexylamine. These compounds have been particularly well explored as solution processable semiconductors that display a wide range of properties including thermochromic phase transitions (Billing & Lemmerer, 2007) and excitonic effects stemming from their multiple quantum well band structure (Kitazawa, 1997). Most of the known hybrid layered perovskites are of the  $\langle 100 \rangle$  type, where the set of directions refer to cuts of the 3D perovskite  $ABX_3$  structure. The primary factor governing the adoption of a layered perovskite is the cross-sectional area of the organic molecule normal to  $\langle 100 \rangle$  compared to the area defined by four adjacent apical halides (about  $40 \text{ \AA}^2$  for Pb-I octahedra), as exposted by Mercier et al. (2009). Steric effects are, therefore, of primary importance and a wide range of relatively non-bulky or small end group organic cations have been demonstrated to be suitable for generating layered perovskites. Rigidity of the organic component can also play a major role in structure determination, since flexible molecules can adopt conformations to maximise hydrogen bonding to the lattice and energetically favourable inter-chain interactions. Flexibility through tilts and distortions to the highly polarisable lead iodide lattice also increases the range of molecules that can successfully fit the layered perovskite structure.

Beyond the two dimensional layered perovskites, a wide range of interatomic interactions and size effects are important for determining the type of structure formed and the also the nature of the lead iodide network in hybrid amine-lead iodides. These factors which include the basicity of the amine, potential for hydrogen bonding, solvate formation,  $\pi$ - $\pi$  interactions in aromatic amines and dispersion forces mean that, for a given organic amine cation, it is not possible to predict the likely resulting dimensionality of the Pb-I network. Indeed even for simple amines the existence of multiple structural phases and solvates for a single organic species indicate that very subtle interactions between the inorganic and organic structural elements exist. In this study, a range of organic cations have been employed to template hybrid lead iodide compounds. One of the most important goals of the field is to generate compounds with light absorption properties spanning the visible spectrum, yet with radically increased stability towards hydrolysis compared with the poorly performing methylammonium lead iodide. In general, lower dimensional lead iodide structures display wider optical band gaps; however use of conjugated or aromatic nitrogen containing heterocycles forming charge-transfer bands with the inorganic framework may be one approach to increase absorption of low dimensional compounds across the visible spectrum (Li, 2012).

## 2. Experimental

### 2.1. Synthesis and crystallisation

Synthesis of precursor iodide salts for each compound was carried out by neutralisation with concentrated aqueous HI (57wt%, Sigma). For 1,2-bis(4-pyridyl)ethane.2HI, 0.001 mol (0.184 g) 1,2-bis(4-pyridyl)ethane (Sigma) was dissolved in 20 mL ethanol in a round bottom flask and kept at 0 °C in an ice bath. 2 equivalents (0.264 mL, 0.002 mol) HI were pipetted dropwise to the flask under stirring. A white precipitate resulted, which was filtered, washed with ethanol and dried at 50 °C in ambient conditions. Yield 0.2603 g, 59.2%. Other iodide salts were prepared in an analogous manner.

#### 2.1.1. 4-Chlorobenzylamine, [ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH<sub>3</sub>]<sub>2</sub>[PbI<sub>4</sub>]

4-Chlorobenzylammonium iodide was synthesised by neutralisation of 4-chlorobenzylamine with hydroiodic acid (57wt% aq.) in ice-cold ethanol. The solvent was removed by rotary evaporation. A three neck round bottom flask equipped with nitrogen inlet and reflux condenser was charged with 6.8 mL HI and 1.7 mL H<sub>3</sub>PO<sub>2</sub>. The acid was degassed for 10 mins and stirred until the colour had changed from brown to yellow. 0.462 g (1 mmol) PbI<sub>2</sub> and 0.539 g (2 mmol) 4-chlorobenzylammonium iodide were added to the flask and the mixture heated to 100 °C under reflux to dissolve the reactants. Upon cooling, a golden crystalline precipitate of 4-chlorobenzylammonium lead iodide (**1**) formed.

#### 2.1.2. 4,4'-Bipyridyl, [H<sub>2</sub>-4,4'-bipyridyl][PbI<sub>4</sub>]

0.236 g of 4,4'-bipyridyl diiodide and 0.264 g PbI<sub>2</sub> were combined with 5 mL hydroiodic acid (57wt% aq.) and sealed in a 23 mL Teflon<sup>TM</sup>-lined stainless steel autoclave. The mixture was heated to 140 °C for 24 hours before cooling to room temperature at a rate of 5 °C / hour. The black crystals of the product (**2**) obtained were filtered, washed with ethanol, and dried at 50 °C.

#### 2.1.3. 4,4'-Bipyridyl DMSO solvate, [H<sub>2</sub>-4,4'-bipyridyl][PbI<sub>3</sub>]<sub>2</sub>.2DMSO

The DMSO solvate crystals of 4,4'-bipyridyl lead iodide (**3**) were obtained by slow evaporation of ethyl acetate into 1 mL DMSO solution containing 0.103 g (0.25 mmol) 4,4'-bipyridyl iodide and 0.115 g (0.25 mmol) PbI<sub>2</sub>.

#### 2.1.4. 1,2-Bis(4-pyridyl)ethane DMF solvate, ; [(H-C<sub>5</sub>H<sub>4</sub>NCH<sub>2</sub>)<sub>2</sub>][PbI<sub>3</sub>]<sub>2</sub>.2DMF

The DMF solvate structure (**4**) was recovered by the slow vapour diffusion of ethanol into a solution of 0.25 mmol (0.11 g) 1,2-bis(4-pyridyl)ethane.2HI and 0.25 mmol PbI<sub>2</sub> (0.115 g) in 1 mL DMF over 12 hours to yield yellow needles up to 1 mm in length.

#### 2.1.5. 1,2-Di(4-pyridyl)ethylene DMSO solvate, [(H-C<sub>5</sub>H<sub>4</sub>NCH<sub>2</sub>)<sub>2</sub>][PbI<sub>3</sub>]<sub>2</sub>.4DMSO

The DMSO solvate for 1,2-di(4-pyridyl)ethylene lead iodide (**5**) was obtained in identical manner to 1,2-bis(4-pyridyl)ethane using 1,2-di(4-pyridyl)ethylene (Sigma) in DMSO with slow vapour diffusion of ethyl acetate.

### 2.1.6. Imidazole, [C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>]PbI<sub>3</sub>

0.224 g Imidazole.2HI and 0.264 g PbI<sub>2</sub> were combined with 5 mL hydroiodic acid (57wt% aq.) and sealed in a 23 mL Teflon<sup>TM</sup>-lined stainless steel autoclave. The mixture was heated to 140 °C for 24 hours before cooling to room temperature at a rate of 5 °C / hour. The yellow crystals of the product (**6**) obtained were filtered, washed with ethanol, and dried at 50 °C.

### 2.1.7. Piperazine, [H<sub>2</sub>-C<sub>4</sub>N<sub>2</sub>H<sub>10</sub>]<sub>2</sub>PbI<sub>6</sub>

Piperazine lead iodide (**7**) was prepared in analogous manner to imidazole: 0.196 g piperazine.2HI and 0.264 g PbI<sub>2</sub> were combined with 5 mL hydroiodic acid (57wt% aq.) and sealed in a 23 mL Teflon<sup>TM</sup>-lined stainless steel autoclave. The mixture was heated to 140 °C for 24 hours before cooling to room temperature at a rate of 5 °C / hour. The yellow crystals obtained were filtered, washed with ethanol, and dried at 50 °C.

## 2.2. X-ray structure determination

Single crystal data for compounds **1-7** were collected at 150 K with an Agilent SuperNova dual tube Eos S2 CCD diffractometer operating graphite monochromated Mo-K $\alpha$  ( $\lambda = 0.7093$  Å) radiation. Structure solution and refinement was carried out in WinGX using XPREP and SHELXS-2013 to solve structures by direct methods and SHELXL-2013 for structure refinement. All H-atoms were refined by the riding model.

**Table 1**

Experimental details

|  | (1)   | (2)  | (3)  | (4)   | (5)   | (6)   | (7)   |
|--|---|--|--|---|---|---|---|
| Crystal data   |   |  |  |   |   |   |   |
| Empirical chemical composition and molecular formula | C <sub>14</sub> H <sub>18</sub> Cl <sub>2</sub> I<br>4N <sub>2</sub> Pb;<br>[ClC <sub>6</sub> H <sub>4</sub> C<br>H <sub>2</sub> NH <sub>3</sub> ] <sub>2</sub> [P<br>bI <sub>4</sub> ] | C <sub>10</sub> H <sub>10</sub> I <sub>4</sub> N <sub>2</sub><br>Pb; [H <sub>2</sub> -<br>4,4'-<br>bipyridyl][<br>PbI <sub>4</sub> ] | C <sub>14</sub> H <sub>22</sub> I <sub>6</sub> N <sub>2</sub><br>O <sub>2</sub> Pb <sub>2</sub> S <sub>2</sub> ;<br>[H <sub>2</sub> -4,4'-<br>bipyridyl]P<br>bI <sub>3</sub> ] <sub>2</sub> .2DM<br>SO | C <sub>9</sub> H <sub>13</sub> I <sub>3</sub> N <sub>2</sub> O<br>Pb; [(H-<br>C <sub>5</sub> H <sub>4</sub> NCH <sub>2</sub> ) <sub>2</sub><br>]PbI <sub>3</sub> ] <sub>2</sub> .2D<br>MF | C <sub>10</sub> H <sub>18</sub> I <sub>3</sub><br>NO <sub>2</sub> PbS <sub>2</sub><br>; [(H-<br>C <sub>5</sub> H <sub>4</sub> NC<br>H <sub>2</sub> ) <sub>2</sub> ][PbI<br>3] <sub>2</sub> .4DM<br>SO | C <sub>3</sub> H <sub>5</sub> I <sub>3</sub> N <sub>2</sub><br>Pb;<br>[C <sub>3</sub> N <sub>2</sub> H <sub>5</sub> ]<br>PbI <sub>3</sub> | C <sub>8</sub> H <sub>24</sub> I <sub>6</sub> N <sub>4</sub><br>Pb; [H <sub>2</sub> -<br>C <sub>4</sub> N <sub>2</sub> H <sub>10</sub> ] <sub>2</sub><br>PbI <sub>6</sub> |
| Mr   | 1000.3  | 873.02   | 1490.29  | 753.13  | 836.26  | 656.98  | 1144.93   |

|                             |   |  |  |  |   |   |   |
|-----------------------------|---|--|--|--|---|---|---|
| Crystal system, space group | Monoclini<br>c, P2 <sub>1</sub>                                     | Monoclini<br>c, I2/a   | Orthorhom<br>bic, Pbca   | Monoclinic,<br>P2 <sub>1</sub> /c                              | Monocli<br>nic, P2 <sub>1</sub> /c                                    | Hexagon<br>al, P6 <sub>3</sub> /m                                     | Monoclini<br>c, P2/n  |
| Temperature (K)             | 150   | 150  | 150  | 150  | 150   | 150   | 150   |
| a, b, c (Å)                 | 8.5992 (3),<br>8.9125 (3),<br>15.8039<br>(6)                        | 7.7839(3)<br>14.1821(5)<br>,<br>15.3644(7)                         | 8.0519 (1),<br>23.4398<br>(3),<br>32.8901<br>(5)                   | 11.8465 (4),<br>17.6887 (6),<br>8.1762 (3)                     | 15.0068<br>(15),<br>16.9568<br>(15),<br>8.1667<br>(5)                 | 15.5643<br>(6),<br>8.0123<br>(5)                                      | 9.8058<br>(3),<br>9.2603<br>(3),<br>12.4081<br>(4)                    |
| β (°)                       | 95.502 (3)  | 90.434(4)  |  | 98.798 (3)   | 95.491<br>(9)   |   | 93.553 (3)  |
| V (Å <sup>3</sup> )         | 1205.64<br>(7)  | 1696.06(12<br>)  | 6207.51<br>(15)  | 1693.16 (10)   | 2068.6<br>(3)   | 1680.92<br>(17)   | 1124.55<br>(6)  |
| Z                           | 2   | 4  | 8  | 2  | 2   | 6   | 2   |
| Radiation type              | Mo Kα   | Mo Kα  | Mo Kα  | Mo Kα  | Mo Kα   | Mo Kα   | Mo Kα   |
| μ (mm <sup>-1</sup> )       | 12.34   | 17.212   | 16.95  | 15.42  | 12.83   | 23.26   | 15.73   |
| Crystal size (mm)           | 0.4 × 0.2 ×<br>0.1  | 0.3 ×<br>0.2 × 0.1   | 0.5 × 0.2 ×<br>0.1   | 0.3 × 0.1 ×<br>0.05  | 0.4 × 0.1<br>× 0.05   | 0.3 × 0.1<br>× 0.05   | 0.4 × 0.3 ×<br>0.4  |
| Data collection             |   |  |  |  |   |   |   |
| Diffractometer              | SuperNova<br>a, Dual,<br>Cu at zero,<br>EosS2<br>diffractom<br>eter | SuperNova<br>, Dual, Cu<br>at zero,<br>EosS2<br>diffractom<br>eter | SuperNova<br>, Dual, Cu<br>at zero,<br>EosS2<br>diffractom<br>eter | SuperNova,<br>Dual, Cu at<br>zero, EosS2<br>diffractomet<br>er | SuperNo<br>va, Dual,<br>Cu at<br>zero,<br>EosS2<br>diffracto<br>meter | SuperNo<br>va, Dual,<br>Cu at<br>zero,<br>EosS2<br>diffracto<br>meter | SuperNov<br>a, Dual,<br>Cu at<br>zero,<br>EosS2<br>diffracto<br>meter |
| Absorption correction       | Multi-scan  | Multi-scan   | Multi-scan   | Multi-scan   | Multi-<br>scan  | Multi-<br>scan  | Multi-<br>scan  |

|  |                               |                               |  |                               |                               |                               |                               |
|--|-------------------------------|-------------------------------|--|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| $T_{\min}, T_{\max}$   | 0.625,<br>1.000               | 0.79148,<br>1.00000           | 0.448,<br>1.000  | 0.626,<br>1.000               | 0.623,<br>1.000               | 0.246,<br>1.000               | 0.687,<br>1.000               |
| No. of measured independent and observed [ $I > 2\sigma(I)$ ] reflections  | 5488,<br>4219,<br>3773        | 2612,<br>2612, 1440           | 15898,<br>7106, 5859   | 7910, 3869,<br>3069           | 7724,<br>4632,<br>2814        | 3203,<br>1277,<br>977         | 5870,<br>2624,<br>2339        |
| $R_{\text{int}}$   | 0.029                         | 0.0232                        | 0.033  | 0.05                          | 0.082                         | 0.034                         | 0.030                         |
| $(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )                 | 0.686                         | 0.682                         | 0.692  | 0.689                         | 0.687                         | 0.676                         | 0.690                         |
| Refinement   |                               |                               |  |                               |                               |                               |                               |
| $R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , S                                    | 0.031,<br>0.054,<br>0.87      | 0.0284,<br>0.054, 0.98        | 0.033,<br>0.067, 1.04  | 0.044, 0.093,<br>1.02         | 0.089,<br>0.197,<br>1.07      | 0.096,<br>0.225,<br>1.12      | 0.027,<br>0.049,<br>1.04      |
| No. of reflections   | 4219                          | 1652                          | 7106   | 3869                          | 4632                          | 1277                          | 2624                          |
| No. of parameters  | 211                           | 78                            | 257  | 142                           | 97                            | 35                            | 87                            |
| No. of restraints  | 1                             | 18                            | 0  | 0                             | 15                            | 0                             | 0                             |
| H-atom treatment   | H-atom parameters constrained | H-atom parameters constrained | H atoms treated by a mixture of independent and constrained refinement | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ ) | 1.50,<br>-1.86                | 0.80, -1.07                   | 1.09, -1.33  | 2.47, -2.47                   | 2.87,<br>-2.29                | 5.09,<br>-10.08               | 1.30,<br>-1.14                |

|                    |                                      |
|--------------------|--------------------------------------|
| Absolute structure | Refined as a partial inversion twin. |
| Flack parameter    | 0.114 (10)                           |

Computer programs: *SHELXL2014* (Sheldrick, 2014). PLATON (Spek, 2005), XPREP (Sheldrick, 1999)

**Table 2**

Bond length range for Pb-I bonds in the  $\text{PbI}_6$  octahedral unit for each compound, these and the bond angle range for apical iodine – lead – equatorial iodine provides a measure of the distortions from ideal octahedral geometry.

| Compound | Organic component (solvate) and compound composition  | Pb-I octahedra bond length range / Å | $I_{\text{ap}}\text{-Pb-}I_{\text{eq}}$ octahedra bond angle range / degrees |
|----------|---|--------------------------------------|--|
| 1        | 4-chlorobenzylamine, $[\text{ClC}_6\text{H}_4\text{CH}_2\text{NH}_3]_2[\text{PbI}_4]$                         | 3.1444(1) - 3.2428(1)                | 86.97(1) - 94.06(1)  |
| 2        | 4,4'-bipyridyl, $[\text{H}_2\text{-4,4'-bipyridyl}][\text{PbI}_4]$  | 3.1233(5) - 3.2765(5)                | 85.261(11) - 96.398(12)  |
| 3        | 4,4'-bipyridyl (DMSO); $[\text{H}_2\text{-4,4'-bipyridyl}]\text{PbI}_3 \cdot 2\text{DMSO}$                    | 3.0201(8) - 3.5200(8)                | 81.60(2) - 97.67(2)  |
| 4        | 1,2-bis(4-pyridyl)ethane (DMF); $[(\text{H-C}_5\text{H}_4\text{NCH}_2)_2][\text{PbI}_3] \cdot 2\text{DMF}$    | 3.1897(1) - 3.3286(1)                | 79.91(1) - 106.82(1)   |
| 5        | 1,2-di(4-pyridyl)ethylene (DMSO); $[(\text{H-C}_5\text{H}_4\text{NCH}_2)_2][\text{PbI}_3] \cdot 4\text{DMSO}$ | 3.1769(3) - 3.3093(3)                | 80.46(1) - 107.64(1)   |
| 6        | Imidazole; $[\text{C}_3\text{N}_2\text{H}_5]\text{PbI}_3$   | 3.2247(2) - 3.2397(2)                | 84.57(5) - 95.28(7)  |
| 7        | Piperazine; $[\text{H}_2\text{-C}_4\text{N}_2\text{H}_{10}]_2\text{PbI}_6$                                    | 3.1995(4) - 3.2819(4)                | 85.313(9) - 102.502(14)  |

Bond length and angle data calculated using PLATON (Spek, 2005)

### 3. Crystal Structure Results

**Figure 1** 4-chlorobenzylammonium lead iodide (**1**) layered perovskite structure viewed in (a) down the  $a$ -axis with  $c$  axis vertical, displaying the interlayer spacing of lead iodide octahedra and (b) down the  $c$  axis with  $a$  axis vertical. Lead iodide octahedra are shaded in grey with iodide ions as dark purple spheres. Carbon (black), nitrogen (light blue), hydrogen (pale pink), chloride (bright green) comprising the organic component are interleaved between the inorganic sheets.



**Figure 2** ORTEP drawing of 4-chlorobenzylammonium lead iodide (**1**) showing the asymmetric unit plus iodide ions to complete the lead iodide polyhedral. Symmetry-related atoms are identified and share the numbering scheme of hydrogen bonding [Table 3](#).

**Table 3**

Hydrogen-bonding parameters for 4-chlorobenzylammonium lead iodide (**1**) [distances in Å and angles in degrees].

| D-H...A               | d(D-H) | d(H...A) | d(D...A)  | <(DHA) |
|-----------------------|--------|----------|-----------|--------|
| N(2)-H(2A)...I(5)#5   | 0.91   | 2.83     | 3.649(13) | 150.5  |
| N(2)-H(2B)...I(3)     | 0.91   | 2.88     | 3.735(13) | 156.8  |
| N(2)-H(2C)...I(2)#3   | 0.91   | 2.70     | 3.578(16) | 161.7  |
| C(10)-H(10A)...I(2)#6 | 0.99   | 3.17     | 4.110(13) | 158.3  |
| N(1)-H(1A)...I(2)#7   | 0.91   | 2.74     | 3.622(12) | 164.9  |
| N(1)-H(1B)...I(1)#8   | 0.91   | 3.01     | 3.682(13) | 131.9  |
| N(1)-H(1B)...I(5)#7   | 0.91   | 3.06     | 3.611(15) | 120.6  |
| N(1)-H(1C)...I(3)#8   | 0.91   | 2.68     | 3.573(17) | 168.6  |

Symmetry transformations used to generate equivalent atoms:

#3 -x+1,y+1/2,-z+2 #5 x+1,y,z #6 x-1,y,z-1 #7 x,y,z-1 #8 -x,y-1/2,-z+1

4-Chlorobenzylammonium lead iodide,  $[\text{ClC}_6\text{H}_4\text{NH}_3]_2[\text{PbI}_4]$ , (**1**) crystallises in  $P2_1$  at 150 K with an interlayer spacing of 15.77 Å and is representative of the layered hybrid perovskites taken from  $\langle 100 \rangle$  cuts of the 3D perovskite lattice. The  $([\text{PbI}_4]^{2-})_n$  sheets are formed from  $[\text{PbI}_6]$  octahedra sharing four vertices in a plane and are charge balanced by *N*-protonated 4-chlorobenzylammonium cations forming slightly interleaved, double sheets between the lead iodide layers, [Figures 1 and 2](#). Many hybrid perovskites show distortions of the octahedra due to stereoactivity of the Pb(II)  $6s^2$  lone pair of electrons, though these effects are generally more pronounced for Sn(II) and Ge(II) than for Pb, and for Cl and Br than I (Mitzi, 1996). As a means to quantify the distortions to the pristine layered perovskite structure, the in-plane rotation  $a$  is given by the M-I-M bond angle, generally around  $160^\circ$  for hybrid lead iodides (Mercier, 2009), while  $a = 154^\circ$  for chlorobenzylammonium iodide. The out-of-plane rotation,  $b$ , or relative tilt of octahedra with respect to the plane of Pb ions is  $91^\circ$ . Comparison to the materials studied by Liu *et al.*, (2004), shows that 4-chloroaniline lead iodide displays a severely distorted Pb-I octahedra and tilted layers  $b = 144^\circ$ ,  $a = 85^\circ$  to accommodate the *p*-chloroaniline, which displays a similar cross-sectional area to 4-chlorobenzylamine, but reduced flexibility with the lack of rotational freedom the methylene unit provides. The Pb-I octahedra show minor distortions with Pb-I bond lengths in the range 3.1444(1) Å- 3.2428(1) Å and  $I_{\text{ap}}\text{-Pb-}I_{\text{eq}}$  angles  $86.89(1)^\circ\text{-}94.06(1)^\circ$ .

**Figure 3** Hydrogen bonding interactions between the NH<sub>3</sub> group on 4-chlorobenzylammonium and the lead iodide inorganic framework, for key see Figure 1 caption. Tilting of the inorganic octahedra is such that NH...I distances are decreased, while the apical iodides on adjacent octahedra tilt away from the –CH<sub>2</sub>- group

The protonated amine group of the chlorobenzylammonium cation “docks” into the lead iodide layer in a manner very reminiscent of the position of the methylammonium cation in the perovskitic methylammonium lead iodide (Weller, 2015), **Figure 3**; four corner sharing PbI<sub>6</sub> octahedra produce a “square antiprismatic box” of iodide ions. The terminal [-CH<sub>2</sub>-NH<sub>3</sub>]<sup>+</sup> element of the chlorobenzylammonium cation is situated and directed towards the one side of this box forming moderately strong hydrogen bonds to the iodide anions, with NH...I distances in the range 2.68 – 3.06 Å. This hydrogen bonding interaction, which is strongest with two apical iodide ions, pulls the terminal [-CH<sub>2</sub>-NH<sub>3</sub>]<sup>+</sup> group towards one side of the box so that the benzyl hydrogen atoms do not interact with the opposing iodide ions, with the CH...I distance greater than 3.10 Å. The chlorobenzylammonium cations alternate in positions either side of the [PbI<sub>4</sub>]<sup>2-</sup> layer along the orthogonal <1 1 0> and <1 -1 0> directions and this also allows the [Cl-C<sub>6</sub>H<sub>5</sub>-] groups to interleave slightly in the interlayer space with the [PbI<sub>4</sub>]<sup>2-</sup> layers directly stacked in the *c*-direction .

The structural chemistry of Pb-I frameworks with N-heterocyclic organic cations has been relatively less well explored, though a few examples have been reported. 4,4'-Bipyridyl lead iodide, [H<sub>2</sub>-4,4'-bipyridyl][PbI<sub>4</sub>], (**2**) has previously been mentioned in one paper (Yin & Cui, 2004); however detailed structural information from this source is not available. In this work the structure of [H<sub>2</sub>-4,4'-bipyridyl][PbI<sub>4</sub>] was found to consist of edge-sharing PbI<sub>6</sub> octahedra forming [PbI<sub>4</sub>]<sup>2-</sup><sub>n</sub> chains oriented along [1 0 0]. The diprotonated bipy molecular cations occupy channels formed between [PbI<sub>4</sub>]<sup>2-</sup><sub>n</sub> chains along in the [1 0 0] direction to give a chequerboard-like structure when viewed along the *a* axis, **Figures 4 and 5**. There is no appreciable hydrogen bonding between the protonated bipy and iodide ions with the shortest NH...I distance at 3.04 Å (**Table 4**). The aromatic rings of the bipy molecular cations are slightly tilted relative to each other with a torsion angle of 28.2°.

**Figure 4** The structure of 4,4'-bipyridyl lead iodide, viewed along the *a* axis with the *c* axis vertical. The 1D chains of edge-sharing lead iodide octahedra are interspersed horizontally and vertically by 1D chains of H<sub>2</sub>-4,4'-bipyridyl molecular cations. For key see Figure 1 caption.

**Figure 5** ORTEP drawing of 4,4'-bipyridyl lead iodide showing the asymmetric unit, iodide ions to complete the lead iodide polyhedral, with symmetry-related atoms identified.

#### Table 4

Hydrogen-bonding parameters for 4,4'-bipyridyl lead iodide (**2**) [distances in Å and angles in degrees].

| D-H...A             | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------|--------|----------|----------|--------|
| N(1)-H(1)...I(2)#7  | 0.86   | 3.04     | 3.664(5) | 131.4  |
| N(1)-H(1)...I(3)    | 0.86   | 3.05     | 3.688(5) | 132.8  |
| C(6)-H(6)...I(3)#7  | 0.93   | 3.23     | 3.803(6) | 121.6  |
| C(3)-H(3)...I(2)    | 0.93   | 3.11     | 3.760(6) | 128.3  |
| C(3)-H(3)...I(3)    | 0.93   | 3.11     | 3.725(7) | 125.3  |
| C(1)-H(1A)...I(2)#7 | 0.93   | 3.13     | 3.720(7) | 123.0  |
| C(1)-H(1A)...I(3)#7 | 0.93   | 3.25     | 3.809(7) | 120.6  |
| C(4)-H(4)...I(2)    | 0.93   | 3.21     | 3.816(6) | 124.6  |
| C(4)-H(4)...I(3)#2  | 0.93   | 3.27     | 3.877(6) | 125.3  |

Symmetry transformations used to generate equivalent atoms:

#2  $x, -y+1/2, z+1/2$  #7  $-x+1, y+1/2, -z+1/2$

A solvate of 4,4'-bipyridyl with lead iodide containing DMSO (**3**) was obtained from solvent interdiffusion. This compound of stoichiometry  $[\text{H}_2\text{-4,4'-bipyridyl}]\text{PbI}_3]_2 \cdot 2\text{DMSO}$  displays staggered chains of edge-sharing Pb-I distorted octahedra separated along [010] by  $[\text{H}_2\text{-4,4'-bipyridyl}]$  dications and along [0 0 1] by DMSO molecules, **Figures 6 and 7**. The lead iodide chains of composition  $[\text{Pb}_2\text{I}_6]_n^{2n-}$  are formed from pairs of  $[\text{PbI}_6]$  octahedra, of composition  $[\text{Pb}_2\text{I}_{10}]$ , which are in turn edge-shared along the  $a$  direction to form a ladder with off-set ‘‘rungs’’ (each rung is a  $[\text{Pb}_2\text{I}_{10}]$  unit). The individual  $\text{PbI}_6$  octahedra are strongly distorted with Pb-I bond lengths between 3.0201(8) Å - 3.5200(8) Å and I-Pb-I bond angles between 81.60(2)° - 97.67(2)°. These distortions have the effect of slightly curving the individual ‘‘rungs’’ of the ladder– the direction of the curve in neighbouring chains repeated along the  $b$ -axis but inverted along the  $c$ -axis, such that the structure has a ‘wave’ like appearance when viewed perpendicular to the  $yz$  plane. The dihedral angle between the pyridyl rings of bipy for **2** is 28.2°, while for **3** it is only 2.7°. This solvate’s columnar structure is rather unusual, but is reminiscent of the  $[\text{Pb}_3\text{I}_9]_n^{3n-}$  chains observed in  $N,N'$ -diethyl-4,4'-bipyridinium and  $N,N'$ -dipropyl-4,4'-bipyridinium lead iodide described in Chen et al. (2011), through in the present case, every  $[\text{Pb}_2\text{I}_6]^{2-}$  unit in the  $[\text{Pb}_2\text{I}_6]_n^{2n-}$  chain is staggered relative to the adjacent pair.

**Figure 6** The DMSO solvate structure of 4,4'-bipyridyl lead iodide (**3**) displays curving of the octahedral columns, running in waves along the  $c$  axis. Atom colours as Figure 1, with oxygen (red) and sulfur (yellow).

**Figure 7** ORTEP view of the DMSO solvate of 4,4'-bipyridyl lead iodide (**3**)**Table 5**

Hydrogen-bonding parameters for 4,4'-Bipyridyl lead iodide DMSO solvate (**3**) [distances in Å and angles in degrees].

| D-H...A               | d(D-H)  | d(H...A) | d(D...A) | <(DHA) |
|-----------------------|---------|----------|----------|--------|
| N(2)-H(2)...S(2)      | 0.86    | 2.86     | 3.679(7) | 160.3  |
| N(2)-H(2)...O(4)      | 0.86    | 1.75     | 2.604(8) | 171.0  |
| C(9)-H(9)...I(4)      | 0.93    | 3.28     | 3.901(6) | 126.4  |
| C(9)-H(9)...I(4)#2    | 0.93    | 3.32     | 3.842(6) | 117.7  |
| C(8)-H(8)...I(3)#5    | 0.93    | 3.20     | 3.833(7) | 126.6  |
| C(7)-H(7)...I(3)#6    | 0.93    | 3.26     | 3.731(6) | 113.6  |
| C(7)-H(7)...I(3)#5    | 0.93    | 3.16     | 3.810(7) | 129.0  |
| C(6)-H(6)...I(5)#5    | 0.93    | 3.20     | 3.831(6) | 127.0  |
| C(3)-H(3)...I(6)      | 0.93    | 3.24     | 3.871(6) | 127.2  |
| C(5)-H(5)...I(5)#5    | 0.93    | 3.12     | 3.790(7) | 130.6  |
| C(4)-H(4)...I(6)      | 0.93    | 3.19     | 3.849(6) | 129.7  |
| C(10)-H(10)...I(4)    | 0.93    | 3.19     | 3.857(7) | 130.2  |
| C(15)-H(15A)...I(7)#7 | 0.96    | 3.29     | 4.094(7) | 142.0  |
| C(15)-H(15B)...O(4)#1 | 0.96    | 2.50     | 3.406(8) | 156.7  |
| C(13)-H(13A)...I(8)#8 | 0.96    | 3.13     | 3.970(9) | 147.6  |
| C(13)-H(13C)...I(6)#2 | 0.96    | 3.25     | 4.083(8) | 145.9  |
| C(11)-H(11A)...I(5)#9 | 0.96    | 3.31     | 4.063(9) | 136.6  |
| N(1)-H(17)...S(1)     | 0.87(7) | 2.81(7)  | 3.657(7) | 167(5) |
| N(1)-H(17)...O(3)     | 0.87(7) | 1.70(7)  | 2.534(8) | 160(6) |
| C(16)-H(16C)...I(7)#9 | 0.96    | 3.32     | 4.217(8) | 155.7  |

Symmetry transformations used to generate equivalent atoms:

#1  $x+1/2, y, -z+1/2$  #2  $x-1/2, y, -z+1/2$  #5  $-x+1/2, y-1/2, z$  #6  $-x+1, y-1/2, -z+1/2$   
 #7  $-x, y-1/2, -z+1/2$  #8  $x, -y+1/2, z-1/2$  #9  $x-1/2, -y+1/2, -z+1$

The DMF solvate of 1,2-bis(4-pyridyl)ethane,  $[(\text{H-C}_5\text{H}_4\text{NCH}_2)_2][\text{PbI}_3]_2 \cdot 2\text{DMF}$ , (**4**) and DMSO solvate of 1,2-di(4-pyridyl)ethylene lead iodide,  $[(\text{H-C}_5\text{H}_4\text{NCH}_2)_2][\text{PbI}_3]_2 \cdot 4\text{DMSO}$ , (**5**) both form structures containing one-dimensional (1D) face-sharing  $\text{PbI}_6$  octahedra in chains of the composition  $[\text{PbI}_3^-]_n$ . **Figures 8, 9 and 10**. This face-sharing motif is commonly found for 1D chains based on  $\text{PbI}_6$  octahedra (Teo *et al.*, 2009) though these may show significant deviation from ideal octahedral geometry, even so far as trigonal prismatic coordination around the lead atom, as found in 1,1'-dimethyl-4,4'-bipyridinium lead iodide (Tang & Guloy, 1999). In the case of **4**, Pb-I bond lengths vary between 3.1897(1) Å - 3.3286(1) Å and I-Pb-I bond angles between 77.69(1)° - 106.82(1)°, representing a significant distortion from perfect octahedral geometry around the lead centre. Similar geometry around lead centres and chain geometry were found in compound **5**. The distribution of solvent molecules and molecular cations (which differ only with the rigidity of one conjugated bond in the middle of the molecular ion in **5**) around the  $[\text{PbI}_3^-]_n$  chains is similar in compounds **4** and **5**. – with two cations and two (DMF) or four (DMSO) alternating around each lead iodide chain and forming a sheathe between it and four (DMSO) or six (DMSO) neighbouring inorganic chains. No significant NH...I hydrogen bonding exists in either of the main residues of these structures (**Tables 6 and 7**).

**Figure 8** (a) The DMF solvate of 1,2-bis(4-pyridyl)ethane,  $[(\text{H-C}_5\text{H}_4\text{NCH}_2)_2][\text{PbI}_3]_2 \cdot 2\text{DMF}$  (**4**), and (b) DMSO solvate of 1,2-di(4-pyridyl)ethylene lead iodide,  $[(\text{H-C}_5\text{H}_4\text{NCH}_2)_2][\text{PbI}_3]_2 \cdot 4\text{DMSO}$ , (**5**). Both solvate structures are viewed down the *c* axis, (*b* axis vertical) which is along the 1D face-sharing lead iodide chains, and can be seen to adopt very similar structure types in the arrangement of both organic and inorganic components.

**Figure 9** ORTEP drawing of  $[(\text{H-C}_5\text{H}_4\text{NCH}_2)_2][\text{PbI}_3]_2 \cdot 2\text{DMF}$  (**4**)

**Figure 10** ORTEP drawing of  $[(\text{H-C}_5\text{H}_4\text{NCH}_2)_2][\text{PbI}_3]_2 \cdot 4\text{DMSO}$ , (**5**)

**Table 6**

Hydrogen-bonding parameters for 1,2-bis(4-pyridyl)ethane lead iodide DMF solvate (**4**) [distances in Å and angles in degrees].

| D-H...A               | d(D-H) | d(H...A) | d(D...A)  | <(DHA) |
|-----------------------|--------|----------|-----------|--------|
| N(1)-H(1)...O(1)      | 0.86   | 1.84     | 2.631(9)  | 151.4  |
| C(4)-H(4)...I(2)#4    | 0.93   | 3.04     | 3.957(11) | 169.3  |
| C(6)-H(6)...I(1)#5    | 0.93   | 3.25     | 3.938(10) | 132.9  |
| C(11)-H(11C)...I(3)   | 0.96   | 3.09     | 3.997(12) | 157.6  |
| C(10)-H(10C)...I(2)#4 | 0.96   | 3.33     | 4.122(11) | 141.2  |

Symmetry transformations used to generate equivalent atoms:

#4  $x-1, y, z$  #5  $-x+2, -y+2, -z+1$ **Table 7**

Hydrogen-bonding parameters for 1,2-di(4-pyridyl)ethylene lead iodide DMSO solvate (**5**) [distances in Å and angles in degrees].

| D-H...A               | d(D-H) | d(H...A) | d(D...A)  | <(DHA) |
|-----------------------|--------|----------|-----------|--------|
| N(1)-H(4)...O(1)#4    | 0.86   | 1.76     | 2.61(2)   | 166.5  |
| N(1)-H(4)...S(5)#4    | 0.86   | 2.95     | 3.777(19) | 163.2  |
| C(1)-H(1)...I(3)#5    | 0.93   | 2.97     | 3.850(19) | 158.4  |
| C(5)-H(5)...S(6)      | 0.93   | 2.94     | 3.52(2)   | 122.1  |
| C(9)-H(9B)...O(2)#6   | 0.96   | 2.54     | 3.50(3)   | 172.0  |
| C(8)-H(8B)...O(2)     | 0.96   | 2.43     | 3.29(3)   | 149.1  |
| C(2)-H(2)...I(2)#7    | 0.93   | 3.14     | 4.02(3)   | 158.0  |
| C(11)-H(11B)...I(4)#8 | 0.96   | 3.24     | 4.02(3)   | 140.3  |
| C(11)-H(11C)...I(4)#9 | 0.96   | 3.28     | 4.20(3)   | 161.4  |
| C(10)-H(10B)...I(2)#8 | 0.96   | 3.23     | 3.96(4)   | 133.7  |

Symmetry transformations used to generate equivalent atoms:

#4  $x, y, z-1$  #5  $-x+1, -y+1, -z$  #6  $x, -y+1/2, z+1/2$  #7  $-x+1, y-1/2, -z+1/2$  #8  $-x+2, y-1/2, -z+1/2$  #9  $-x+2, -y+1, -z$

Imidazolium lead iodide (**6**),  $[\text{C}_3\text{N}_2\text{H}_5]\text{PbI}_3$ , likewise forms 1D face-sharing chains, in this case six imidazole ions are arranged hexagonally around the octahedral chain and the compound crystallises in hexagonal space group  $\text{P6}_3/\text{m}$ . Distortions of the  $\text{PbI}_6$  octahedra are far less pronounced than in compounds **4** and **5** (Table 2). Viewed down the chain, along the  $c$  axis, Figures 11 and 12, the iodide ions adopt a fully staggered conformation, unlike in compounds (**4**) and (**5**), (Figure 8) in which the iodides are partially eclipsed.

**Figure 11** Face-sharing chain structure of  $[\text{PbI}_3]^-$  in imidazolium lead iodide (**6**) viewed down the  $c$  axis ( $b$  axis horizontal) which is parallel to lead iodide chains.

**Figure 12** ORTEP drawing of imidazolium lead iodide

**Table 8**

Hydrogen-bonding parameters for imidazolium lead iodide (**6**) [distances in Å and angles in degrees].

| D-H...A             | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------|--------|----------|----------|--------|
| C(3)-H(3)...I(4)    | 0.93   | 3.23     | 3.73(5)  | 115.6  |
| C(3)-H(3)...I(4)#13 | 0.93   | 2.95     | 3.81(5)  | 155.3  |
| N(1)-H(1)...I(3)#6  | 0.86   | 3.23     | 3.95(6)  | 142.8  |

Symmetry transformations used to generate equivalent atoms: #6  $y, -x+y, -z+1$  #13  $-x+y+1, -x+1, z$

The basic structural model consists of chains of face sharing  $\text{PbI}_6$  octahedra separated by weakly hydrogen bonded imidazolium cations. The orientational disorder in the imidazolium cations is also linked to rotational disorder of the  $[\text{PbI}_3]^-$  infinite chains along their main axis. This results in significant local positional disorder of the iodide ions which the basic structural model does not fully represent, leading to significant electron density peaks ( $\sim +5\text{e}^-/\text{\AA}^3$ ) and holes ( $\sim -10\text{e}^-/\text{\AA}^3$ ) associated with the three iodide ion positions. Disordering iodine over these possible sites produces a better model reducing the electron and hole density and improves the fit parameters marginally. However, this much more complex model still does not fully account for the local positional disorder and, therefore, only the simpler structural model for compound (6) is presented in this work. This disorder may be associated with rotational disorder of the imidazolium cation ring over the five possible orientations and in this study this was modelled using a planar cyclopentadienyl ring with 1.07 occupancy for each “carbon” atom position.

Piperazinium lead iodide (7) forms yellow crystals containing isolated  $[\text{PbI}_6]^{4-}$  octahedra under hydrothermal conditions in aqueous hydroiodic acid. The diprotonated piperazinium molecular cations are packed in herringbone fashion along the (110) plane, [Figures 13 and 14](#). Examples of hybrid inorganic-organic structures containing isolated  $[\text{PbI}_6]^{4-}$  octahedra are not nearly so extensively described in the literature as 1D and 2D frameworks; however, one key example is the dihydrated methylammonium lead iodide  $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$  (Vincent, 1987), which is a well-studied material found in the degradation of perovskite-type solar cells under humid conditions (Leguy, 2015). The methylammonium lead iodide dihydrate displays far less distortion from ideal octahedral geometry (Pb-I range: 3.1995(4) Å - 3.2819(4) Å, I-Pb-I bond angles 85.313(9)° - 102.502(14)°) likely due to the conformational requirements of incorporating the six-ring of piperazine into the inter-octahedral void.

**Figure 13** Piperazinium lead iodide (7) displaying isolated  $[\text{PbI}_6]^{4-}$  octahedra with significant distortions from ideal octahedral geometry.

**Figure 14** ORTEP drawing of piperazinium lead iodide (7) displaying one isolated  $[\text{PbI}_6]^{4-}$  octahedron and cyclohexane-like piperazinium ion.

### Table 9

Hydrogen-bonding parameters for imidazolium lead iodide (6) [distances in Å and angles in degrees].

| D-H...A             | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------|--------|----------|----------|--------|
| N(1)-H(5A)...I(3)#2 | 0.89   | 2.75     | 3.596(4) | 158.1  |
| N(1)-H(5B)...I(2)#3 | 0.89   | 3.31     | 3.890(4) | 125.1  |
| N(1)-H(5B)...I(3)#4 | 0.89   | 3.07     | 3.691(4) | 128.6  |
| N(1)-H(5B)...I(4)#4 | 0.89   | 3.12     | 3.672(4) | 122.3  |
| N(2)-H(6A)...I(2)   | 0.89   | 2.76     | 3.582(4) | 154.6  |
| N(2)-H(6B)...I(2)#5 | 0.89   | 3.21     | 3.777(4) | 124.1  |
| N(2)-H(6B)...I(4)   | 0.89   | 3.03     | 3.629(4) | 125.9  |
| C(4)-H(4A)...I(3)#2 | 0.97   | 3.12     | 3.923(5) | 140.8  |
| C(4)-H(4B)...I(2)#5 | 0.97   | 3.08     | 3.744(5) | 126.8  |
| C(4)-H(4B)...I(4)#5 | 0.97   | 3.22     | 3.915(5) | 129.9  |
| C(2)-H(2A)...I(3)#4 | 0.97   | 3.17     | 3.771(5) | 121.5  |
| C(2)-H(2A)...I(4)#2 | 0.97   | 3.13     | 3.842(5) | 131.5  |
| C(2)-H(2B)...I(2)   | 0.97   | 3.12     | 3.906(5) | 139.4  |
| C(3)-H(3A)...I(3)#1 | 0.97   | 3.12     | 3.885(5) | 137.2  |
| C(3)-H(3A)...I(4)   | 0.97   | 3.29     | 3.886(5) | 121.6  |
| C(3)-H(3B)...I(3)#6 | 0.97   | 3.18     | 3.912(6) | 133.9  |
| C(3)-H(3B)...I(4)#2 | 0.97   | 3.28     | 3.880(5) | 121.6  |
| C(1)-H(1A)...I(2)#3 | 0.97   | 3.20     | 3.886(6) | 129.6  |
| C(1)-H(1A)...I(4)#5 | 0.97   | 3.31     | 3.935(5) | 124.3  |
| C(1)-H(1B)...I(2)#7 | 0.97   | 3.17     | 3.900(5) | 133.3  |
| C(1)-H(1B)...I(4)#4 | 0.97   | 3.27     | 3.899(5) | 123.8  |

Symmetry transformations used to generate equivalent atoms:

#1  $-x+3/2, y, -z+3/2$  #2  $-x+1, -y+1, -z+1$  #3  $-x+1/2, y, -z+3/2$  #4  $x-1, y, z$  #5  $-x+1, -y+2, -z+1$  #6  $x-1/2, -y+1, z-1/2$  #7  $x-1/2, -y+2, z-1/2$

#### 4. Conclusions

With the growing focus of research on next generation of sustainable energy materials hybrid inorganic-organic photovoltaic materials containing  $\text{PbI}_6$  octahedra have become of increasing technological importance. As well as studying the photoactive materials themselves and developing



new functional semiconducting compounds understanding how these materials can be processed directly from solutions and how they degrade through the formation of solvates are topics that will be central to their deployment into usable devices.

A wide range of structural motifs are accessible through alteration to the connectivity between octahedral units, template by specific organic cations. 4-Chlorobenzylammonium lead iodide is typical of the layered 2D perovskite structures adopted by sterically undemanding, linear-terminating organic cations. Of note is the way in which the  $-\text{CH}_2\text{-NH}_3$  end group interacts with the lead iodide layer in a similar way to the methylamine cation in the photovoltaic MAPI forming three  $\text{NH}\dots\text{I}$  hydrogen bonds with the  $\text{PbI}_6$  iodide ions. The aliphatic end group,  $\text{R-CH}_2\text{-NH}_3$  is sufficiently narrow and flexible to dock into the perovskite layer and form these hydrogen bonds. However, for organic amine cations with a larger cross-sectional profile corner sharing  $\text{PbI}_6$  octahedra seems to become a less favourable structural feature possibly due to the inability of the protonated amine end groups to form suitable hydrogen bonded coordination geometries. This leads to the formation of lower dimensional structures, including predominantly 1D polymeric lead iodide chains, with no hydrogen bonding between the protonated amine and iodide ions. For a small organic cation with high charge density such as the diprotonated  $[\text{H}_2\text{-piperazinium}]^{2+}$  cation it is possible to stabilise a rather unusual structure containing isolated  $[\text{PbI}_6]^{4-}$  octahedra.

The ability of hybrid organic-inorganic lead (II) iodides and their solvates to adopt structures in which very different structural motifs for the inorganic lead-iodide networks exist is of some significance. These structural units range all the way from fully vertex sharing  $\text{PbI}_6$  octahedra, through various vertex, edge and face sharing chains to discrete  $[\text{PbI}_6]^{4-}$  octahedra. One reason why studying these different structures and understanding the factors that stabilise them, such as hydrogen bonding between the protonated amine and iodide anions, is to comprehend their phase stability and ability to undergo solvation. Thus compounds such as formamidinium lead iodide (FAPI) rapidly interconverts at room temperature between the yellow and black phases – the former containing  $[\text{PbI}_3]^-$  chains, seen in structures (4) and (5) here, and the latter fully vertex linked octahedra in a perovskite structure. This very facile phase transformation has inhibited the investigation and use of FAPI for solar cell applications. (Binek, 2015). Similarly methylammonium lead iodide undergoes rapid hydration from a perovskitic phase to a monohydrate containing  $[\text{PbI}_3]^-$  chains and a dehydrate containing discrete  $[\text{PbI}_6]^{4-}$  octahedra (Leguy, 2015); again this is an important factor limiting the development of solar cells using this material. Through the development of the structural chemistry of hybrid organic-inorganic lead (II) iodides and their solvates, as presented in this paper, useful insights into these phase transformation and solvation routes will become possible.

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