Variable dimensionality in ‘hollow’ hybrid tin iodide perovskites†

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In this paper we present two new hybrid Sn iodide perovskite structures inspired by our previous work using TzH⁺ as a structure-directing agent, which has previously led to the discovery of a wide variety of structural novelty.11–13 Our nominal target composition was (TzH)SnI₃, which we assumed might adopt a 3D structure related to that observed in (GuH)₀.₅(TzH)₀.₅SnI₃. To our surprise the reaction produced a novel structure type based on a ‘hollow’ B-site deficient perovskite, (TzH)₁₁(H₃PO₂)SnI₅₃ (1). While the B-site deficient perovskite structure has been reported previously,14,15 1 represents the first example of a layered variant of this family. On leaving the same reaction mixture for 2 months, a 3D ‘hollow’ perovskite (TzH)₃SnI₅ (2) is the dominant product.

Details of the synthesis and characterisation are provided in the ESI.† In brief, the same reaction mixture produces 1 after ~1 h and 2 after ~2 months. The crystal structures of 1 and 2 were determined by single crystal X-ray diffraction at 93 K and 173 K, respectively: crystallographic details given in Table 1. While the amine and coordinated solvent, H₃PO₂, positions in 1 have been identified fully, it has not been possible to fully assign the C/N positions of TzH⁺ as partial disorder precludes definitive atom assignment. In 2, only the tin iodide framework has been included in the final refinement; the level of disorder is higher and although fragments can be assigned, no satisfactory and complete model of the amine moieties was found. Nevertheless, CHN analysis supports the proposed composition, with three intact TzH⁺ moieties, hence we conclude there is no degradation of the amine during the prolonged reaction. Fig. 1 shows the crystal structures of 1 and 2 highlighting the B-site deficiency common to both compositions and the difference in connectivity between the 2D layered and 3D structures. For clarity, amine positions have been omitted. A key distinction between the two structures is the incorporation of a neutral H₃PO₂ molecule in 1, which acts to ‘cap’ and separate the triple perovskite-like blocks.

In our previous work11,13 we discussed the significant effect that ionic size, lone-pair effects and hydrogen-bonding environments can have on both cationic ordering behaviour and sub-
Table 1  Crystallographic data and refinement details for 1 and 2

|   | 1       | 2       |
|---|---------|---------|
| Temperature | 93 K | 173 K |
| Formula | C$_{22}$N$_{13}$H$_{24}$PO$_2$Sn$_{2}$I$_{23}$ | C$_6$N$_3$H$_{12}$Sn$_3$I$_7$ |
| Formula weight | 4423.95 | 1335.97 |
| Density/g cm$^{-3}$ | 3.220 | 2.801 |
| Crystal system | Triclinic | Triclinic |
| Space group | PI | PI |
| $\alpha$/Å | 14.0051(14) | 6.403(4) |
| $\beta$/Å | 14.7298(13) | 14.2301(10) |
| $\gamma$/Å | 22.5350(20) | 14.680(11) |
| $\alpha^{10}$ | 83.978(5) | 91.42(3) |
| $\beta^{10}$ | 85.573(5) | 93.54(3) |
| $\gamma^{10}$ | 88.147(6) | 90.10(3) |
| V/Å$^3$ | 4608.0(7) | 1334.6(13) |
| Z | 2 | 2 |
| Measured ref. | 130.747 | 36.319 |
| Independent ref. | 16.815 | 4844 |
| R(int) = 0.0869 | R(int) = 0.1379 |
| R | 794 | 85 |
| GOOF | 1.128 | 1.837 |
| R1 = 0.0593 | R1 = 0.1758 | wR2 = 0.4900 |

$^a$ C/N positions in 1 have not been fully assigned as disorder precludes definitive atom assignment. While only the tin iodide framework of 2 has been refined, the formula and formula weight has been calculated based on the assumed (TzH)$_3$Sn$_2$I$_7$ composition.

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The mean distortion level ($\Delta d$) and bond angle variance ($\sigma^2$) of each octahedron in both compositions were calculated (details are provided in ESI†) and the values shown in Table 2. It can be noted that the most extreme octahedral distortions in 1 occur for Sn4 and Sn5, which are the two sites in the ‘inner’ layer of the triple perovskite block. Comparison of the structural distortions of 1 and 2 to previously reported materials is important in attempting to understand the adoption of the 2D and 3D structure-types, respectively. While at present there are five examples of ‘hollow’ B-site deficient tin iodide perovskites based on the FASnI$_3$ or MASnI$_3$ framework (FA$^+$ = formamidinium and MA$^+$ = methylammonium), the crystal structure of the tin iodide framework of only one of these has thus far been determined, namely HEA$_{0.5}$FA$_{1-x}$Sn$_{0.67}$I$_{2.33}$ (HEA$^+$ = hydroxyethylammonium). 1 is the first of these structure-types to include resolved amine positions. The mean distortion level in both 1 and 2 is greater than in either HEA$_{0.5}$FA$_{1-x}$Sn$_{0.67}$I$_{2.33}$ or the related Pb-based composition, MA$_{0.55}$HEA$_{0.45}$Pb$_{0.62}$I$_{2.82}$. While a greater distortion is expected in Sn-based structures compared to related Pb-based materials the magnitude of the difference does not solely account for this. We hypothesise that the presence of only a single small amine, TzH$^+$, in both 1 and 2 likely results in a greater distortion of the octahedra to optimise the hydrogen-bonding environments and stabilise the structure. This is in contrast to the linear HEA$^+$ present in both known materials which apparently somewhat precludes this distortion.

In summary, we have prepared two new examples of ‘hollow’ B-site deficient tin halide perovskites. In (TzH)$_3$Sn$_2$I$_7$ we introduce the first 2D layered structure of this type and the first crystal structure featuring resolved amine positions. In
(TzH)₃Sn₂I₇ we present the first structure of this type templated by a single organic cation. The occurrence of two distinct compounds in this reaction sequence may be due to a structural change from 1 to 2 over time, but other processes such as the delayed precipitation of 2 or the initial presence of both 1 and 2 simultaneously followed by dissolution of 1 cannot be ruled out. 2 represents the first 3D ‘hollow’ perovskite templated using a single cation. The versatility of 1,2,4-triazolium as a structure-directing agent in hybrid perovskites has resulted in the discovery of several previously unseen structures that likely would not have been realised otherwise. Moreover, the first observation of the inclusion of H₃PO₂ as an active ‘capping’ agent provides food-for-thought in the design of dimensionally-reduced perovskites. This work prompts further study of the structure-directing effects of both small disc-shaped amines and hypophosphorous acid in the pursuit of interesting new structure-types, ultimately with prospects for property manipulation and control.

**Conflicts of interest**

There are no conflicts to declare.

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