On the Demystification of "HPbI₃" and the Peculiarities of the Non-innocent Solvents H₂O and DMF

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Abstract. Detailed investigations by XRD reveal that the precursor "HPbI₃" that was obtained by reaction of aq. conc. hydroiodic acid HI and PbI₂ in DMF is $(CH_3)_2NH_2PbI_3$. $(CH_3)_2NH_2^+$ is formed by solvent reaction as already described in the literature but not properly assigned. Attempts to synthesize HPbI₃ by gas phase reaction of PbI₂ with aq. conc. HI yielded light-yellow crystals of the oxonium salt H₁₈O₈Pb₃I₈ (*Pbam*, *Z* = 2, *a* = 10.075, *b* = 30.162, *c* = 4.5664 Å). The crystal structure of H₁₈O₈Pb₃I₈ consists of trimeric ribbons of edge-sharing PbI₆ octahedra. These ribbons $[Pb_3I_8]^{2-}$ are separated by protonated fragments of crystalline ice $[H_{18}O_8]^{2+}$ or $(H_2O)_6(H_3O^+)_2$. $H_{18}O_8Pb_3I_8$ can also be precipitated from PbI₂ and aq. conc. HI. H₁₈O₈Pb₃I₈ is not

Introduction

For a couple of years, hybrid organic-inorganic lead halide perovskites $APbX_3$, $MAPbI_3$ (MA = methylammonium, CH₃NH₃) in particular, are of great interest. The application of MAPbI₃ as an excellent light harvester in solar cells^[1] has induced a strong boost on the research of such materials. In recent years, the power conversion efficiency (PCE) of such perovskite solar cells (PSCs) was enhanced to over 20%^[2] through optimization on the cell architecture and the composition of the absorber material. One great advantage of PSCs is the easy processing that is done close to room temperature. Solubility and reactivity of the components enable the use of simple organic solvents (DMF, DMSO, ...) and gas phase reactions (HI, CH₃NH₃I, ...) close to ambient conditions.

This intensive research activity has also led to the use of different precursor materials, solvents, and reaction conditions to form MAPbI₃.^[3] In 2015 *Wang* et al. claimed "*HPbI₃*" as a "*new precursor compound for highly efficient solution processed perovskite solar cells*".^[4] Subsequently, several continuing publications referred to "HPbI₃" as a precursor and gave more or less detailed information on the nature of "HPbI₃".^[5] *Wang* et al. made experiments with PbI₂ and HI in DMF and characterized the remaining solid by thermogravimetry (TG),

stable at room temperature but transforms within a few days to lightyellow $(H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2$ with $x \approx 0.23$ ($R\bar{3}m$, Z = 3, a = 4.5554, c = 29.524 Å). The crystal structure represents a CdCl₂-type layer structure with H_2O/H_3O^+ in between. Charge compensation is achieved by Pb²⁺ vacancies. Via topotactic reaction $(H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2$ releases H_2O/HI and forms crystals of the pristine PbI₂. All steps were characterized by P-XRD, IR/Raman spectra, and UV/Vis spectra. $H_{18}O_8Pb_3I_8$ acts as a precursor for the synthesis of MAPbI₃ because the reaction with gaseous CH₃NH₂ yields MAPbI₃, so it can mimic a composition "HPbI₃".

powder X-ray diffraction (P-XRD), and X-ray photoelectron spectroscopy (XPS). From the observed weight loss (in the range of 240 to 345 °C) of 23.7% they conclude the reaction of HPbI₃ into PbI₂ and HI (theoretical weight loss: 21.7%) and a PbI₂:HI ratio of 1:1.1. The XPS measurements also showed an PbI₂:HI ratio of around 1:1. Furthermore, they measured a P-XRD pattern. From comparison of some individual reflections they concluded a layer structure similar to PbI₂ with an increased distance between the layers because of the intercalation of H⁺. According to the ratio Pb:I of 1:3 and the similarity to KPbI₃ and CsPbI₃ they assumed a layer structure with PbI₆ octahedra connected by common edges and corners (NH₄CdCl₃ type).^[6] In the course of the reaction the color changed from dark yellow (PbI₂) to light yellow ("HPbI₃"). The material named as "HPbI₃" showed an increased solubility in DMF compared to PbI₂ and an improvement of the film quality and solar cell efficiency of 16% by converting the precursor to $FAPbI_3$ (FA = formamidinium).

With direct reference to the work of *Wang* et al. the group of *Pang* et al. studied the transformation of the "HPbI₃" precursor with methylamine gas (CH₃NH₂) into MAPbI₃.^[7] They characterized the "HPbI₃" compound also by P-XRD and claimed that "*Pawley fitting shows an orthorhombic (space group P6₃mc) structure*..." In contrast to *Wang* et al. they assumed from the P-XRD and high-resolution transmission electron microscopy (HR-TEM) data a structural model that is based on the hexagonal perovskite that consist of 1D chains of face sharing PbI₆ octahedra with protons in between. As an additional proof they showed that "HPbI₃" could be transferred into MAPbI₃ by the reaction with methylamine gas, whereas KPbI₃ could not be transferred.

Long et al.^[8] obtained "HPbI₃" by mixing PbI₂ and excess HI (probably conc. aq. HI) in DMF. They postulated a "solvate HPbI₃·xDMF" with $x \le 1$. For both samples they described

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.201800267 or from the author.



needle-shaped light-yellow single crystals. Single crystal investigations revealed a hexagonal unit cell with very similar lattice parameters for HPbI₃ (a = 8.7339, c = 8.1779 Å) and the solvate HPbI₃·xDMF (a = 8.7517, c = 8.1802 Å). The refinement in space group $P6_{3}mc$ (no. 186) revealed the positions of Pb and I. The cations were not localized because of the weak scattering power (H⁺) and severe orientation disorder (DMF). The similar volume of the unit cell of the two compounds was explained by the high mobility of H⁺. The subsequent treatment of HPbI₃ with excess CH₃NH₂ yielded MAPbI₃ that was characterized by P-XRD and yielded a working device with a PCE of 16%.

In a very recent paper *Zhang* et al. mentioned $PbI_2 \cdot xHI$ that was synthesized from PbI_2 /conc. HI/DMF.^[9] They reported a P-XRD pattern for "HPbI_x", which is very similar to the hexagonal pattern of *Pang* et al. and *Long* et al. assigned to HPbI₃. Additionally, they report on a P-XRD pattern for a phase "PbI₂•xHI", that showed no similarity to any known phase.

The great significance of "HPbI₃" as a precursor is demonstrated by the fact that it is mentioned in several reviews^[10] or used without further characterization.^[11] Furthermore, the idea to "recover" moisture-sensitive perovskites like MAPbI₃ by transformation to "HPbI₃" might be an important advantage in processing of the PSC.

On the whole the situation for the precursor "HPbI₃" is inconsistent according the published data and also to our experience with hybrid perovskites.^[12] On the one hand there was clear evidence, that a compound acting as "HPbI₃" is an important intermediate during the formation of FAPbI₃ and MAPbI₃. On the other hand the existence of HPbI₃ as a well-defined crystalline compound seemed to be quite implausible, because then a "naked" proton has to act as a cation. One indication for this point is the lack of knowledge on the ionic radius of H⁺. Therefore, we have investigated the reactivity of the system HI/PbI₂/DMF and tried to obtain HPbI₃ from PbI₂ and aq. conc. hydroiodic acid as it was assumed in the literature. The samples were characterized by XRD investigations of powders and single crystals, vibrational spectroscopy, and UV/Vis spectroscopy. The results show that a compound "HPbI3" is not formed but reversible reactions with the solvents DMF and H₂O, respectively, mimic its intermediate existence.

Results and Discussion

Formation of (CH₃)₂NH₂PbI₃ from HI/PbI₂/H₂O/DMF

The first part of our results deals with the role of DMF in the system PbI₂/HI/H₂O. *Pang* et al.^[7] published a hexagonal unit cell and lattice parameters of a = 8.765(1) and c =8.177(2) Å for "HPbI₃" and very similar values for the DMF adduct HPbI₃•xDMF (a = 8.7517, c = 8.1802 Å). This was not comprehensible because H⁺ and DMF should show significantly different volumes. In the case of a 1D perovskite the size of the chain of face-sharing PbI₆ octahedra should be similar and the lattice parameter a relates to the cation size. A comparison to literature revealed very similar lattice parameters for the hexagonal dimethylammonium (DMA) compound $(CH_3)_2NH_2PbI_3$ [a = 8.769(1), c = 8.188(2) Å].^[13] The intensities were similar to the published P-XRD and the calculated P-XRD pattern of DMAPbI₃ fits perfect the published P-XRD pattern of *Wang* et al.^[4] and *Pang* et al.^[7]

Furthermore, it is a well-known phenomenon that DMF decomposes into formic acid and DMA, especially in acids.^[14] Eppel et al. already showed the synthesis of DMAPbI₃ from PbI₂/HI/DMF.^[15] They also showed that DMAPbI₃ crystallize in the orthorhombic space group $Cmc2_1$ with a pseudo hexagonal metric [a = 8.7560(8), b = 15.1670(1), c = 8.1830(4) Å; $b \approx \sqrt{3}a$], that may explain the confusion by *Pang* et al.^[7] Also the transformation of DMAPbI₃ by methylamine gas into MAPbI₃ has recently be shown in the literature.^[16] Additionally, the higher solubility of "HPbI₃" is obvious, as it is known that the solubility of PbI₂ is increased in the presence of iodides.^[17] The decomposition temperature of the TG measurement by Pang et al.^[7] fits with the one reported from Eppel et al.^[15] for DMAPbI₃. The weight loss for the formation of PbI₂ is calculated as 27.3%, i.e. slightly higher than observed by Pang but within the experimental range.

In order to proof our guess we reexamined the "HPbI₃" powder by solving PbI₂ and aq. HI in DMF. We have precipated yellow needles/rods by overlaying the solution with ethyl ether. The measurement of a selected single crystal yielded the known structure of DMAPbI₃ (Tables S1–S3, Supporting Information). The refinement of the room temperature data was done assuming the hexagonal unit cell and space group $P6_3/mmc$, as we observed neither super structure reflections, nor a splitting of the reflection profiles or a reduction of the Laue class. Positions of Pb and I were obtained from direct methods, N and C were localized from difference Fourier synthesis. The organic cation is disordered. This model corresponds to the data given by *Mancini* et al.^[13] We have found no evidence for a symmetry reduction to the orthorhombic non-centrosymmetric model in $Cmc2_1$ as given by Eppel et al.^[15] and also no reason for the symmetry reduction to $P6_3mc$. Figure 1 shows the excellent agreement of the experimental



Figure 1. Experimental and calculated diffraction pattern DMAPbI₃ (Mo- K_{α_1} radiation).

Journal of Inorganic and General Chemistry

Zeitschrift für anorganische und allgemeine Chemie

P-XRD pattern to the theoretical pattern calculated from the sc-XRD data (see Supporting Information).

"HPbI₃"/H₁₈O₈Pb₃I₈ from aq. conc. Hydroiodic Acid and PbI₂

When it became clear that the reaction of PbI₂/HI/H₂O in DMF yields no compound "HPbI₃" we tried to synthesize HPbI₃ directly from conc. hydroiodic acid. In the literature^[7–9,11b,18] several groups have described the synthesis of "HPbI₃" by gas phase reaction of HI and PbI₂ with the evaporation of gaseous HI from conc. aq. hydroiodic acid. When PbI_2 was placed beside an open container with conc. aq. HI (57%) in an exsiccator, we observed the crystal growth of light-yellow rods in the powder sample of PbI₂. Single crystal investigations by XRD revealed an unknown orthorhombic unit cell. The preliminary structure determination produced a model with trimeric chains of PbI_6 octahedra $[Pb_3I_8]^{2-}$. The residual electron density between these chains were interpreted as water molecules that were interconnected by hydrogen bonds. According to the requirement of charge neutrality a part of the water molecules should be labelled as oxonium cations H₃O⁺. With this model in mind we added PbI₂ directly to conc. aq. hydroiodic acid and obtained well-developed light-yellow single crystals that showed the same orthorhombic unit cell as the crystals formed before by vapor transport. The refinement resulted in a composition H₁₈O₈Pb₃I₈.

The crystal structure (Figure 2) displays stripes of edgesharing PbI₆ octahedra running in direction of the short *c* axis. The motif can be seen as the transition from the NH₄CdCl₃ type, where the chains of edge-sharing octahedra form dimers and the pristine PbI₂ with layers of edge-sharing octahedra. With respect to the NH₄CdCl₃ type there is one additional row of PbI_{6/3} octahedra (each additional iodine is connected to three Pb atoms). Vice versa the layers in PbI₂ are separated by additional I⁻ anions into stripes. The stripes are arranged in a fishbone-like manner with the H₃O⁺/H₂O subunits in between.



Figure 2. Crystal structure of $H_{18}O_8Pb_3I_8$, projection in direction (001); black: Pb, turqois: I; red: O.

Pb–I distances reflect the usual findings for connected polyhedra (Figure 3). The shortest distance is observed for the terminal distance Pb2–I4 (2.98 Å) and the longest distance to the threefold connected iodine in *trans* position (Pb2–I1: 3.55 Å). Intermediate distances result for the other twofold (Pb2–I3: 3.16 Å) and threefold connected iodine atoms (3.21 / 3.23 / 3.34 Å). According to the position within the ribbon, the PbI₆

octahedron around Pb1 is nearly regular, while the octahedron around Pb2 is distorted in a 1+2+2+1 pattern. This distortion is typically for a lone pair activity of a ns² cation like Pb²⁺.



Figure 3. Pb–I and H₃O⁺/H₂O subunits in H₁₈O₈Pb₃I₈.

The O–O distances between 2.49 and 2.75 Å (Figure 3) are typical for water molecules, which are linked by hydrogen bonds.^[19] The H₃O⁺/H₂O subunits represent a cut-out of the crystal structure of ice I (O–O: 2.762 Å).^[20] The short distance O3–O4 is probably caused by a preferred localization of the additional H⁺. In general, the positions of the hydrogen atoms could not be determined, but it is known from vibrational spectroscopy and MD simulations, that the O–O distances are shortened in oxonium cations like the Zundel cation H₅O₂⁺ or the Eigen cation H₉O₄⁺.^[21] We expect an interaction of the H₃O⁺/H₂O subunits to the [Pb₃I₈]^{2–} chains via O–H···I hydrogen bridges. The shortest O–I distances in MAPbI₃ and other hybrid iodoplumbates.

The explicit characterization of $H_{18}O_8Pb_3I_8$ as the first product from the gas phase reaction of aq. conc. hydroiodic acid with PbI₂ demonstrates, that hydroiodic acid acts under this conditions not as a simple source of HI leading to the formation of HPbI₃, but H₂O is also present in the gas phase. This is not a surprise, because concentrated hydroiodic acid is known as an azeotrop with a boiling point maximum of 127 °C under normal pressure. Furthermore, the formation of oxonium cations H₃O⁺ is in line with the property of conc. hydroiodic

acid as a very strong Brønsted acid. So species of the series $(H_2O)_x(PbI_2)_y(HI)_z$ are conceivable under the reported reactions conditions.^[22] $H_{18}O_8Pb_3I_8$ is the representative for x = 6, y = 3, and z = 2. As Figure 2 demonstrates it can be expected that the values of x, y, and z depend on the pattern for the arrangement of Pb_mI_n motifs and H_3O^+/H_2O subunits as well as the demand for charge neutrality.

$(H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2 (x \approx 0.23) / (H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$

Single crystals of H₁₈O₈Pb₃I₈ are not stable in air. The welldeveloped rods precipitated from conc. hydroiodic acid transform to smaller crystals of irregular shape. The P-XRD pattern of the freshly prepared single crystals were in good agreement to the calculated pattern (Figure S4, Supporting Information), but powdered samples showed additional lines after a few hours (Figure S6, Supporting Information). The irregular crystals were characterized by sc-XRD and revealed a rhombohedal unit cell with a = 4.56 and c = 29.53 Å. The structure solution in $R\bar{3}m$ yielded for the positions of Pb and I a CdCl₂type structure ($R_1 = 0.071$, $wR_2 = 0.166$). Difference fourier synthesis gave a residual electron density between the layers of 6.2 e^{-1} Å⁻³ on a site 2/3, 1/3, 0, that was interpreted as oxygen and reduced the R values ($R_1 = 0.042$, $wR_2 = 0.108$). The displacement parameter of Pb was significantly enlarged in comparison to I (factor 2). The refinement with a free site occupation factor for Pb resulted in reasonable values for the displacement parameter and a further reduction of the R values $(R_1 = 0.020, wR_2 = 0.031)$. The interpretation of this model is shown in Figure 4.



Figure 4. Crystal structure of $(H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2$ (left) with corrugated layer of H_3O^+/H_2O and layer of PbI₆ octahedra; black: Pb, turqois: I; red: O.

There are layers of edge-sharing PbI₆ octahedra in a CdCl₂type arrangement with partially occupied Pb2+ sites. The site occupation factor is 78.4(5)%. Between the layers there are H₂O molecules that are connected via hydrogen bridges to a corrugated layer. According to charge neutrality there are additional protons. Assuming a ratio Pb:I of 1:3 (see below) the formula can be written as $(H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2$ with $x \approx$ 0.226(5) or $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$ if the relation to H₁₈O₈Pb₃I₈ is retained. The structure repesents an intercalation of H₃O⁺/H₂O into PbI₂ with a change of the anion stacking from hcp to ccp. In comparison to PbI₂ the distance between the layer is enlarged by 40% or 2.84 Å per H_3O^+/H_2O layer. Because of the Pb²⁺ deficit and the corresponding H⁺ between the Pb/I layers both layers are charged. The topology of the H_3O^+/H_2O layer is very similar to the situation in $H_{18}O_8Pb_3I_8$. The transition from $H_{18}O_8Pb_3I_8$ to $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$ leaves the composition nearly unchanged and requires only small shift of the atoms. Furthermore, the volumes related to one iodide atom are also very similar [H₁₈O₈Pb₃I₈: 86.73 Å³; $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$: 88.6 Å³], so it is comprehensible, that the shape of the H₁₈O₈Pb₃I₈ crystals is maintained in the course of the transformation.

When $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$ was stored in air for several days the light-yellow color changed to orange-yellow and the P-XPD pattern showed the formation of PbI₂ (Figure S7, Supporting Information). A similar observation was made in the course of the single crystal measurement. The single crystal of $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$ is stable for several hours but during a long-term measurement that was done to compensate the weak scattering power caused by the small crystal size, the reflection profiles of (H₃O)_{0.5}(H₂O)_{1.5}Pb_{0.75}I₂ started to get broader, showed diffuse scattering halos, and new reflections occurred.^[23] The indexing revealed the hexagonal primitive unit cell with slightly enlarged *c* lattice parameter [a = 4.552(2)]and c = 7.105(6) Å] compared to the unit cell of the pristine PbI₂. The refinement ($P\bar{3}m$, CdI₂-type) was biased by the broad reflection profiles $(R_1 = 0.082, wR_2 = 0.228),$ but the results showed clearly, that a single crystal of $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$ transforms to a single crystal of PbI₂ by a topotactic reaction. A comparison of the two orientation matices shows, that both *ab* planes remain parallel. This at a first view surprising result is in line with the observation, that the ions I^- as well as $Pb^{2+}(!)$ have a remarkably high mobility in MAPbI₃ and related compounds.^[24]

Our investigations show, that PbI₂, H₁₈O₈Pb₃I₈, and $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$ can be transformed into one another according to the conditions of reaction (Figure 5). A gas phase reaction transforms binary PbI₂ into H₁₈O₈Pb₃I₈. The fact, that powder samples of PbI₂ result in small but well-developed single crystals of H₁₈O₈Pb₃I₈ underline the importance of mobilization of Pb²⁺ and I⁻ by HI/H₂O. In contrast to a first guess and many statements in the literature conc. hydroiodic acid is not only a resource for HI, but also for H₂O. The compound, that is formed at room temperature in a closed system (exsiccator) contains HI and H₂O in a ratio 1:4. This is close to the molar ratio as is present in conc. hydroiodic acid with 57% HI (1:5.5) and corresponds to the composition of the azeotrop.



 $\label{eq:Figure 5. Scheme for the transformations PbI_2 \rightarrow H_{18}O_8Pb_3I_8 \rightarrow (H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2 \rightarrow PbI_2 \mbox{ and the synthesis of MAPbI_3 from } H_{18}O_8Pb_3I_8 \ / \ (H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2 \rightarrow PbI_2 \mbox{ and the synthesis of MAPbI_3 from } H_{18}O_8Pb_3I_8 \ / \ (H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2 \rightarrow PbI_2 \mbox{ and the synthesis of MAPbI_3 from } H_{18}O_8Pb_3I_8 \ / \ (H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2 \rightarrow PbI_2 \mbox{ and the synthesis of MAPbI_3 from } H_{18}O_8Pb_3I_8 \ / \ (H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2 \rightarrow PbI_2 \mbox{ and the synthesis of MAPbI_3 from } H_{18}O_8Pb_3I_8 \ / \ (H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2 \rightarrow PbI_2 \ (H_3O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2O)_{0.5}(H_2$

"HPbI₃" is introduced to the literature as a precursor for MAPbI₃ and FAPbI₃. Our experiments have shown, that the gas phase reaction with conc. hydroiodic acid yields not HPbI₃, but $H_{18}O_8Pb_3I_8$ instead. Nevertheless, a simple acid-base reaction with gaseous CH_3NH_2 should result in MAPbI₃. When a sample of $H_{18}O_8Pb_3I_8$ was placed beside a concentrated aqueous solution of CH_3NH_2 we observed immediately the formation of black MAPbI₃. The fast reaction results from the high vapor pressure of CH_3NH_2 , that is at room temperature much higher than in the case of aq. conc. hydroiodic acid. Subsequently, the sample became a yellow "jam". Single crystal XRD measurements revealed MA_4PbI_6 ·2H₂O and MA_4PbI_6 . After annealing at 60–100 °C a black solid was formed, that was identified as MAPbI₃ with very few PbI₂.

Things might be different with the use of gaseous HI. Here, it was shown, that surpassing of gaseous HI over MAPbBr₃ or MAPbCl₃ leads to the formation of MAPbI₃, in the case of the bromide even in a topotactic reaction peserving the shape of the single crystals.^[25]

UV/Vis Spectroscopy

Optical spectra of PbI_2 , $H_{18}O_8Pb_3I_8$, and $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$ were recorded for further characterization and are shown in Figure 6. The spectra confirm the visual impression, that the reaction of PbI_2 to $H_{18}O_8Pb_3I_8$ results

in a change of color from orange-yellow to light-yellow, because the absorption edge shifts from 525 nm to 475 nm. Also the reaction of $(H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2$ back to PbI₂ changes the color, while the transformation from $H_{18}O_8Pb_3I_8$ lets the color unchanged. The evaluation was done with the assumption of a direct band gap. There are other equations for indirect bandgap semiconductors.^[26] The bandgap increases from 2.3 eV to about 2.6–2.7 eV.

IR and Raman Spectra

Vibrational spectra of PbI_2 , $H_{18}O_8Pb_3I_8$, and (H₃O)_{0.5}(H₂O)_{1.5}Pb_{0.75}I₂ were recorded for further characterization (see Figure 7). The strong IR-active frequencies around 3480 cm⁻¹ are due to O-H valence modes and only very weak in the Raman spectrum. The sharp modes around 2800 cm⁻¹ are probably due to the oxonium cation. The modes around 1600 cm⁻¹ (IR and Raman) are bending modes of H₃O⁺/H₂O. The modes around 500 cm⁻¹ are due to rotational modes.^[27] Significant differences occur for the very strong Raman-active Pb-I valence modes between 123 and 72 cm⁻¹ according to the different connectivity of PbI₆ octahedra. The highest frequency observed for H18O8Pb3I8 as the only compound is with terminal Pb-I bonds. The higher frequency of (H₃O)_{0.5}(H₂O)_{1.5}Pb_{0.75}I₂ in comparison to PbI₂ can be explaind by the missing Pb²⁺ because some of the I⁻ are only connected to two octahedra instead of three.

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Figure 6. UV/Vis spectra of PbI₂, $H_{18}O_8Pb_3I_8$, and $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$ measured in diffuse reflection (top) and corresponding Tauc plots (bottom, see text).

Conclusions

The development of suitable precursors for the synthesis of hybrid organic inorganic perovskites (HOIPs) is a central question for the fabrication of PSCs. We have shown that claimed "HPbI₃" does not have the expected composition, when it is synthesized using DMF as a solvent. All the observed behavior in several publications that base on "HPbI₃" as a precursor is explained by the fact that (CH₃)₂NH₂PbI₃ is formed as intermediate compound. In a subsequent reaction the DMA⁺ cation is transformed to methylamonium CH₃NH₃⁺. Although this reaction of DMF including the formation of HOIPs was already described in the literature this was not taken into consideration when "HPbI₃" was introduced as an existing precursor. The reason is the missing substantial characterization of the intermediate species in the course of the device manufacturing.

In general, solvents used in processing PSCs are not as innocent as sometimes expected. We have shown that in the presence of H₂O HI acts not as an active gaseous phase forming "HPbI₃" as it is supposed in some publications. Instead, H₃O⁺ and higher aggregates (H₃O⁺)_m(H₂O)_n are formed. Neverthe-



Figure 7. Vibrational spectra of PbI_2 , $H_{18}O_8Pb_3I_8$, and $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$.

less, the occurrence of "HPbI₃" can be mimicked by reversible addition and release of H_2O , but according to the moisture sensitivity of MAPbI₃ and related perovskites, this should be obeyed in the course of processing PSCs and also the interpretation of experimental results.

We have synthesized and characterized H₁₈O₈Pb₃I₈ as the first example for a well-defined compound of the system H₂O/ HI/PbI₂. The structure can be easily described by a combination of the structural features of the binary components PbI₂ and H₂O (i.e. ice I), that are separated by "additional" HI into a fishbone-like arragment of stripes. At room temperature H₁₈O₈Pb₃I₈ transforms within a few hours without significant change of the composition to (H₃O)_{0.5}(H₂O)_{1.5}Pb_{0.75}I₂. This layer structure is related to a CdCl₂-type structure for the Pb-I substructure with vacant sites on the Pb²⁺ positions. The charge compensation takes place by intercalated layers of H₃O/ H₂O, that represent cutouts of the structure of ice with additional protons. (H₃O)_{0.5}(H₂O)_{1.5}Pb_{0.75}I₂ releases in a topotactic transformation HI/H₂O and forms PbI₂ closing the cycle that started with the uptake of HI/H2O from conc. aq. hydroiodic acid. This topotactic decomposition can be important

for the precipitation of MAPbI₃ or related HOIPs in a preferred orientation.

According to our results we expect the existence of variety of compounds in the system H₂O/HI/PbI₂. The fishbone-like pattern allows an expansion of the neutral parts according to the formula (H₃OI)₂(PbI₂)_n(H₂O)_{2n}, where the PbI₂/H₂O layers are separated by the additional I⁻ anions and H₃O⁺ cations, respectively. H₁₈O₈Pb₃I₈ represents the example with n = 3. For the subsequent transformation to the intercalation compound (H₃O)_{2x}(H₂O)_{2-2x}Pb_{1-x}I₂ the value of *n* relates to the extent of the deficit *x*.

Taking the release of H₂O at elevated temperatures into account representatives of the system H₂O/HI/PbI₂ like H₁₈O₈Pb₃I₈ / (H₃O)_{0.5}(H₂O)_{1.5}Pb_{0.75}I₂ can serve as new precursors for the synthesis of HOIPs with "HPbI₃" as a vitual precursor. As a proof of principle we passed gaseous CH₃NH₂ over H₁₈O₈Pb₃I₈ / (H₃O)_{0.5}(H₂O)_{1.5}Pb_{0.75}I₂ and observed instantly blackening of the light-yellow starting materials due to the formation of MAPbI₃. Gentle heating to 60–100 °C resulted in crystalline MAPbI₃ with small amounts of PbI₂. However, our investigations show the importance of a substantial characterization of intermediate products for a comprehensive unterstanding of the processes in the course of the fabrication of a PSC device.

Experimental Section

DMAPbI₃: PbI₂ (461 mg, 99%, Acros Organics) was dissolved in 0.7 mL DMF (99.8%, Roth). Subsequently, hydroiodic acid (0.2 mL, 57% aq. solution, Acros Organics) was added and the solution was overlaid with ethyl ether. After a few minutes, light yellow crystals of DMAPbI₃ were formed.

 $H_{18}O_8Pb_3I_8$ / $(H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2$: Initially, a mixture of both compounds was synthesized by placing powdered PbI₂ (1.0 g) in an open glass vessel. This vessel with PbI₂ was enclosed into a larger container with an excess of conc. hydroiodic acid (57% aq. solution) in a separate open vessel, so that the equilibrium gas phase (H₂O/HI) could slowly diffuse via the gas phase into the provided PbI₂. After 1 week small yellow crystals were grown from PbI₂.

H₁₈O₈Pb₃I₈: Pure H₁₈O₈Pb₃I₈ was obtained by cooling a hot solution of PbI₂ (3.3 g) in 5 mL hydroiodic acid (57% aq. solution) to room temperature. The bright yellow crystals were isolated by suction filtration and dried by pressing between filter papers. All characterizations of H₁₈O₈Pb₃I₈ were done instantly. After 3 d, when the powder still looked unchanged, the measured P-XRD showed only reflections of (H₃O)_{2,x}(H₂O)_{2-2,x}Pb_{1-x}I₂ [or (H₃O)_{0.5}(H₂O)_{1.5}Pb_{0.75}I₂, respectively], so all characterizations were repeated. One sample was washed with ethyl ether and dried in vacuo. The responding P-XRD showed only reflection of PbI₂.

 $(H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2$ or $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$: Well-developed light-yellow platelets of $(H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2$ / $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_2$ were obtained by dissolving the mixture of $H_{18}O_8Pb_3I_8$ / $(H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2$ (see above) in acetone and slow evaporation of the solvent.

MAPbI₃ from H_{18}O_8Pb_3I_8 / (H_3O)_{2x}(H_2O)_{2-2x}Pb_{1-x}I_2: A sample of the initially synthesized mixture was placed in a glass next to CH_3NH_2 (40% aq. solution, Merck). The bright yellow solid turned instantly

black (MAPbI₃) and after a while it changed to a colorless-yellow mash-like solid. From this "mash" single crystals of MA_4PbI_6 ·2H₂O and MA_4PbI_6 were isolated. The "mash" turned back into black (indicating the formation of MAPbI₃) by heating on a hotplate at about 60–100 °C. Very few PbI₂ as by-product was detected by P-XRD.

P-XRD: The products were characterized by powder XRD (STOE Stadi P, Mo- K_{a1} radiation, Ge (111) monochromator, silicon microstrip detector Mythen 1 K, Debye-Scherrer setup, transmission). Unit cell refinement was done using the STOE WinXPOW software.

Single Crystal XRD: Measurements of single crystals were done using a diffractometer equipped with an image plate detector (IPDS II, Fa. STOE, Darmstadt, Germany)^[28] or with a Bruker APEX II diffractometer with a CCD detector and a microsource.^[29] The structure solution (direct methods) and refinements were done with the SHELXL software package.^[30] For DMAPbI₃, we preferred a refinement in the hexagonal space group $P6_3/mmc$. Refinements in the noncentrosymmetric subgroup $P6_3mc$ or the orthorhombic space group $Cmc2_1$ yielded no improvement beyond the standard deviations and the DMA cation remained disordered. Further details are listed in the Supporting Information (Tables S1–S3).

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-434387 (for $H_{18}O_8Pb_3I_8$) and CSD-434388 [for $(H_3O)_{0.5}(H_2O)_{1.5}Pb_{0.75}I_3$].

IR and Raman Spectra: IR and Raman spectra were recorded with a Bruker FRA 106/S module with a Nd:YAG laser ($\lambda = 1064$ nm).

UV/Vis Spectra: Diffuse reflectance spectra were recorded with a Thermoscientific Evolution 600 equipped with an integration sphere. The baseline was measured against SPECTRALON[®]. For the measurement, a powdered sample was pressed into a pellet inside the sample holder.

Supporting Information (see footnote on the first page of this article): SI contain additional data for sc-XRD measurement and experimental and calculated P-XRD patterns.

Acknowledgements

This work was supported by BMBF (Project "Meso-PIN", 03 SF0484 D)

Keywords: HPbI₃ precursor; Oxonium cation; Lead; Noninnocent solvent; Hybrid perovskite; Single crystal

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Received: June 20, 2018 Published online: Journal of Inorganic and General Chemistry

Zeitschrift für anorganische und allgemeine Chemie



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On the Demystification of "HPbI₃" and the Peculiarities of the Non-innocent Solvents H_2O and DMF

