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Amine Additive Reactions Induced by the Soft Lewis Acidity of Pb²⁺ in Halide Perovskites. Part I: Evidence for Pb-Alkylamide Formation

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Metal halide perovskite materials (ABX₃) employed in optoelectronic devices have rapidly achieved high efficiencies. Their performance can be partially attributed to intrinsic defects being electronically benign. Despite the inertness of defects within the bulk, such as ion vacancies, solution processing additives and surface passivation have been shown to enhance material properties. Thus, detailed knowledge of additive chemistry is desirous to elucidate passivation mechanisms and facilitate further improvements. In particular, the soft Lewis acid nature of Pb²⁺ has been overlooked heretofore as a key feature of amine-lead chemistry in perovskite preparations. In Part I of this study, we demonstrate that acid-base reactions between PbI₂ and aliphatic amines yield alkylammonium and Pb-alkylamide species. The alkylammonium and alkylamide products are capable of occupying A-site cation and anion vacancies, respectively. Subsequent incorporation of these impurities at perovskite crystal surfaces or formation of non-perovskite phase inclusions likely influence the perovskite layer morphology and properties which are invstigated in Part II. These results reveal a new mechanism by which optoelectronic properties of perovskites can be chemically modified. Additionally, the general concept of acidification of organic molecules solvated to Pb²⁺ promoting unexpected reactions is applied to explain amine reactions with other additives, such as formic acid. Understanding acid-base reactions induced by PbI₂ complexing to protic molecules is useful to comprehend and predict defect/impurity chemistry in a wide variety of perovskite precursor formulations.

Introduction

Rapid increase of metal, mainly Pb, halide perovskite (formula ABX₃, X = halide) based optoelectronic device performance owes largely to empirical improvements in electron/hole transport layers, ink additive engineering, and various post processing treatments.[1-3] Despite achieving high performance, short shelf lifetimes of perovskite inks and low operational stability of devices are paramount challenges to be overcome for commercialization of this technology.[2,4,5] Additives are most often included in perovskite solutions with the intention of influencing perovskite crystallization during thin film deposition.[2,6-9] Alternatively, the surface of as-deposited thin films can be exposed to gaseous or liquid additives to alter the properties of the film and improve performance of the finished devices.[10-12] Many different types of solvent mixtures and additives are now widely used without consideration of the full extent of chemical reactions that can occur with perovskite constituents. Among myriad additives reported, amines are becoming increasingly common and perovskite thin films can be intentionally or unintentionally exposed to amines during various stages of fabrication and characterization.

It was discovered that gaseous methylamine treatment dissolves solid methylammonium lead triiodide (MAPbI₃) into a liquid which can be useful for healing poor film morphologies.[13] The solubilizing benefits of amines led to their use as an additive in N,N dimethylformamide (DMF) and acetonitrile (ACN) based perovskite inks resulting in improved solar cell efficiencies.[9,14,15] These studies revealed that crystallization and morphology are directly influenced by amines, but there is speculation that chemical passivation occurs simultaneously.[15,16] Additionally, post-deposition exposure of films to butylamine, poly-ethylenimine, or ethylendiamine were very effective at improving photoluminescence quantum yield resulting in enhanced device performance and/or stability.[12,16,17] As molecular additive engineering with amines becomes an area of focus for

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Scheme 1. (a) General mechanism in anhydrous conditions by which a protic molecule (HA) is acidified upon coordination to PbI_2 (denoted by **H** and dashed line) which can induce deprotonation by a suitable base (B). (b) Example of reaction when the same molecule, butylamine, acts as both the acid and the base. (c) Example for a reaction between HA and B (formic acid and butylamine in DMF) which would be unfavorable in the absence of PbI_2 but is promoted by the Lewis acidity of PbI_2.
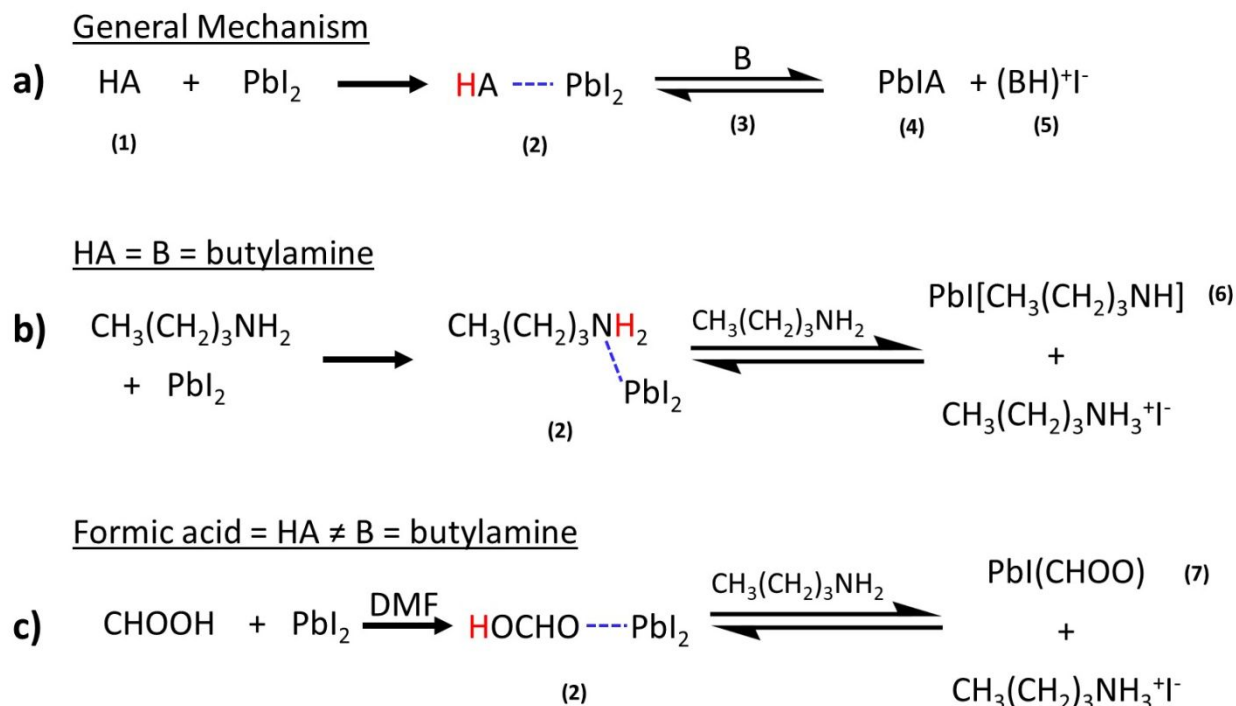
advancing perovskite technology, the detailed chemistry with Pb halides and other additives will become of greater importance.

In this study, we identify underappreciated acid-base reactions between Pb halide salts and aliphatic amines. Counterintuitively, mixing PbI_2 with amines results in the generation of an acidic alkylammonium molecule. The chemical reaction is driven by the Lewis/soft acidity of the Pb^{2+} cation in which the N-H protons are acidified by Pb^{2+} upon formation of the $PbX_2 \bullet$ amine coordination complex. A proton is then abstracted by a Brønsted base; in this case, a second amine molecule which generates an alkylammonium halide molecule and a Pb-alkylamide bond (generally referred to as ammonium and amide hereafter). It is known from studies on amino acid/Pb reactions that the soft acid characteristics of Pb^{2+} lead to the formation of Pb-amide bonds preferentially over Pb-carboxylate bonds.[18,19] The Pb-amide represents a dative bond that is more covalent in nature than a coordination complex bond and can potentially fulfill the role of a halide anion on the surface of the perovskite crystal. Thus, the reaction products in small amounts are capable of occupying both A-site cation and anion surface vacancies while precipitating new phases at larger concentrations. Furthermore, this concept is applied to acidification of formic acid in the presence of PbI_2 promoting deprotonation by amines which would otherwise be unfavorable in DMF. Elucidating this chemical mechanism is important for understanding the effects that additives and additive combinations have on the composition, morphology, and optoelectronic properties of metal halide perovskite thin films.[20]

Results and Discussion

Acidification of Protic Additive Molecules.

Based on established transition metal halide chemistry, we propose Scheme 1 outlining the reaction mechanism between PbI_2 and various additives.[21] The general mechanism for anhydrous conditions is depicted in Scheme 1a, although one could easily envision H_2O as either reactants HA or B. In this scheme, a protic molecule (denoted by HA) acting as a weak Brønsted acid, (1), is not deprotonated by a weak base, B, under normal conditions. However, in the presence of PbI_2, the pK_a of (1) is lowered by the formation of a coordination complex (2) with PbI_2. It then becomes favorable for a weak Brønsted base (3) to deprotonate the acidified complex (2) forming the conjugate base (4) and conjugate acid salt with iodide (5). Scheme 1b shows a plausible reaction for the case of a single additive, butylamine, which can act as both the acid and the base (i.e. HA = B) producing a Pb-butylamide bond (6) and a butylammonium iodide molecule. While this reaction is well known to occur for many transition metals, reports of the formation of simple Pb-alkylamides by this mechanism are limited.[21] Scheme 1c illustrates a heterogenous reaction in which HA ≠ B exemplified by formic acid and butylamine, respectively. In DMF, carboxylic acids ($pK_a \approx 13.5$) would not be expected to be deprotonated by amines (alkylammonium $pK_a \approx 10.3$).[22] However, in the presence of PbI_2, formic acid can be acidified by coordinating to Pb^{2+} and deprotonated by a sufficiently strong base to form insoluble PbI(formate) (7). This

work focuses mainly on the reaction in Scheme 1b with butylamine and characterization of the PbI-butylamide product. We then demonstrate Scheme 1c occurs in DMF when HA = formic acid. These results provide important insight into chemical reactions occurring in perovskite solutions that can only be predicted by considering the combined effects of solvent, additives, and precursor properties.

Figure 1. Photographs of PbI_2, TBAI:PbI_2 (molar ratio 1:1), and BAI:PbI_2 (molar ratio
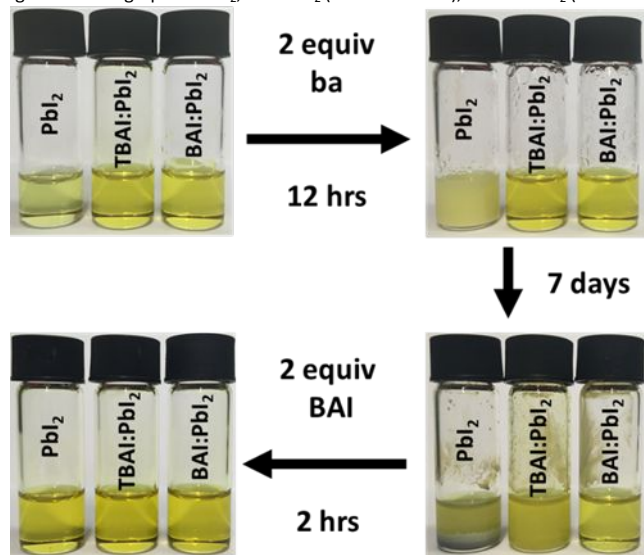
1:1) dissolved in DMF reacting with 2 equivalents of butylamine (ba) additive at 55 ºC. After one week, the resulting precipitates were fully reversible by the addition of excess BAI.

Case of HA = B = Amines.

We begin with reactions of amines with PbI_2 in various solvents (reaction in Scheme 1b). Understanding amine reactions with PbI_2 is important for several reasons: 1) perovskite solutions are often prepared non-stoichiometric with excess PbI_2,[23,24] 2) PbI_2 inclusions are present or form easily upon the release of MAI,[24,25] 3) defects in $MAPbI_3$, such as undercoordinated Pb surface sites and MAI deficiencies, are likely similar in reactivity to PbI_2,[3] and 4) reacting with bulk PbI_2 produces enough material to be able to easily characterize the products. High solubility of PbI_2 in amines was easily demonstrated by dissolving concentrated PbI_2 in butylamine (~500 mg/mL) at refrigeration temperatures, approximately 5-10 ºC (Fig. S1). When the PbI_2/butylamine solution temperature was elevated, a large amount of pale-yellow precipitate formed which did not redissolve upon cooling. In a DMF solution, (200 mg/mL PbI_2 in DMF with 2 molar equivalents butylamine) became turbid within 12 hours. We infer that the precipitate is the result of a chemical reaction, as Pb halides are extremely soluble in both DMF and aliphatic amines. We hypothesize that the precipitate is a Pb-iodo-butylamide, compound (6) in Scheme 1b which will be verified below. Amine/amide reactions as revealed qualitatively by precipitate formation and/or color changes were observed for a variety of primary and secondary amines as well as different PbX_2 salts (see Fig. S2 and S3). Tertiary amines lacking an acidic proton, such as triethylamine, were not reactive with PbI_2. No precipitate was observed for a reaction between PbI_2 and methylamine in DMF but, as will be

shown later, a reaction still took place. In general, the length/structure of the alkyl groups of an aliphatic amine is not expected to strongly affect the reaction in Scheme 1b other than influencing kinetics through steric hindrance.

As DMF is the most-employed solvent for perovskite processing, we use it to study amine/amide reactions of PbI_2 with butylamine in similar conditions. In anhydrous DMF at 55 ºC, PbI_2 reacts with butylamine on a time scale of several hours to days as shown in Fig. 1. Including one molar equivalent of tetrabutylammonium iodide (TBAI) as an additive, a soluble iodide source lacking acidic protons, slows the precipitate formation. Days passed before the TBAI:PbI_2 solution showed signs of Pb-amide formation. Given extended reaction time (~ 1 month at RT), the final product of the TBAI:PbI_2 sample is very similar in appearance to the control (Fig. S4). In contrast, the precipitation is nearly fully inhibited when equimolar butylammonium iodide (BAI) is dissolved with the PbI_2. The effect of BAI was anticipated since relatively stable inks and quality films of $MAPbI_3$ have been processed by ACN/methylamine solvent mixtures.[14] Furthermore, the precipitate in the control and TBAI containing solutions were fully redissolved by addition of BAI demonstrating equilibrium chemistry and good reversibility. Thus, to take advantage of the solubilizing properties of amines for perovskites, both solution "pH" and temperature must be kept low. While we intentionally used a large excess of amines to guarantee enough product to characterize, small amounts of precipitates were observed via the Tyndall effect for butylamine concentrations as low as 0.2 molar equivalents with respect to PbI_2 (Fig. S5). Methylammonium iodide was also effective at inhibiting reactions with butylamine while formamidinium iodide, a much weaker acid, was not (Fig. S6). Finally, simulating a sub-stoichiometric formulation, a solution of butylamine/MAI/PbI_2 in a 0.5:0.5:1 molar ratio in DMF developed a precipitate (Fig. S6) as well indicating this reaction is especially pertinent to typical PbI_2 rich precursor ink formulations.

The effect of TBAI can be understood in the context of soft acid/base interactions. Iodide is a soft base with very high affinity for soft acids and can significantly slow the kinetics by competing with amines for coordination with Pb^{2+} to make $[PbI_3]^-$.[26] With iodide present, the PbI_2•amine complex becomes much more labile. However, excess iodide (TBAI vs. BAI) alone was not able to sufficiently prevent the amide reaction from occurring. The strength of soft basicity and the resulting adduct bond is quantified by the donor number (DN).[7,26,27] Relative to DMF (DN = 26.6 kcal/mol), 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone (DMPU, DN = 33 kcal/mol) slowed the
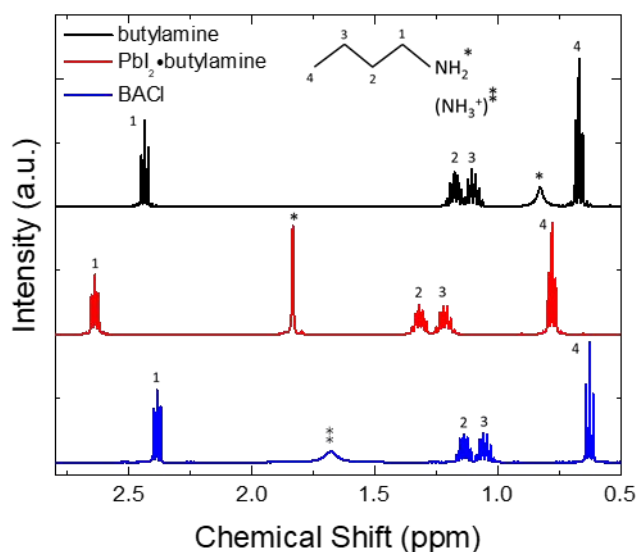
Figure 2. Chemical shifts of the N-H protons measured by ^{1}H-NMR of butylamine, butylammonium, and PbI$_2$•butylamine coordination complex in deuterated chloroform. The magnitude of the downfield shifts corroborates the acidification of butylamine complexed to Pb^{2+}.

butylamine/PbI$_2$ reaction supporting the role of competitive soft acid-base interactions.[7,26,27] For better or for worse, primary and secondary alkylamines (donor number ≈ 42-50 kcal/mol) will ultimately prevail over most other organic molecules.[27] Thus, a convenient organic molecule additive that would inhibit the amide reaction by completely blocking amine solvation yet be volatile enough to leave the perovskite film during deposition are scarce or non-existent.

Reversibility of the reaction with BAI supports the acid-base chemistry proposed in Scheme 1b. To further assess the plausibility of Scheme 1b, ^{1}H-NMR was performed on the PbI$_2$•butylamine complex which was isolated by reacting PbI$_2$ with butylamine (no DMF) followed by extraction with deuterated chloroform. Note that BAI is insoluble in chloroform and continually precipitated out as the PbI$_2$•butylamine complex reacted with excess butylamine. The ^{1}H-NMR spectra of butylamine, PbI$_2$•butylamine adduct, and butylammonium are contrasted in Fig. 2. Relative to free butylamine, the N-H protons (indicated with *) in the PbI$_2$•butylamine complex are shifted significantly downfield corroborating an increase in acidity. The narrowing of the N-H peak is typical of coordination complexes due to the inhibition of hydrogen bonding/proton exchange. Furthermore, the downfield shift of the N-H protons in the coordination complex is even greater than that of butylammonium. Thus, the relative pK$_a$'s suggested by the ^{1}H-NMR measurements strongly support the plausibility that proton transfer to a second butylamine molecule would be favorable in solvents like chloroform. However, the pK$_a$ of acids can change considerably due to counter ion (e.g. Cl vs. I) and, more importantly, solvent choice so the reaction products in DMF require further characterization.[22]

As the reaction progressed, aliquots of the reaction mixture of PbI$_2$/butylamine in DMF were drop casted and characterized

by XRD as shown in Fig. 3a. The sample prepared immediately after butylamine addition contains peaks solely from PbI$_2$ (main
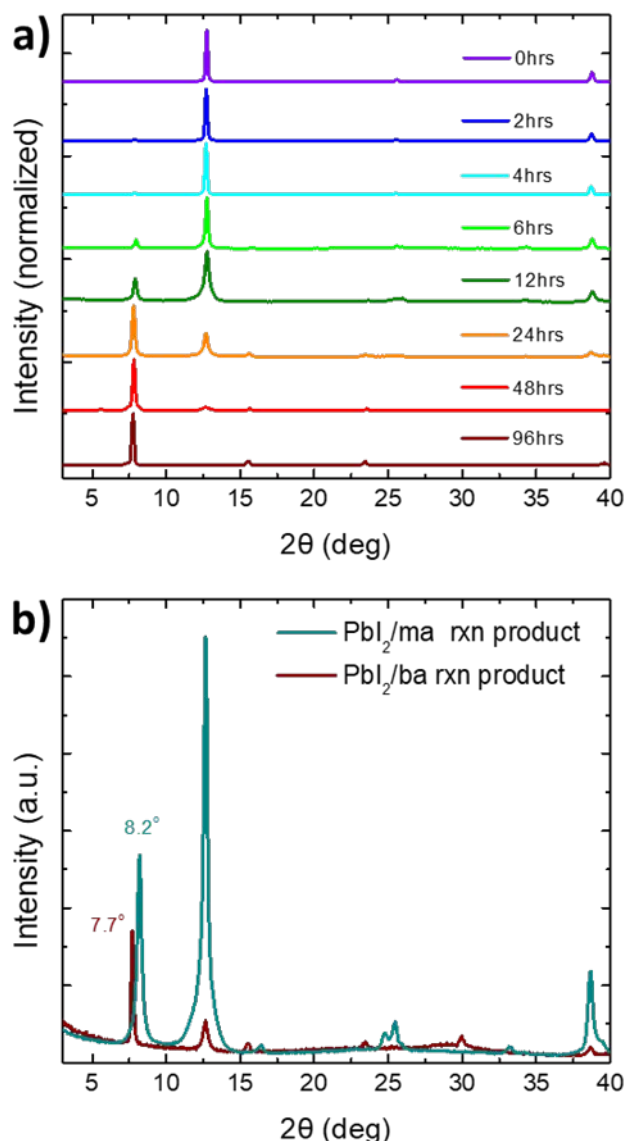

Figure 3. (a) Normalized XRD patterns of drop cast samples of a PbI$_2$/butylamine (1:2) solution in DMF as a function of reaction time showing a gradual shift from PbI$_2$ to a new phase potentially containing Pb-butylamide moieties. (b) Comparison of XRD of the PbI$_2$/methylamine (ma) reaction product to PbI$_2$/butylamine (ba) reaction product.

peak at 2θ = 12.7^o). However, after only 2 h at 55 ^{o}C, a new phase with a peak at approximately 7.7^o begins to emerge. The ratio of this unidentified phase to PbI$_2$ increases over the course of several days until there is no longer crystalline PbI$_2$ in the samples. In order to rule out the new phase simply being a result of PbI$_2$•butylamine coordination/solvation, several measures were taken. First, ^{1}H-NMR of a fresh solution of PbI$_2$/butylamine in deuterated-DMF showed that the butylamine completely complexes to the PbI$_2$ within 15 min (recall the DN of butylamine is much larger than DMF). Thus, the time scale of the formation of the unidentified phase in Fig. 3a does not match the rate of amine solvation. Second,
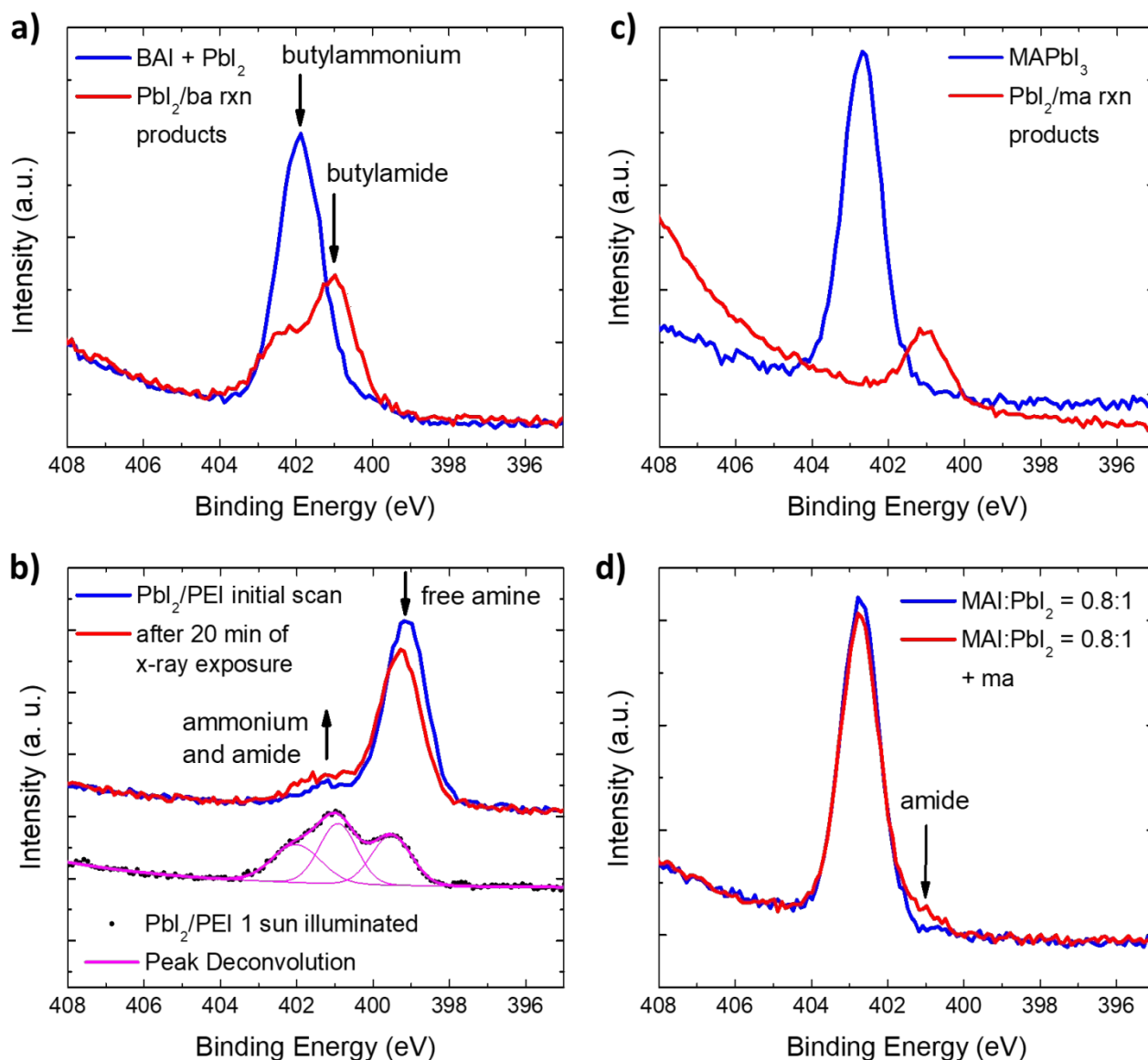
Figure 4. N 1s XPS of (a) drop cast samples of BAI:PbI_2 (1:1 ratio in DMF) and the supernatant of the PbI_2/butylamine reaction in DMF, (b) a thin film bilayer of PbI_2/linear-PEI showing *in situ* changes in relative intensity of the free amine peak (BE ≈ 399.5 eV) and amide/ammonium peaks (BE > 400 eV), (c) thin films of an $MAPbI_3$ control (1:1 MAI:PbI_2 ratio) and PbI_2/methylamine reaction in DMF showing amide formation with methylamine, and (d) amide formation in a non-stoichiometric MAI:PbI_2 solution in DMF after the addition of methylamine.

PbI_2•amine coordination complexes are known to decompose at room temperature[28] and the drop cast samples in Fig. 3 were annealed at 110 °C for 20 min to remove free or solvating butylamine. Third, a film of drop cast PbI_2 was solvated by a gaseous butylamine atmosphere at room temperature, quickly encapsulated in PMMA, and characterized by XRD (Fig. S7). The PbI_2•butylamine solvate displayed a primary peak at roughly 2θ ≈ 4.2° which was absent in the films drop cast from the PbI_2/butylamine reaction in DMF. Unsurprisingly, the peak at 4.2° due to the PbI_2•butylamine solvation complex decreased quite rapidly during the course of the measurement despite PMMA encapsulation. It is worth noting that the PbI_2 exposed

to butylamine vapor formed a small amount of the Pb-amide product peak apparent from a peak at 2θ = 7.7°, comparable to the amount formed after 1 h in solution with DMF, which did not decrease appreciably over time. Finally, addition of methylamine:ethanol mixture (33 wt% methylamine) to a PbI_2 solution in DMF reacted to form a similar phase as the butylamine/butylamide reaction, but with a primary peak at 2θ = 8.2° (Fig. 3b). The larger scattering angle is consistent with the smaller d-spacing due to the smaller size of methylamine. Note that no precipitate was observed with methylamine which means the reaction could easily go unnoticed.

X-ray photoemission (XPS) measurements identify significant nitrogen content (nitrogen must be > 1 atomic % on the surface to resolve with XPS) after 4-6 hours of reaction time (Fig. S8). Negligible oxygen content rules out the direct involvement of water impurities in the reaction (Fig. S9). The XPS spectrum of the N 1s region of the PbI_2/butylamine product after complete reaction is shown in Fig. 4a. The peak clearly contains two distinct N species. The high binding energy (BE) peak (≥ 402 eV) is identified as butylammonium by comparison to a drop cast film of BAI:PbI_2. We attribute the lower BE peak (≈ 401 eV) to the Pb-amide species.[29,30] To rule out the presence of residual butylamine, a solid-state PbI_2/linear-polyethylenimine (PEI) thin film heterojunction was also characterized (Fig. 4b). The free amine peak is located at < 400 eV (see also an Au/PEI control in Fig. S10) which strongly suggests the peak at 401 eV arises from amide N. Note that three distinct N species have been previously measured in $MAPbI_3$ films *via* XPS.[31] A peak observed at 401.2 eV was particularly prominent in films processed from an ACN/methylamine solvent system.[32] In addition, the PbI_2/PEI sample was observed to react *in situ* during XPS measurements. After 20 minutes of X-ray exposure during consecutive scans, the free amine peak intensity decreased concurrent with an increase in intensity of the high BE features. The photosensitivity of the amine/amide reaction was characterized by irradiating the PbI_2/PEI heterojunction with AM1.5G simulated solar illumination for 2 hours in an N_2 atmosphere. Consistent with the N 1s peaks observed for butylamine conversion to butylammonium and butylamide in Fig. 4a, peak deconvolution of the 1 sun irradiated PbI_2/PEI sample revealed a best fit with peaks centered at 399.5 eV, 400.9 eV, and 402 eV. Illumination clearly accelerates the conversion of the PEI amine groups to ammonium and amide species. Furthermore, the absence of solvent molecules in this solid-state reaction prove that the BE features at 402 eV and 401 eV arise solely due to a reaction between aliphatic amines and PbI_2.

Similar N species at BE ≈ 401 eV were observed in a film of PbI_2/methylamine reacted in DMF (Fig. 4c). Curiously, methylammonium was absent, possibly suggesting that the amide species segregate to PbI_2/perovskite surfaces or interfaces. Additionally, a thin film spin coated from an MAI deficient ink (MAI:PbI_2 ratio = 0.8:1 in DMF) in which the 20% excess PbI_2 was allowed to react with the methylamine additive for 1 week contained a considerable amount of amide species. This condition of excess PbI_2 is highly relevant for typical perovskite ink formulations.[23,24] More importantly, Fig. 3a and Fig. 4c clearly demonstrate the plausibility of amide incorporation in fresher solutions (aged less than 1 day) using amine additives, likely at concentrations below the detection limit of XPS. The amide incorporation in $MAPbI_3$ films was correlated to photoluminescence improvements (Fig. S11) which is consistent with reports of amine passivating perovskite surfaces.[9,15]

Finally, the insoluble PbI-butylamide product was isolated by decanting the DMF and repeated ACN washings to solubilize and selectively remove ammonium halides which, in turn, help to dissolve unreacted PbI_2. The N 1s XPS spectra of the materials

soluble and insoluble in ACN indeed indicate that ammonium and amide components were segregated by this method (Fig. S12). We hypothesize from Scheme 1b that the insoluble material is composed of a Pb-halide-butylamide of the formula: $PbI[NH(CH_2)_3CH_3]$. This material resembles a class of materials referred to as coordination polymers and are commonly synthesized from transition metal halides.[33-35] The precipitate collected after subsequent DMF and ACN washing was characterized by thermal gravimetric analysis (TGA) shown in
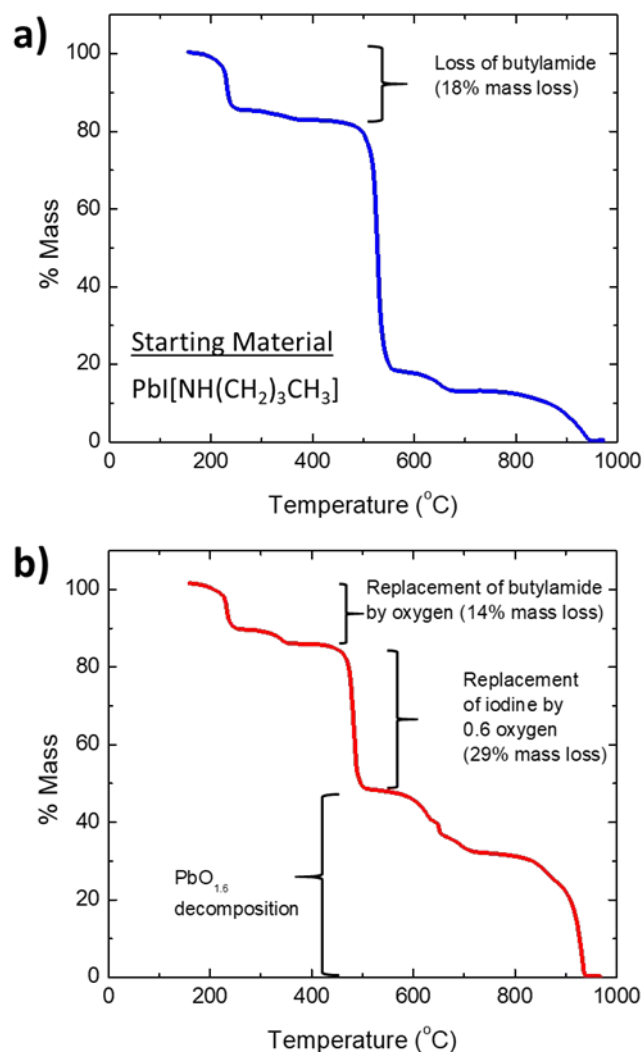

Figure 5. TGA of the isolated precipitate from the reaction of PbI_2 and butylamine in DMF under (a) N_2 and (b) ambient air. The mass losses indicated for (a) butylamide removal and (b) replacement of butylamide by oxygen confirm the hypothesized starting composition of $PbI[CH_3(CH_2)_3NH]$.

Fig. 5 (for PbI_2 controls see Fig. S13). The TGA samples were held at 150 °C for 10 min before starting the scan in order to remove any residual coordinating solvent molecules including DMF.[7] Under N_2 flow (Fig. S13), the PbI_2 control begins to sublime at 430 °C (5% mass loss). Under air flow the mass loss of PbI_2 at 450 °C corresponds to replacement of the two iodide by oxygen to make $PbO_{1.6}$, the expected stoichiometry for the temperature range 400-500 °C.[36] At higher temperatures, the

$PbO_{1.6}$ continues to decompose in several more steps (presumably to $PbO_{1.4}$, $PbO_{1.2}$, and PbO).[36] In contrast, the butylamine reaction product begins to decompose at approximately 230 °C, much lower temperature than PbI_2. Based on Scheme 1b, we hypothesize that the insoluble PbI_2/butylamine reaction product is likely a PbI-butylamide as opposed to a Pb diamide.[21,29,30] Assuming this stoichiometry, the 18% mass loss between 200-400 °C correspond strikingly well to the expected change due to loss of the amide group in N_2 (Fig. 5a) and 14% mass loss due to replacement by oxygen in air (Fig. 5b). The

Figure 6. ^{1}H-NMR at (a) high and (b) low chemical shifts of combinations of formic acid (fa), butylamine (ba), and PbI_2 in deuterated DMF (d7-DMF). The spectra indicate that the presence of PbI_2 induces proton transfer from formic acid to butylamine in d7-DMF whereas no reaction is observed for the formic acid + butylamine control.

expected mass losses for PbI_2•butylmaine solvation complexes are listed in Table S1. As both DMF and butylamine should be

expelled from the material below 150 °C, the agreement of TGA in N_2 and air strongly support that the chemical composition of the insoluble PbI_2/butylamine reaction product is indeed the singly substituted $PbI[NH(CH_2)_3CH_3]$.[7]

Most of the discussion of the Lewis acidity of Pb^{2+} and PbI_2 in perovskite literature has focused on Lewis acid-base coordination complexes or adducts with aprotic Lewis bases like DMF, dimethylsulfoxide, thiourea, and pyridines.[6-8,10,11] These dative perovskite-organic coordination bonds have been shown to form with molecules such as pyridines, phosphine oxides, sulphur moieties, esters, etc. resulting in passivation of surface traps and non-radiative recombination centers.[7,8,10,11] In contrast, this work indicates another option, demonstrating the plausibility of Pb-amide bond formation in perovskite solutions and subsequent incorporation in thin films. The Pb-amide bond is similar yet distinct from a coordination complex bond (e.g. Pb•amine, Pb•pyridine) in that it is more covalent in nature. The higher energy of Pb-amide bond is reflected in the thermal decomposition onset > 200 °C whereas PbI_2•pyridine complexes are known to decompose at < 100 °C.[28] We assert that post-thin-film-deposition amine treatments are susceptible to amide formation at PbI_2 inclusions or undercoordinated Pb surface defects, which are proposed non-radiative recombination sites.[11,37] Note that an ammonium is simultaneously produced for every amide such that both an A-site and X-site vacancy can be annihilated *via* the same reaction. Additionally, the density of states at the valence and conduction band extrema are composed mainly of Pb and iodide orbitals while the A-site sublattice does not contribute to band edge electronic states.[38] Thus, a molecule covalently bonded to Pb at a perovskite surface is a potentially ideal passivating agent. The properties or benefits of small amounts of Pb-amide species in perovskite films are as yet unknown but are the subject of a follow up study.[20] However, the demonstration of perovskite solar cells with high power conversion efficiencies from processes utilizing amines motivates obtaining a deeper understanding of amine/amide chemistry with Pb halides.

Case of HA ≠ B.

We demonstrate the generality of the mechanism identified in the amine/amide reaction by applying it to heterogeneous reactions (i.e. the acid and base are dissimilar molecules) induced by PbI_2 that are otherwise unfavorable. The situation is exemplified in Scheme 1c by the reaction between formic acid and amines which have both been employed in perovskite processes independently.[9] Additionally, the presence of formate has recently been identified in perovskite films (before annealing) fabricated from aged perovskite inks in which hydrolysis of DMF released dimethylamine and formic acid.[5] In DMF, formic acid is not acidic enough to be deprotonated by an aliphatic amine.[22] However, the acidity is increased upon complexation with PbI_2 which drives deprotonation. Upon the addition of a small amount of butylamine, a solution of PbI_2/formic acid in DMF instantaneously forms a precipitate. Indeed, ^{1}H-NMR spectra of a formic acid/butylamine mixture in deuterated DMF shows that proton exchange does not occur
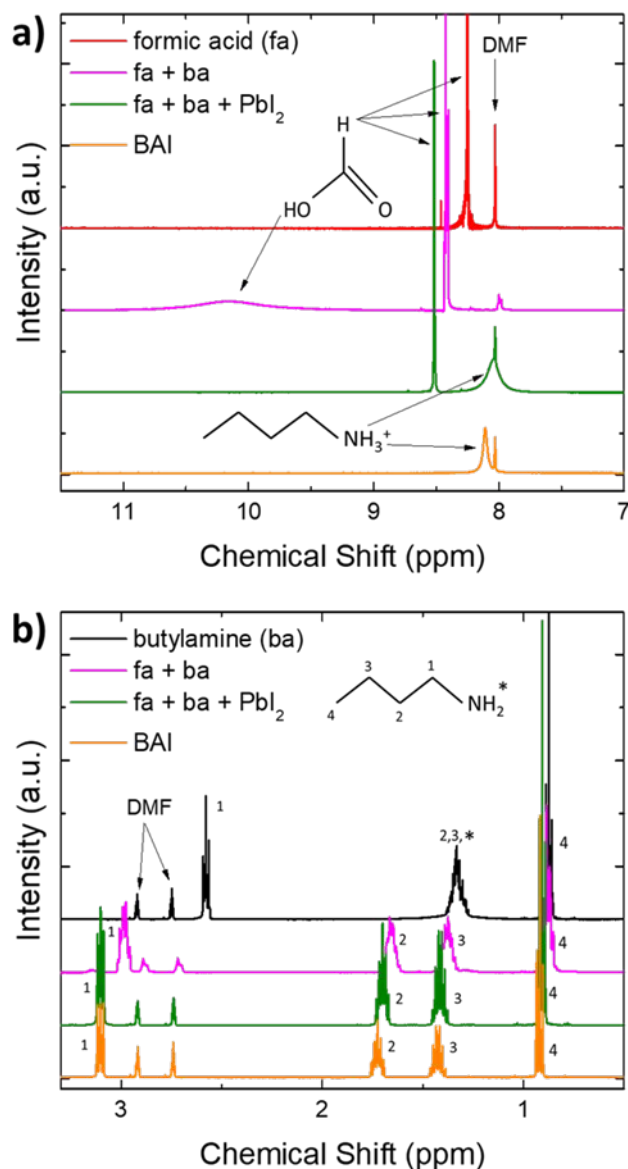
(Fig. 6). In fact, the hydrogen bonding between formic acid and butylamine make the acidic proton on formic acid observable as a broad peak at 10.1 ppm. The rapid exchange of the proton between oxygens in a carboxylic acid make them very difficult to detect in the formic acid control. However, the supernatant of a reaction of PbI_2/formic acid/butylamine in deuterated-DMF reveals a butylammonium peak at approximately 8.1 ppm which corresponds well to a BAI control. Note that formic acid DN = 19 kcal/mol so the PbI_2•formic acid complex would be expected to be a very labile species in the presence of DMF and butylamine.[27] Despite the relatively low concentration of the PbI_2•formic acid complex in DMF, it is effectively deprotonated by butylamine to produce PbI(formate) and BAI. As hydrolysis of DMF releases dimethylamine and formic acid, the importance of understanding impurity reactions, the products induced by the Lewis acidity of PbI_2, the influence on perovskite film crystallization, and effects on device stability cannot be underestimated.

Conclusions

In summary protic molecules commonly used as halide perovskite processing additives are acidified when solvated to an acidic Pb^{2+} center. This change in pK_a induces proton transfer to a suitable base molecule leading to unanticipated chemistry in perovskite precursor solutions. We demonstrate the Lewis acidity of PbI_2 causes proton transfer from carboxylic acids to amines in DMF. More importantly, an acid-base reaction between amines and PbI_2 releases protons to produce Pb-amide and ammonium species in solution which can be incorporated into thin films. Formate and amide impurities may play a significant role in the crystallization, morphology, and properties of perovskite thin films fabricated from different processes and ink formulations as well as the differences in film properties resulting from variable aging time of solutions. The insight provided by this work into different types of dative bonds that can form from additive chemistry in perovskite films elucidates a new approach for covalently bonding amide groups to undercoordinated Pb sites and also raises questions regarding the role of these complexes in resulting devices. As the processing of perovskite films becomes more complex, understanding and predicting the detailed structure/bonding of impurities is paramount for advancing performance and stability of metal halide perovskite based optoelectronic devices.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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