

Organoammonium-Ion-based Perovskites Can Degrade to Pb⁰ via Amine–Pb(II) Coordination

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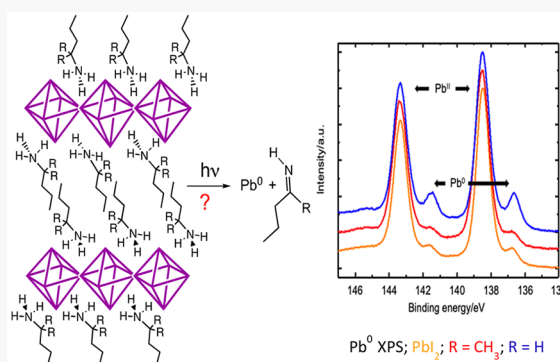


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Supporting Information

ABSTRACT: The degradation of alkylammonium Pb^{II} halide perovskites, in the dark and upon irradiation near room temperature, involves coordinated amine as the dominant reducing agent to yield Pb⁰ near room temperature, as determined by X-ray photoelectron spectroscopy (XPS). The reduction of Pb^{II} first involves amine coordination, supported by ²⁰⁷Pb nuclear magnetic resonance (NMR) analysis. It is shown that a Pb^{II}–amide complex is the immediate precursor of Pb^{II} reduction. Its oxidized counterpart, the imine, is formed and is characterized by NMR and gas chromatography–mass spectrometry. The “redox” process requires a β-C–H bond of the alkylamine. Amine species devoid of this moiety do not similarly reduce Pb^{II} to Pb⁰. The conversion of an alkylammonium moiety to the Pb^{II}–amide is proposed to occur through a sequence of photoassisted proton-transfer reactions to a lead-coordinated ligand, which is substantiated through XPS-observed Pb^{II} reduction in a family of lead bromide/iodide 2D perovskites.



Organic-based lead halide perovskites have been broadly investigated^{1,2} for photovoltaics,³ light-emitting diodes,^{4,5} and lasers⁶ and as substrates for fundamental studies of optical and electronic properties.^{7–10} They display defect tolerance, band-gap tunability, and practicable solution processing, but their long-term stability can be problematic and is clearly a prerequisite for practical device utilization. In particular, forming Pb⁰ can be deleterious during fabrication¹¹ or under operating conditions.^{12–15} Sterically small alkylammonium cations (such as methylammonium) are commonly found in crystalline “3D” bulk perovskites; larger ones with broader structural variation are used as spacers in “2D” layered or mixed “2D/3D” species.^{8,16–18} While it is commonly assumed that an ammonium lead iodide perovskite can degrade to an amine, HI and PbI₂ that subsequently yields I₂ and Pb⁰,^{13,19,20} an under-appreciated pathway for formation of Pb⁰ is based instead on the fundamental chemistry of Pb–N bonding:^{12,21} Pb^{II} and amine nitrogen are “soft” Lewis acids and bases, respectively, and Pb^{II}–amine coordination is expected to be strong. Here we show that reduction of Pb^{II} to Pb⁰ can occur by a “redox” reaction in a Pb^{II}–coordinated amine, both in the model system, PbI₂, and in a family of 2D perovskites. Indeed, we find that this amine-involved pathway is favored compared with the unimolecular decomposition of PbI₂ to Pb⁰ either in the dark or, more substantially, upon irradiation near room temperature (Figure 1). The key to proving the role of the

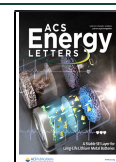
amine as the critical reducing agent in our “redox” proposal is the unambiguous identification of its oxidized organic product, the Schiff base. Simply demonstrating the formation of Pb⁰¹² is insufficient. We further provide evidence to suggest that a Pb^{II}–amide complex is intermediate in the overall sequence for Pb^{II} reduction and that the reduction of Pb^{II} occurs only when a β-C–H moiety is present in the amide ligand. It is especially significant that every step in this sequence involves only simple proton transfer, which apparently is favored under device-relevant stress conditions.

Our proposed pathway for the amine-derived reduction of Pb^{II} is based on a series of simple proton-transfer reactions (Scheme 1) in which it is hypothesized that the coordination of an amine to Lewis-acidic Pb^{II} should result in the acidification of Pb–N–H groups and also any “β-X–H” groups that are present. The final, and key, step in our scheme, the rapid reduction of Pb^{II} to Pb⁰, is proposed to occur in the coordination sphere of a lead–amide complex. Were this step not fast, direct observation of the amide complex might be possible. Reduction is proposed to occur by the deprotonation

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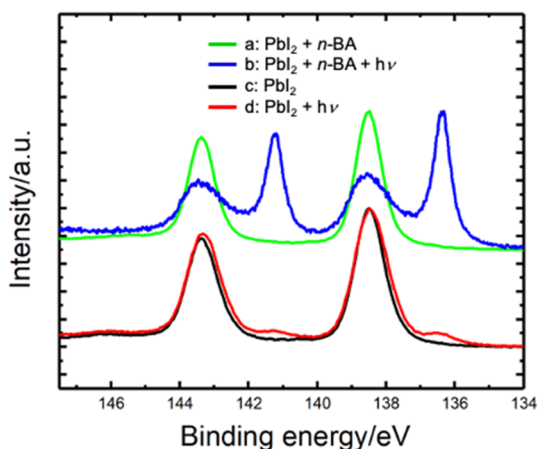
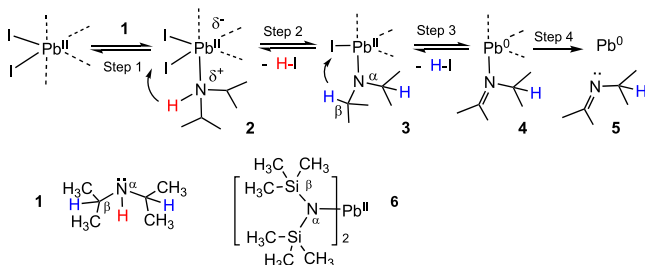


Figure 1. X-ray photoelectron Pb(4f) spectra showing the reduction of Pb^{II} to Pb⁰. (a) Control: PbI₂ before irradiation. (b) PbI₂ following irradiation (1.5 W LED control at 375 nm; intensity ca. 25 mW/cm²) for 18 h. PbI₂ in the presence of *n*-butylamine (c) before irradiation and (d) upon irradiation. Peaks at ca. 136.5 and 141.5 eV correspond to Pb⁰, and peaks at ca. 138.5 and 143.5 eV correspond to Pb^{II}.

Scheme 1. Reduction of Pb^{II} to Pb⁰ by the Reaction between PbI₂ and Di-*iso*-propylamine (1)^a



^aAmine coordinates to PbI₂. N–H becomes acidified in adduct 2, as does β -*iso*-propyl C–H (in blue). The proton transfer from N to iodide gives amide complex 3 with the loss of HI. The transfer of β -*iso*-propyl C–H (in blue) to iodide gives imine complex 4 with the loss of HI and the concomitant reduction of Pb^{II} to Pb⁰, identified by XPS. Imine 5 is identified by NMR and GC-MS. Complex 6 is used for the atomic layer deposition of PbI₂.

of “ β -X–H” with the loss of HI. This effectively oxidizes the amine to its dehydrogenated analog, imine 5. We began our studies by examining the chemistry of PbI₂, which is a model for organo-lead perovskites, where it is present as an adduct that is either inadvertently²² or intentionally^{23,24} present in perovskite-based devices. We also examined amines as our first substrate class because they are either added to perovskite formulation mixtures^{25,26} or used in postprocessing.^{27,28}

To prove that amine–Pb^{II} complexes are readily formed from PbI₂, we probed for coordination by ²⁰⁷Pb NMR in *N,N*-dimethylformamide (DMF) solution. Pb/amine ratios were set at ca. 1:1. As shown in Figure 2, the reaction with *n*-butylamine (*n*-BA) shows a signal at 1220 ppm that is downfield from that for PbI₂ (955 ppm), as are the signals for the coordination of di-*iso*-propylamine (DiPA; 1090 ppm) and *tert*-butylamine (*t*-BA; 1132 ppm). We attribute the downfield shifts to the replacement of an iodide by a more electronegative nitrogen-based ligand. We relate these differences in ²⁰⁷Pb chemical shifts to the relative steric sizes of the three amine ligands: Cone angles for *n*-alkylamines (106°), *tert*-butyl amine (113°),

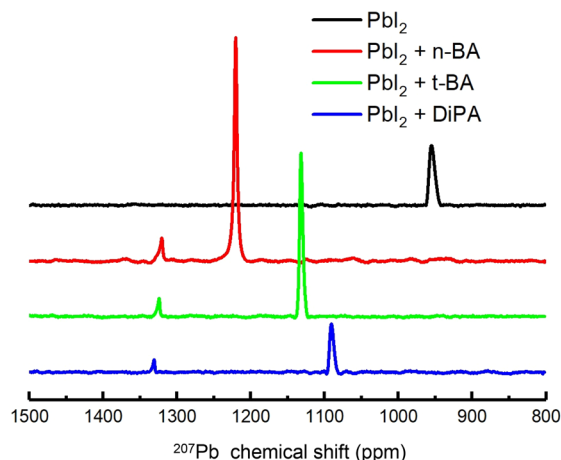


Figure 2. ²⁰⁷Pb NMR spectra for the reaction between PbI₂ and *n*-butylamine (*n*-BA), di-*iso*-propylamine (DiPA), and *tert*-butylamine (*t*-BA). All spectra were recorded as 0.8 M solutions in DMF, with lead and amine ratios set at ca. 1:1.

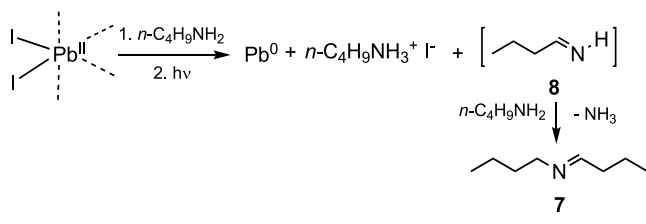
and di-*iso*-propylamine (137°) track the relative peak intensities for their complexes in the ²⁰⁷Pb NMR spectra from least sterically crowded to most.²⁹ These shifts also correlate with a reduction in nitrogen electronegativity related to the alkyl group donor structure.

Having demonstrated the possibility for lead–amine coordination, we next tested the validity of our overall proposal that rests on the rapid reduction of Pb^{II} to Pb⁰ via a lead–amide complex formed between PbI₂ and an *ex situ* prepared amide, lithium di-*iso*-propylamide (LDA), to give 3 by simple ligation. When a solution of LDA in tetrahydrofuran (THF)/hexanes was added to a suspension of PbI₂ in this solvent mixture at room temperature, the reaction mixture became orange followed by the rapid precipitation of a copious black solid. If the LDA solution was instead added at –20 °C and then allowed to warm, no reaction ensued until ca. –10 °C, when a rapid change to orange and then precipitation occurred. After methanol was added to quench any residual LDA, the solid was separated and studied by XPS to confirm its identity as Pb⁰ (Supporting Information, Figure S1). The supernatant was recovered and analyzed by nuclear magnetic resonance (NMR) and gas chromatography–mass spectrometry (GC-MS) (Supporting Information, Figures S2–S5) to show the presence of 5 as the major organic product, which proves our central contention for Pb^{II} reduction. It is also important to note here that [bis(trimethylsilyl)amido]lead(II) 6, which does not have β -C–H bonds, can be prepared from the corresponding lithium amide and isolated as a reagent for use in the atomic layer deposition of lead diiodide.³⁰

Step 2 in Scheme 1 is the conversion of the lead–amine complex 2 to an amide. Given the high reactivity of 3, we can infer with certainty the intermediate formation of 3 by noting its products of decomposition, Pb⁰ and, definitively, 5. In contrast with this latter step that rapidly proceeds even at 0 °C, the treatment of a suspension of PbI₂ with *n*-butylamine at room temperature resulted only in its dissolution, presumably forming the analog of 2. When, however, this solution was placed between two sheets of ITO/glass and irradiated at 375 nm (1.5 W LED light source; illumination intensity ca. 25 mW/cm²) for 1 h, Pb⁰ was produced (Supporting Information, Figure S6).

To show further that the reduction to Pb^0 requires an amine and, in particular, one that contains a $\beta\text{-C-H}$ bond, solid PbI_2 and suspensions of PbI_2 in di-*iso*-propylamine, *tert*-butylamine, or dimethylbutylamine or in solution with *n*-butylamine (PbI_2 is soluble in *n*-butylamine) were irradiated in plain glass vials under the same conditions as previously described (Supporting Information, Figure S7). In no case was Pb^0 seen in the absence of irradiation, even if the reaction mixtures were heated to 80 °C. Pb^0 formation on irradiation was observed with di-*iso*-propylamine and, in particular, with *n*-butylamine. As expected, **5** was present in the di-*iso*-propylamine-containing supernatant (Scheme 1). *n*-Butylidenebutylamine (**7**), the adduct of the expected imine (**8**) with excess *n*-butylamine, was found in that supernatant (Scheme 2)³¹

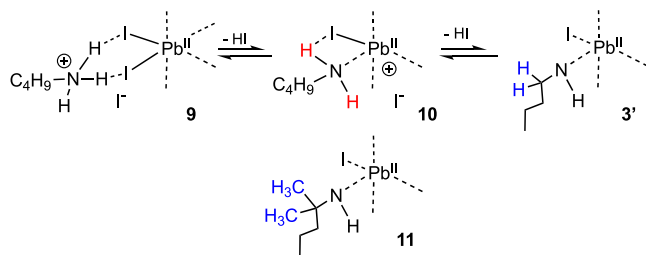
Scheme 2. Irradiation of *n*-Butylamine and PbI_2 Gives Imine **8, Which Adds a Second Equivalent of *n*-Butylamine to Give **7**, Identified by GC-MS and NMR by Comparison with Authentic Material**



(Supporting Information, Figures S8 and S9). Significantly, no Pb^0 was observed in the similarly treated PbI_2 suspension in *tert*-butylamine or in dimethylbutylamine, which have no $\beta\text{-C-H}$ bonds. Here unidentified colorless solids resulted. These results further emphasize the role of $\beta\text{-C-H}$ bonds in the “redox” formation of Pb^0 (Step 3 of Scheme 1). They also show that Step 2 of Scheme 1 is photoassisted.

Translating the role of amines in the reduction of Pb^{II} to establish the role of ammonium halide adducts is paramount with regard to understanding the reactivity of the materials that are based on layered 2D or 2D/3D perovskites.^{1,8,18} These layers are separated by alkylammonium ions, including linear^{18,32,33} and aminoalkyl-aromatic,^{18,34–39} -cycloalkyl,¹⁸ and -heterocyclic ions.^{18,35} These can be related to our model through a series of proton-transfer reactions (Scheme 3).

Scheme 3. *n*-Butylammonium ion ($n\text{-BA}^+$) is Hydrogen-Bonded to the Perovskite (9**) and Is Converted to the Corresponding Amine Adduct (**10**) Simply by $(\text{N-H})^+$ Group Deprotonation by Iodide, Which Also Yields HI^a**



^aA second similar loss of HI opens a site on Pb^{II} for amine coordination (**3'**). Complex **11**, which has no $\beta\text{-C-H}$ bonds, cannot act as a similar reducing agent.

We chose to examine *n*-butylammonium ($n\text{-BA}^+$) 2D perovskites ($n = 1$)¹⁶ as representative materials, several of which we characterized by X-ray diffraction (XRD) (Supporting Information, Figure S10). All studies were done on spin-cast thin films. We used four halide stoichiometries^{38–40} to further probe the effect of the ammonium salt and the key proposed role of proton transfer from the salt to the “ PbX_4 ” unit. We find by XPS analysis (Supporting Information, Figure S11) that for two of these cases, Pb^0 is formed in the dark, but more Pb^0 is produced on irradiation for all four. It is significant that the formation of Pb^0 , both in the dark and upon irradiation, is greatest for the iodide-based perovskite $n\text{-BA}_2\text{PbI}_4$. It decreases with the increasing incorporation of Br in place of iodide and is lowest for $n\text{-BA}_2\text{PbBr}_4$ (Figure 3). We believe these data are consistent with the first steps shown in the Scheme 3: The iodide species should be more basic than the bromide-substituted species given the relative electro-

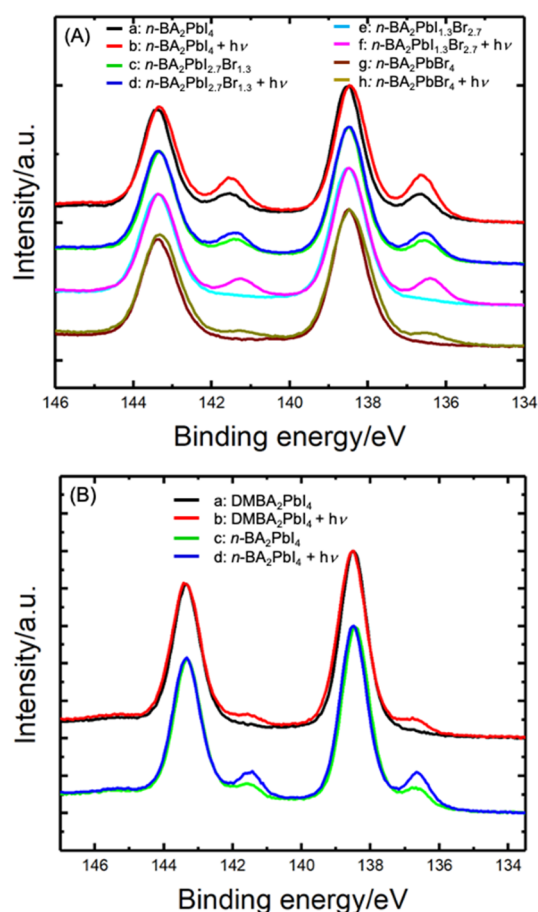


Figure 3. (A) $\text{Pb}(4f)$ XPS showing the effect of *n*-butylammonium ($n\text{-BA}^+$) on the reduction of Pb^{II} to Pb^0 , both in the dark (18 h) and following irradiation (1.5 W LED at 375 nm; intensity *ca.* 25 mW/cm^2), for 18 h for a series of 2D perovskites and a PbI_2 control. (a) $n\text{-BA}_2\text{PbI}_4$ in the dark, (b) irradiated $n\text{-BA}_2\text{PbI}_4$, (c) mixed halide species $n\text{-BA}_2\text{PbI}_{2.7}\text{Br}_{1.3}$ in the dark, (d) irradiated $n\text{-BA}_2\text{PbI}_{2.7}\text{Br}_{1.3}$, (e) $n\text{-BA}_2\text{PbI}_{1.3}\text{Br}_{2.7}$ in the dark, (f) irradiated $n\text{-BA}_2\text{PbI}_{1.3}\text{Br}_{2.7}$, (g) $n\text{-BA}_2\text{PbBr}_4$ in the dark, and (h) irradiated $n\text{-BA}_2\text{PbBr}_4$. (B) XP $\text{Pb}(4f)$ spectra contrasting the effects of *n*-butylamine (BA) versus dimethylbutylamine (DMBA) on the reduction of Pb^{II} to Pb^0 , both in the dark (18 h) and following irradiation (1.5 W LED at 375 nm), for 18 h. (a) $\text{DMBA}_2\text{PbI}_4$ in the dark, (b) irradiated $\text{DMBA}_2\text{PbI}_4$, (c) $n\text{-BA}_2\text{PbI}_4$ in the dark, and (d) irradiated $n\text{-BA}_2\text{PbI}_4$.

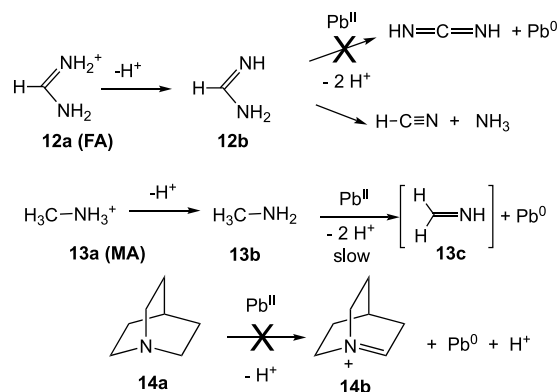
negativities of the two halides. Note, in particular, the relatively small amount of Pb^0 formed with the β -C–H-devoid ammonium $\text{DMBA}_2\text{PbI}_4$ (**11**) compared with the linear ammonium $n\text{-BA}_2\text{PbI}_4$, which is attributed to the irradiative reduction of PbI_2 itself (cf. Figure 1).

We have shown that the commonly invoked pathway for the formation of Pb^0 upon irradiation of a simple hybrid organic–inorganic lead halide perovskite, decomposition to amine plus PbI_2 , and then photolysis to Pb^0 and I_2 is inefficient compared with a direct amine-based pathway. We further showed that Pb^{II} is reduced to Pb^0 by a process of β -hydrogen elimination in a key Pb–amide complex intermediate. This process is analogous to the base-assisted dehydrohalogenation of an alkyl halide. It is a reductive process that is well known in the organometallic chemistry of transition metals in that when Pb^{II} acts as a “leaving group” following β -hydrogen loss from the amide complex, it retains the pair of electrons that had been in the Pb–N bond. The organic product, the imine, is the formal oxidized product of lead reduction. It is important to note that starting from an organoammonium-ion-incorporated perovskite, several steps involving the likely reversible loss of HI are required to yield first the coordinated amine and then the key lead–amide intermediate.

We demonstrated that the decomposition of a *bona fide* lead–amide complex to Pb^0 is fast. If all reversible steps leading to the loss of HI were favorable, then we would expect the rapid reduction of our 2D perovskite-based Pb^{II} in the dark, which is contrary to observation. Thus we propose that the role of irradiation is to “pump” proton-transfer reactions⁴¹ to favor HI loss in each step in Scheme 1. In support of this proposed role of proton transfer, we showed that replacing iodide with bromide imparted photochemical stability to our 2D material. Finally, and of perhaps greater significance, we found that an alkylammonium iodide can be used to make a crystalline 2D material that is even more stable to photochemical degradation because the amine is devoid of β -C–H bonds.

To predict classes of ammonium species whose chemistry might preclude the ultimate formation of Pb^0 requires an analysis of the nature of the organic product that would be formed by putative β -C–H bond elimination. Indeed, there are classes of ammonium species that do contain β -C–H bonds, yet they do not react following deprotonation by β -C–H elimination to give Pb^0 , for example, the common perovskite “A-site” organic cation formamidinium (FA, **12a**), where autodecomposition of the formamidine parent (**12b**) to HCN and ammonia is rapid⁴² (see also Supporting Information, Figure S12), or methylammonium (MA, **13a**), where β -C–H elimination from methylamine (**13b**) would be slow because of the highly reactive, unsubstituted parent imine product, methylenimine,⁴³ **13c** (see also Supporting Information, Figure S13) (Scheme 4). Irradiation of inorganic cesium perovskite, formed from CsI and PbI_2 , gave no Pb^0 , showing the key role of an amine as a reducing agent (Supporting Information, Figure S14). Finally, there are families of sterically constrained, tertiary amines, such as 1-azabicyclo[2.2.2]octane (**14a**), where β -elimination would yield a highly strained “bridgehead” olefin (**14b**).⁴⁴ Through the consideration of these facets of structure, the design and implementation of amine-based groups that do not promote the deleterious formation of Pb^0 can be envisaged.

Scheme 4. β -C–H Elimination to Give Pb^0 is Unfavorable for **12b**, Where Decomposition to HCN and NH_3 is Rapid, **13b**, where β -C–H Elimination Would Be Very Slow Because of the High Energy of the Parent Imine **13c**, and **14a**, Where the “Bridgehead” Olefin **14b** is Highly Strained



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.1c00714>.

Complete experimental procedures, five XPS figures, one XRD figure, four sets of NMR spectra, two sets of GC-MS data, and two sets of photographs of lead halide reduction (PDF)

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Notes

The authors declare no competing financial interest.

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