Chemically Controlled Crystal Growth of $(\text{CH}_3\text{NH}_3)_2\text{AgInBr}_6$

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We report the successful crystal growth of a previously unknown mixed-metal organic compound (CH$_3$NH$_3$)$_2$AgInBr$_6$. This phase, which is not obtained by direct combination of reactants, is crystallized through the use of Pb$^{2+}$ (from CH$_3$NH$_3$PbBr$_3$) to modulate the soluble intermediates and force formation of (CH$_3$NH$_3$)$_2$AgInBr$_6$. Our results provide insights into mechanism and design-driven crystal growth and discovery of new halide materials that are chemically related to perovskites with photovoltaic and related applications.

Organic-inorganic methyl ammonium metal halides are of particular interest in the search for photoactive materials attributed to their rich structural and electronic behavior. The properties have been observed to be strongly correlated with the intricate interactions between the organic and inorganic subunits. Structural dynamics within the perovskite structure have important implications for the operation mechanism of solar cells. They are thought to enhance charge carrier lifetime and open-circuit voltage, and affect hysteresis during current-voltage measurements. More specific to mixed metal-organic hybrids, it has been observed that organic-inorganic halide compounds, (MA)$_2$MM'X$_6$ (M = K, Ti, Ag; M' = Bi, Gd, Y; X = Cl, Br), are not as synthetically accessible as the inorganic derivatives (Cs$_2$MM'X$_6$ (M = Ag, M' = Bi, In, Sb; X = Cl, Br)). That is due to the substantial difference between reactivity and decomposition and/or vaporization temperatures of the organic starting materials and those of the inorganic reagents, precluding high-temperature techniques and thus limiting synthetic options. (MA)$_2$KBICl$_6$ and (MA)$_2$TIBiBr$_6$ have been synthesized by directly combining appropriate reagents hydrothermally. The synthesis of (MA)$_2$TIBiBr$_6$, however, resulted in significant amounts of a by-product ((MA)$_3$Bi$_2$Br$_9$). This issue was improved in the synthesis of (MA)$_2$AgBiBr$_6$ by adding MAPbBr$_3$, which was thought to serve as an *in situ* seed for the crystal growth. This synthetic technique, however, did not selectively yield (MA)$_2$AgBiBr$_6$ and, as a secondary phase, (MA)$_3$Bi$_2$Br$_9$ was also formed. Furthermore, the role of MAPbBr$_3$ in the synthesis has not been fully described and understood. Here, we demonstrate synthesis strategy to rationally design a chemical reaction to create a product with desired structural units and/or physical properties. By implementing this strategy, we selectively synthesized and grew crystals of the new mixed metal halide (MA)$_2$AgInBr$_6$, which does not form as a major phase by a straightforward combination of starting materials, through the addition of MAPbBr$_3$. Rather than acting as an *in situ* seed, as has been previously postulated, we demonstrate that the key role is the formation of a complex intermediate species that selects a distinct reaction pathway. Thus, it offers a handle on how to design the synthesis of new hybrid halides. In addition, this material undergoes a structural phase transition at T = 135 K, that is driven by the dynamic rotational disorder of MA units, i.e., the disordered MA groups pick one bonding interactions (N-H---Br). Initial synthetic attempts to prepare (MA)$_2$AgInBr$_6$ via direct combination or hydrothermal methods were unsuccessful due to decomposing and yielding AgBr and (MA)$_3$InBr$_7$. Yet, in one reaction, trace signs of a phase with composition (MA)$_3$AgInBr$_5$ was observed. To identify optimal synthesis conditions and gain better insight into the synthetic chemistry of (MA)$_2$AgInBr$_6$, a series of experiments were performed and they are summarized in Table S1. The key observation is that the presence of PbBr$_3$/MAPbBr$_3$ is crucial for directing the selective formation of (MA)$_2$AgInBr$_6$. That the desired phase requires lead to form, despite it being a spectator species that is not in the final product, implies that it must be affecting the species in...
solution. For the reactions that do not involve lead, we find that three equilibrium reactions (1-3, Table S2) provide a good approximation of the equilibria present during the synthesis of (MA)2AgInBr6 from a concentrated HBr solution.

For each reaction mentioned in Table S2, there are an equilibrium constant $K_{eq}$ and a reaction quotient $Q$. If the reaction condition could be altered in a way such that the reaction quotient $Q_1 \sim Q_2 \sim Q_3$, (MA)2AgInBr6 would then crystallize. As the limiting reactants are [Ag+] and [In3+], (MA+) was changed to be either in excess or deficient to test whether the equilibria (1-3) were shifted to the favor of (MA)2AgInBr6 creation. As presented in Table S1, the changes in the concentrations do not selectively yield the formation of (MA)2AgInBr6 as a major phase (Experiment (Exp) 1-6, Table S1). Instead, the presence of lead in MAPbBr3 is crucial for directing the synthetic reaction to form (MA)2AgInBr6 (Exp 7-9, Table S1). MAPbBr3 can be introduced to the synthesis either by providing PbBr2 and MABr (Exp 7-8, Table S1) or addition of ex-situ MAPbBr3 crystals (Exp 9). Further, the fact that (MA)2AgInBr6 crystals were grown hydrothermally implies thermodynamic stability under the conditions during growth. It is not sufficient to add previously-prepared (MA)2AgInBr6 to act as a seed: growth of new material fails in the absence of PbBr2/MAPbBr3 (Exp 10, Fig. S1), with a significant fraction of the input crystalline (MA)2AgInBr6 decomposing into AgBr and (MA)InBr3. Together, our results imply that PbBr2/MAPbBr3, despite not being incorporated in the final product, guides the synthesis of (MA)2AgInBr6. The most likely mechanism is that the presence of PbBr2 modulates the formation of intermediates in solution, either by reducing the effective concentration of In3+ by binding, or increasing the solubility of AgBr (which is relatively insoluble, $K_{sp} = 5.4 \times 10^{-18}$) and thus available concentration of Ag+, or some combination of the two.

To better understand the role of PbBr2/MAPbBr3 in the formation of (MA)2AgInBr6, we attempted to identify a hypothesized ‘activated complex’, which modulated intermediate during the reaction via UV-Vis spectroscopy (Fig. S2). The UV-Vis spectra show that there are several equilibria present in the system, with transitions between discrete species (rather than shifts in absorption bands that would indicate formation of highly polymeric intermediates). Thus, to a good approximation, Jobs analysis can be used to identify the chemical compositions of the ‘activated complex’ [(MA)2Ag(In+1Pb)n], which is present as a dominant species in the system. We find that addition of lead significantly changes spectra in the presence of AgBr, and thus focus on potential intermediates containing Ag. The absorption maxima of (MA)2AgBr5, MABr and MAPbBr3 solutions are observed at 245, 275 and 308 nm, respectively. With MABr in 100-fold excess, the ratio of Ag: Pb in (Ag2:2Pb) was determined to be 1:1 (x = 0.5) at the extrema (maximum or minimum) of the plots of the absorbance at a given wavelength as a function of the Pb composition (x) (Fig. 1). The amount of MA (y) in ([MA]2AgPb)) was then identified to be 6 at the maxima of the plot (Fig. 1). This analysis resulted in the chemical composition of [(MA)2AgPbBr6] of the ‘activated complex’. The Lewis base strength of ligands likely present in the synthesis reaction can be arranged in order CH3NH3 > Br⁻ > CH3NH2⁺. Under the acidic environment (concentrated HBr) of the synthesis, CH3NH3 (if present) is protonated, leaving Br- ligands most favourable to form chemical bonds to the central metal cations in the activated complex. For illustrative purposes, the symmetry arrangement of [(MA)6AgPb]Br9 consistent with the UV-Vis spectra is shown in Fig. 1C.

![Fig. 1](image)

**Fig. 1.** Jobs analysis using UV-Vis spectroscopy (A-B). Absorbance at 308 nm and 245 nm (A) as a function of Pb composition (x) in (MA)6AgPb, with excess MABr; Absorbance at 275 nm (B) as a function of MA amount (y) in (MA)2AgPb. The lines are fit to the data. (C) Proposed symmetry of the ‘activated complex’ with the chemical composition determined by Jobs analysis.

Thus, we find that, in the presence of MAPbBr3, there are two additional equilibrium reactions (4-5, Table S2) involved in the synthesis of (MA)2AgInBr6. PbBr2/MAPbBr3 shifts the equilibrium (MA)2AgBr5(1g) + Pb2+(aq) + 2MA+(aq) + 4Br-(aq) ⇌ [(MA)2AgPbBr6(1g)] (4), Table S2) to the formation of [(MA)2AgPb]Br3 ‘activated complex’. (MA)2AgPbBr3, in turn, facilitates the (MA)2AgInBr6 creation in (MA)2AgInBr6(1g) ⇌ 2MA+(aq) + [Ag]+(aq) + In3+(aq) + 6Br-(aq) (1), Table S2). And MAPbBr3 is also recovered with the formation of (MA)2AgInBr6. It is indicative of the Pb2+ cations in MAPbBr3 playing two roles in this synthesis: (i) binding with free MA cations in solution, thus inhibiting the formation of (MA)InBr by-product and (ii) interacting with the Ag+ cations through the bridging Br in [(MA)2AgPb]Br3, thereby making Ag+ available in solution. The
synthetic chemistry is illustrated in Fig. 2. Our results elucidate the vital roles of MAPbBr₃ in the synthesis, which does not simply serve as an in situ seed for crystal growth as thought previously.

![Fig. 2 Reaction scheme illustrating the synthetic chemistry of (MA)₂AgInBr₆](image)

With single crystals of (MA)₂AgInBr₆ in hand, its crystal structures were fully characterized by single-crystal X-ray and neutron diffraction, as well as Rietveld powder XRD refinements (Fig. S5, Table S3-S5). Despite the apparent formula, (MA)₂AgInBr₆ (A₂BB'X₄) does not form with a double perovskite structure. This is attributed to a too large A/B cation ratio. Instead, (MA)₂AgInBr₆ crystallizes in the high symmetry trigonal space group P6₃m1 (Fig. 3). The material exhibits a 1-dimensional chain of face-sharing alternating octahedra of [AgBr₆] and [InBr₆] and the MA cations are located in the empty space formed between the chains. This structure is similar to those of BaNiO₃ and CsNiBr₃, which are composed of 1-dimensional chains of face-sharing [NiO₃] and [NiBr₆] octahedra, respectively. It is difficult to resolve the positions of light atoms, such as C, N and H, in the presence of the heavier Ag, In and Br atoms by X-ray diffraction alone. Neutron single-crystal diffraction was also used to resolve the structural orientation of the MA cations. The MA units are disordered about the the 2d sites, which are of C₂ᵥ point group symmetry. Each of the C and N atoms is assigned a partial occupancy of 1/6 accordingly. The hydrogen atoms were refined with rigid body RIGU restraints to account for the positional disorder and a rotational motion of the MA cations around the C–N axis. Similar disorder has also been observed in MAPbBr₃. Although (MA)₂AgInBr₆ and other known hybrid halides ((MA)₂MBr₆ (M = K, Tl, Ag, In B' = Sb, Bi, X = Br, Cl)), the crystal structures of these hybrid materials are more diverse (from infinite 1-dimensional chain to 3-dimensional structures), compared to those of the other reported caesium mixed-metal halides Cs₂BB'X₆ (B = K, Tl, Ag, In B' = Sb, Bi, X = Br, Cl). This may be due to the spatial anisotropy and dynamic disorder of the CH₃NH₃⁺ units that have selective hydrogen-bonding interactions with the electronegative bromide atoms of the inorganic framework, thus driving the bonding patterns and structural features of the material at different temperatures.

To describe vibrations as well as confirm the C₃ᵥ symmetry of MA in the HT structure, IR study was performed (Fig. S4). The vibrational modes observed in the IR spectra are consistent with those expected for the MA cation in C₃ᵥ symmetry (Γ \text{vib} = 5A₁ + A₂ + 6E). The vibrational modes for (MA)₂AgInBr₆ were assigned and compared with MAPbBr₃. The NH₃-related vibrational modes are stronger (in larger wavenumbers) than the corresponding CH₃ vibrations. That is attributed to the larger electronegativity of N compared to that of C, forming stronger N–H bonds, thereby enhancing the change in dipole moments associated with the NH₃ vibrations.

To determine optical bandgap for the material, the UV-Vis spectra were collected. The results indicate that (MA)₂AgInBr₆ exhibits bandgap with absorption edge value of 3.8 eV (Fig. S5).}

![Fig. 3 Low-temperature (LT) crystal structure of (CH₃NH₃)₂AgInBr₆. (A) showing infinite 1-D chains of face-sharing AgBr₆ and InBr₆ octahedra and CH₃NH₃⁺ (MA) units; (B) showing a 2-D buckled honeycomb-lattice of the MA units. High-temperature (HT) structure of (MA)₂AgInBr₆ is similar to LT structure, except the MA cations are disordered. (C)(MA)₂AgInBr₆ crystal](image)
temperature-dependent structural analysis on single crystals is challenging as crystals tend to develop multiple domains (twins) due to mechanical strain occurred with changing temperature. In the low temperature (LT) data, the crystal was found to be a four-domain twin. By incorporating the correct twin law, the least-squares refinements were significantly improved and converged. The LT structure crystallizes in the low symmetry trigonal space group $P\overline{3}$. The nature of the structural transition is driven by the dynamic disorder of the MA units, i.e., the disordered MA cations pick one orientation over the others at low temperature, directing the structural change through the hydrogen-bonding interactions (N–H···Br) (Fig. 4). The MA units in both structures are patterned on a 2-D buckled honeycomb lattice, illustrating an example of proton ordering in two dimensions (Fig. 3). The order of protons occurring simultaneously at six sites, rather than just adjacent sites, gives rise to the directional movement of the Br atoms in the LT structure compared to those in the HT structure while the positions of Ag and In stay essentially unchanged.

The presence of hydrogen atoms in the structures was located from negative nuclear scattering density. In HT structure, due to dynamic disorder of the MA cation, six possible –NH$_3^+$ positions of MA cation generate N–H···Br bonding interactions with H···Br distances range from 2.75(5) to 2.81(7) Å. In LT structure, the hydrogen bonding distances reduce to 2.760(3) and 2.805(4) Å. Hydrogen bonding interactions are depicted in Fig. 4 (and Table S4-S5).

![Diagram of hydrogen bond interactions](image)

**Fig. 4** Hydrogen bond interactions in high temperature (HT) (two major microstates) and low temperature (LT) structure of (CH$_3$NH$_3$)$_2$AgInBr$_6$. Hydrogen bond geometry ($D$(donor)–H···A(acceptor)) for N1–H1···Br1 at LT from neutron diffraction: $D$–H 1.011(3) Å, H···A 2.760(3) Å, 2.805(3) Å; $D$–A 3.5142(9) Å, 3.6468(5) Å; D–H···A 131.7(3)°, 141.02°.

In addition to the structural analysis, the nature of the phase transition was studied by the specific heat measurements. In a plot of $C_p$ vs. T, Fig. 5, there is a peak indicative of the structural phase transition at T = 135 K and no hysteresis is observed from the heating and cooling curves (Fig. S8). In addition, there is group-subgroup relationship between the HT and LT crystal structures ($P\overline{3}m1 \leftrightarrow P\overline{3}$). Thus, this is likely a second-order phase transition. In addition, the changes in entropy were estimated from a plot of $C_p/T$ vs. T to be $\Delta S = 5.79$ J mol f.u.$^{-1}$ K$^{-1} \approx \ln 2$ after subtracting phonon contribution, which was approximated from a coefficient/T (Fig. 5). This is roughly half the value expected for one degree of freedom (two microstates) per methylammonium unit, implying significant correlations in MA$^+$ cation motion above the phase transition. This is not unexpected, as the one dimension columns of Ag/InBr$_6$ octahedra enforce a coupling between adjacent MA$^+$ ions (through the hydrogen bonding interactions).

![Graph of $C_p/T$ vs. T](image)

**Fig. 5** (A) Heat capacity ($C_p/T$) of (CH$_3$NH$_3$)$_2$AgInBr$_6$ as a function of temperature, showing a structural phase transition at 135 K; (B) the changes in entropy estimated from the integration of the peak after subtracting phonon contribution.

**Conclusions**

In short, we have found that PbBr$_2$/MAPbBr$_3$ can be used to induce the formation of new organic-inorganic hybrid materials. The key mechanism is not acting as a seed for preferential crystal growth, but rather affecting the equilibrium distribution of species in solution, allowing for selective control of the thermodynamically stable phase (Fig. 2). Further, we find that the spatial anisotropy and dynamics of the MA units gives rise to the sensitivity of crystal structures and thus properties to temperature. That paves an avenue to discover unconventional physical phenomena of hybrid materials containing organic components with dynamic motions. Our results provide insights into the mechanisms and design-driven synthesis and discovery for new organic-inorganic halide materials that are chemically related to perovskites with photovoltaic and related applications.
Conflicts of interest
There are no conflicts to declare.

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References