

Influence of Dimethyl Sulfoxide on the Structural Topology during Crystallization of PbI_2

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ABSTRACT: Hybrid metal–organic halides are an exciting class of materials that offer the opportunity to examine how fundamental aspects of chemical bonding can influence the structural topology. In this work, we describe how solvent adducts of lead halides can influence the crystallization and subsequent annealing of these hybrid phases. While the size and shape of organic molecules are known to govern the final topology of the hybrid, we show that the affinity of solvent molecules for Pb ions may also play a previously underappreciated role.

The past decade has seen halide perovskites play a major role in advancing photovoltaic technology. This is largely attributed to their large absorption coefficients,^{1,2} long-lived and highly mobile charge carriers,^{3–5} and plentiful opportunities for tailoring the properties through modifications to the structural framework. Yet, perhaps most importantly, it is the ease of processing that has made this technology so accessible and attractive for large-scale fabrication. This combination of highly efficient charge transport and ease of deposition makes these solution-processable semiconductors attractive for a variety of applications, which include photovoltaics, light-emitting diodes, and transistors.^{6–8}

Methylammonium lead(II) triiodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$; MAPbI₃) is readily dissolved in organic solvents such as dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and γ -butyrolactone, which makes it highly amenable to spin-coating nanometer-thick films. Yet, these solvents can also act as Lewis bases, which creates the possibility of competing phases during crystallization and complicates the phase diagram when precipitating from nonaqueous conditions. Indeed, previous reports of solvent adduct formation as in the case of $(\text{DMSO})_2\text{PbI}_2$ ⁹ and intermediate phases with trapped solvent molecules clearly highlight this challenge.^{10–12} Although some groups have leveraged these intermediates as a way to obtain superior film coverage,^{10,13,14} it remains unclear how these phases can transform so readily into the bulk perovskite phase while maintaining high-quality film coverage.

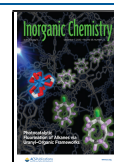
Solution-processed films of MAPbI₃ are commonly obtained by either a one- or two-step method. In the former, a solution containing both lead(II) iodide (PbI_2) and methylammonium iodide (MAI) is spin-coated onto a substrate, which after annealing produces a black film corresponding to the perovskite phase. Alternatively, in the two-step method, a solution of PbI_2 is first deposited and annealed on a substrate, after which the resulting film is soaked in a solution of MAI to form the final perovskite phase. The majority of modern procedures for high-performance photovoltaic cells fabricated from either method utilize an antisolvent washing step to induce rapid crystallization.¹⁵ The one-step procedure has the benefit of better

control over stoichiometry, and it has been reported that the solubility of PbI_2 is increased by the presence of MAI in some solvents, where the more concentrated solution results in thicker films. Conversely, the two-step method has been used to obtain films of improved quality due to the slower reaction between the two components.^{10,16,17}

The crystal structure of $(\text{DMSO})_2\text{PbI}_2$ was first reported in 1980,⁹ but more recently Seok and co-workers began to examine these phases in the context of lead halide perovskites.^{13,18} The same authors later identified an additional intermediate phase, which was assigned the formula $(\text{DMSO})\text{PbI}_2$ based on elemental analysis and thermogravimetric analysis (TGA) data.¹⁸ Nakamura and colleagues later studied intermediate phases in the transformation from PbI_2 to MAPbI₃ in solar-cell device fabrication conditions in either DMSO or DMF, providing the first description of the crystal structure for $(\text{DMSO})\text{PbI}_2$.¹² In this work, we expand on these previous reports to establish a structural relationship between lead(II) iodide and the Lewis adducts that can form with DMSO to gain insight into why these phases form and how they can influence the formation of metal–organic halides. This is complementary to the work of Nakamura and colleagues—where they examine in situ transformations from DMSO–MAI– PbI_2 intermediates to MAPbI₃—while our focus is on the structural relationships between PbI_2 and DMSO adducts prior to the introduction of MAI. Both solvent adducts were prepared using procedures adapted from the literature, and the resulting crystal structures were found to be in good agreement with those previously reported (see the [Supporting Information](#)). We present a detailed crystallographic analysis of the topotactic relationships between $(\text{DMSO})_2\text{PbI}_2$, $(\text{DMSO})\text{PbI}_2$, and PbI_2 (Figure 1) and

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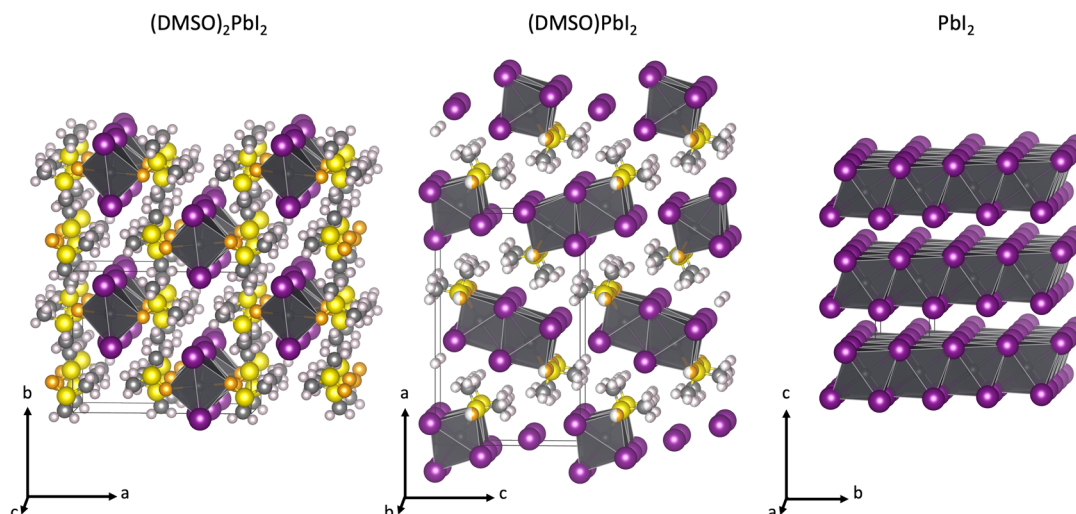


Figure 1. Crystal structures of $(\text{DMSO})_2\text{PbI}_2$, $(\text{DMSO})\text{PbI}_2$, and PbI_2 . Color code: Pb-centered octahedra, dark gray; I, purple; O, orange; S, yellow; C, light gray; H, lilac.

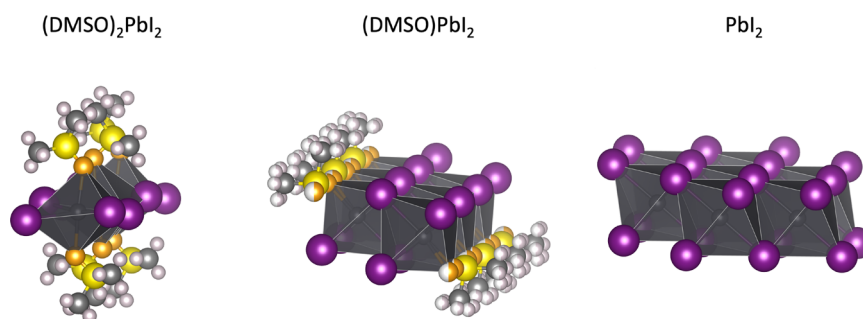


Figure 2. Coordination environment for $(\text{DMSO})_x\text{PbI}_2$ upon the removal of DMSO molecules.

use this approach to illustrate a transformation pathway that requires minimal atomic rearrangement during the removal of DMSO.

To begin, the MAXSUB program from the Bilbao Crystallographic Server (BCS)^{19,20} was first used to confirm that a direct group–subgroup relationship does not exist between PbI_2 , $(\text{DMSO})\text{PbI}_2$, or $(\text{DMSO})_2\text{PbI}_2$. The BCS program COMSUBS^{19,20} was then used to identify subgroups that were common to two space groups for a given index. For PbI_2 and $(\text{DMSO})\text{PbI}_2$ ($P\bar{3}m1$ and $Pnma$), the common subgroups with an index of 4 are $P2_1/c$, $P2_1/m$, Pc , Pm , $P2_1$, $P\bar{1}$, and $P1$. For $(\text{DMSO})\text{PbI}_2$ and $(\text{DMSO})_2\text{PbI}_2$ ($Pnma$ and $Pccn$), the common subgroups with an index of 1 are $Pna2_1$, $P2_1/c$, Pc , $P2_1$, $P\bar{1}$, and $P1$.

These results were evaluated using the BCS program TRANSPATH,²¹ which tries to identify a transition pathway between two structures that do not have a group–subgroup relationship. Despite the fact that there are several subgroups common to PbI_2 and $(\text{DMSO})\text{PbI}_2$, TRANSPATH was unsuccessful at identifying a plausible transition pathway. This is likely due to the large atom translations and high strains associated with the loss of the first solvent molecule.

The ISOTROPY Software Suite^{22,23} program, COMSUBS,²⁴ was therefore used to evaluate the potential pathways for transformation between PbI_2 and $(\text{DMSO})\text{PbI}_2$. This resulted in many possible pathways using the previously identified common subgroup $P2_1$. One such pathway that involved minimal atomic movement was deemed the most plausible. Figure S1 shows Bärnighausen trees presenting the group–

subgroup relationships between PbI_2 and $(\text{DMSO})\text{PbI}_2$ and the subgroup common to them. To better demonstrate this transformation between the two structures, animated images have been provided in the Supporting Information (SI). Note that the Bärnighausen trees presented herein show the relationship between the structures of interest (the aristotypes) and their common subgroups (the hettotypes). The hettotypes discussed here are not maximal subgroups of the aristotypes, but adding these intermediate steps to the figures would confuse rather than clarify the transformation pathways.

A similar procedure applied to the $(\text{DMSO})\text{PbI}_2$ -to- $(\text{DMSO})_2\text{PbI}_2$ transformation was unable to identify a plausible pathway. For example, COMSUBS identified pathways that corresponded to complete structural reorganizations where essentially all bonds were broken and the atoms passed within unreasonably small distances of each other. Given that both structures contain the structural motif of Pb-centered polyhedra connected into chains, it seems implausible to completely break and reassemble the bonds. Close inspection of the structures allows one to identify how they relate but requires the adoption of a nonstandard space group setting of $(\text{DMSO})_2\text{PbI}_2$, which is not allowed in the TRANSPATH and COMSUBS programs.

While the transformation from $(\text{DMSO})\text{PbI}_2$ to $(\text{DMSO})_2\text{PbI}_2$ is less straightforward, it can be understood by applying a few stepwise modifications. First, the space group setting of $(\text{DMSO})_2\text{PbI}_2$ was changed from $Pccn$ (No. 56) to $Pbnb$ (No. 56-6), allowing both structures to have their infinite chains parallel to the crystallographic b axis. Second, a shift of the origin was applied to each structure so that Pb atoms are

coincident with the lattice points. Third, both unit cells had to be doubled in size but in different crystallographic directions (see the SI for further explanation). For $(\text{DMSO})_2\text{PbI}_2$, we used a $2 \times 1 \times 1$ supercell ($a = 27.3956 \text{ \AA}$, $b = 8.7607 \text{ \AA}$, and $c = 10.8575 \text{ \AA}$), while we used a $1 \times 2 \times 1$ supercell for $(\text{DMSO})\text{PbI}_2$ ($a = 17.7962 \text{ \AA}$, $b = 9.0224 \text{ \AA}$, and $c = 11.1382 \text{ \AA}$). Finally, the space group symmetries were lowered to a common subgroup of $P1$.

With the structural motifs oriented in the same direction, half of the Pb atoms sitting at equivalent locations in the cells with similar cell metrics, it is far easier to identify the atomic motions necessary for the transformation to occur. From inspection of the cell parameters, one can observe that the major change occurs in contraction of the a axis upon the removal of 1 equiv of DMSO. The corresponding Bärnighausen trees and transformation pathway animation are presented in the SI. Further inspection of points along the transformation pathway indicate that a higher symmetry is adopted; the pathway can be described in $P2_1/c$, one of the other previously identified common subgroups.

Having established a common basis in which each phase can be directly compared, the topological relationships become more evident (Figure 2). The structure of $(\text{DMSO})_2\text{PbI}_2$ consists of $\text{Pb}(\text{DMSO})_2\text{I}_4$ octahedra that share edges to form infinite chains running along the c axis. Within the octahedra, the iodide sits within the basal plane to form a pseudo-square-planar environment with DMSO molecules in the apical positions, which holds the chains together through hydrogen-bonding interactions to neighboring iodides, as illustrated in Figure 1. Upon heating, one of the apical DMSO molecules begins to depart, creating chains of unsaturated square pyramids that begin to condense toward each other (through an approximately $1/4a + 1/4b + 1/8c$ shear), most likely due to electrostatic attraction and loss of the previously mentioned hydrogen bonds, to create the $(\text{DMSO})\text{PbI}_2$ structure. This process is repeated again as the second DMSO molecule is lost from the remaining apical position of the square pyramids and the chains completely collapse into the layered structure of PbI_2 . While this does not represent a traditional topotactic transformation, where the host framework is completely retained,^{25,26} it is clear that the local motifs are primarily retained and therefore have a significant influence on the final structure.^{27,28}

So, although the process of removing DMSO superficially appears to involve significant atomic translations, the rigid inorganic units simply condense during the removal of DMSO. The Pb-centered polyhedra do not undergo a major reorganization; a single Pb–O bond is replaced with a bond to an iodide on a neighboring polyhedron. Hence, these adducts represent a compromise between the locally coordinated solvent molecules and the creation of a long-range close packing of the anionic substructure.

Herein lies a crucial fundamental observation for understanding the topology of new hybrid metal–organic halides. Crystallization of these hybrids involves the condensation of complex ions in solution that frequently involve the coordination of noninnocent solvent molecules.²⁹ The formation of dative bonds with neutral solvent molecules competes with the creation of a dense anionic substructure that optimizes the electrostatic interactions. This competition can influence—and if properly understood may even be exploited to template—the connectivity of the inorganic moieties to the hybrid structure. This idea is supported by the prevalence of chainlike inorganic frameworks found in hybrid structures with large organic molecules.³⁰

As a final note, it is important to discuss experimental evidence for or against the transformations presented herein. One must remember that the fabrication environment for a photovoltaic device is complex, and subtle procedural differences can have a large impact on the device performance. This is further distinguished from the formation of free-standing crystals or polycrystalline samples and any subsequent treatment or analysis. This is why it is of utmost importance to report detailed synthetic procedures so that researchers can assess the difficulty of reproducibility.³¹

For example, there are reports indicating that spin-coating a solution containing DMSO and PbI_2 can result in either amorphous films (presumably containing both DMSO and PbI_2 components) or a crystalline solvent adduct.^{10,14} Even if coherent long-range order is absent, the local coordination environments are expected to remain. Presumably, the difference in these observations might be influenced by solution variables (reagent purity, solution concentration, additives, etc.), spin-coater settings, or environmental variables (relative humidity, substrate identity, or treatment), among other possibilities. While experimental evidence supports interconversion between the discussed phases, it is not clear whether such transitions happen directly, whether additional intermediate amorphous or crystalline phases are involved, or whether the transformations involve a nucleation and ripening type of mechanism. We have replicated the observations of Seok and colleagues that show via *ex situ* powder X-ray diffraction and TGA that DMSO can be removed stepwise, but direct observation of the transformation of these phases has not been observed.¹⁸

In summary, we have explored the crystallographic relationship between lead(II) iodide and two Lewis adducts that form during crystallization in the presence of DMSO. We determined that these phases are related through common structural subgroups and have highlighted physically reasonable transformation pathways that describe the atomic translations involved with the removal of incorporated solvent molecules. Understanding these kinds of fundamental structural relationships provides insight into how these intermediates can facilitate the transformation to specific hybrid phases and how the orientation of the intermediate phases may direct the orientation of the final product. While it is well understood that the size and shape of the organic molecule has a significant influence over the final topology of metal hybrids, this work highlights a more subtle role that solvation can play during crystallization.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02056>.

Additional details of the crystallographic analysis (PDF)

PbI_2 to $(\text{DMSO})\text{PbI}_2$ animation (AVI)

$(\text{DMSO})\text{PbI}_2$ to $(\text{DMSO})_2\text{PbI}_2$ animation (AVI)

Accession Codes

CCDC 2019920–2019925 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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