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Guest-Activated Forbidden Tilts in a Molecular Perovskite Analogue

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Supporting Information

ABSTRACT: The manipulation of distortions in perovskite structures is critical to tailoring the properties of these materials for a variety of applications. Here we demonstrate a violation of established octahedral tilt rules in the double perovskite analogue $(NH_4)_2SrFe(CN)_6 \cdot 2H_2O$. The forbidden tilt pattern we observe arises through coupling to hydration-driven Jahn−Teller-like distortions of the Sr coordination environment. Access to novel distortion mechanisms and the ability to switch these distortions on and off through chemical modification fundamentally expands the toolbox of techniques available for engineering symmetry-breaking processes in solid materials.

Symmetry-breaking processes have long played a central role in the design of functional materials. An important example is the ferroelectric instability of perovskite ceramics such as $BaTiO_3$ and $PbZr_xTi_{1-x}O_3$, which is responsible for their switchable polarization and dielectric and piezoelectric responses.[1−3] The ABX_3 perovskite structure is also famously susceptible to symmetry-lowering via correlated tilts of corner-sharing $[BX_6]$ octahedra.[4] One of the most exciting recent developments in the field has been the realization that clever combinations of different tilt instabilities can be exploited in the design of new classes of functional ceramics,[5] including multiferroics and negative thermal expansion materials.[6,7] The development of so-called "tilt engineering" strategies relies on a deep collective understanding of the different possible symmetry-breaking processes accessible through octahedral tilt mechanisms and their various combinations.[8]

In this context there is an important conceptual difference between the corner-sharing perovskite structure and its contemporary molecular analogues: systems in which the X anion connecting neighboring coordination octahedra is molecular rather than monatomic. Whereas an intrinsic limitation for oxide perovskites is that tilt directions (clockwise/anticlockwise) must alternate for neighboring octahedra if network connectivity is to be retained,[8−10] the use of molecular spacers allows for new tilt patterns where this strict alternation is no longer observed.[11,12] Formally this distinction is captured by the associated distortion periodicities **k**, given relative to the simple cubic ABX_3 aristotype. In corner-sharing perovskites, tilts usually couple at either $\mathbf{k} = [1/2, 1/2, 0]$ or $[1/2, 1/2, 1/2]$; these are the conventional "in-phase" and "out of phase" tilts described by Glazer notation.[13] The entire family of periodicities $\mathbf{k} = \langle 1/2, 1/2, \xi \rangle$ is actually allowed,[14] although so-called "unusual" tilt systems with $\xi \neq 0$ or 1/2 are much rarer in practice.[10] In molecular perovskites, however, tilts can actually be associated with arbitrary **k** and hence result in symmetry-lowering processes inaccessible to oxide perovskites. We use the term "forbidden" to describe these particular tilt patterns since their periodicities fall outside the set allowed for corner-sharing perovskites. Examples of such distortions are now known for both azide[15,16] and dicyanometallate[17] perovskites, with the same degrees of freedom accessible to formate perovskites[18] and Prussian Blue analogues.[19] So, in principle, there is enormous scope for tilt engineering strategies in molecular perovskites. What remains to be shown is the extent to which there exists genuine chemical control over the activation and nature of these forbidden tilts.

Here we study the structural chemistry of ammonium strontium ferrocyanide, $(NH_4)_2SrFe(CN)_6$, a molecular analogue of well-known double perovskites such as Sr_2FeMoO_6.[20] We show that simple (de)hydration of this material is sufficient to switch on and off forbidden tilt systems. The underlying mechanism involves coupling of tilts to the specific pattern of $Sr-OH_2$ bonds formed during hydration. A similar mechanism is observed in the related Ba-containing framework (first reported in ref 21) except that the increase in cation radius drives a different hydration pattern, in turn affecting the symmetry of the forbidden tilt systems activated. So not only do we show how to access unconventional tilt order for these molecular perovskites, but also we establish a methodology through which simple chemical modification might eventually be used to manipulate physical properties that depend on the nature of activated tilts.

Mixing aqueous solutions of $(NH_4)_4Fe(CN)_6$ and $SrCl_2$ in a 2:1 stoichiometric ratio yields crystals of $(NH_4)_2SrFe(CN)_6 \cdot 2H_2O$ (**1**·$2H_2O$). Upon heating to around 300 K under dry N_2, water is eliminated from the structure in a single-crystal-to-single-crystal transformation, yielding the dehydrated framework $(NH_4)_2SrFe(CN)_6$ (**1**). This transformation is entirely reversible on rehydration (see Supporting Information). The structures of **1** and **1**·$2H_2O$ were determined using single-crystal X-ray diffraction, and the reversibility of hydration assessed using powder X-ray diffraction (see Supporting Information for further details).

Compound **1** crystallizes with a double perovskite structure consisting of octahedrally coordinated Sr^{2+} and $Fe(CN)_6^{4-}$ ions

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that alternate in three dimensions [Figure 1(a)]. Each NH_4^+ cation, analogous to the perovskite A-site cation, occupies a pseudocubic cavity. The structure has $P2_1/n$ symmetry, which is actually very common for oxide double perovskites.[22,23] This particular symmetry results from a combination of rocksalt-type cation order with activation of the (conventional) $a^-a^-c^+$ Glazer octahedral tilt system.[9] The presence of octahedral tilts in **1** can be rationalized in terms of tolerance factor arguments.[24] Hydrogen-bonding interactions between NH_4^+ ions and the N-terminus of neighboring cyanide bridges induce bending of the Fe−CN−Sr linkages at the N atom, distorting the framework away from a conventional Prussian blue structure to give Fe−N−Sr angles of 140−145°.

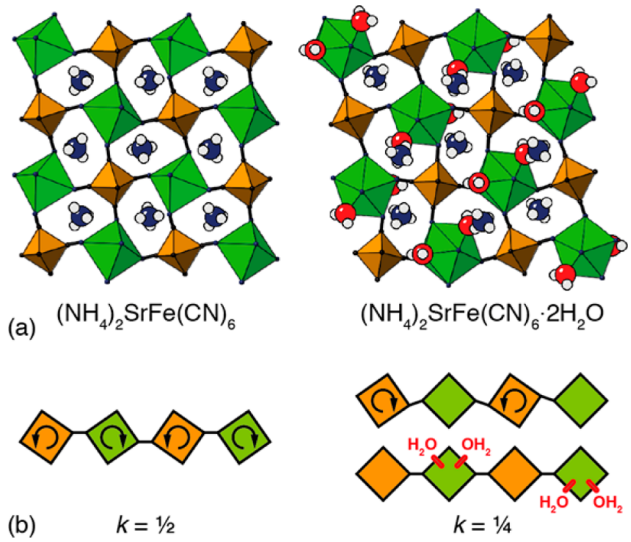

Figure 1. (a) Representations of single layers of the **1** (left) and **1**·$2H_2O$ (right) crystal structures, viewed along a unique perovskite axis of each structure. Sr polyhedra are shown in green, Fe in orange, cyanide bridges in black, NH_4^+ in blue and white, and H_2O in red and white. See Figure S1 for images showing multiple layers. (b) The structure of **1** is that of a conventional double perovskite, with octahedra of the same type tilted in phase with respect to each other (left). Forbidden tilt systems appear in **1**·$2H_2O$ due to the distortive effect of the H_2O molecules on the Sr geometry, with each Fe tilted out of phase with respect to the neighboring Fe in each repeating Sr··· Fe··· chain (right).

The hydrated phase **1**·$2H_2O$ has a structure with the same basic framework connectivity as **1** but in which the coordination number of Sr^{2+} has increased from six to eight in order to accommodate two additional H_2O molecules. The particular H_2O arrangements we observe are different from those in the orthorhombic modification[25] of $(NH_4)_2SrFe(CN)_6{\cdot}2H_2O$ (accessed via an alternative synthetic route and having a different framework connectivity related to the $KLnFe(CN)_6{\cdot}nH_2O$ phases[26]) and lead instead to a monoclinic structure with $C2/c$ symmetry. For our study it is convenient to consider the hydration pattern in **1**·$2H_2O$ in terms of a correlated distortion of B-site coordination environments of the underlying perovskite-like lattice. Analysis using the ISOTROPY software suite[27] gives that this distortion, when couched in group theoretical terms, is described by the Λ_3 irreducible representation (irrep[28]) at **k** = [1/4, 1/4, 1/4] with reference to the parent cubic structure. Importantly, activation of a distortion with this particular irrep accounts entirely for the space group symmetry of **1**·$2H_2O$; in other words, it is the primary order parameter.

This same group theoretical analysis also accounts for the coupling between hydration-induced distortions and octahedral tilts. In particular, there are two forbidden tilt systems of the correct symmetry to couple to the Λ_3 hydration pattern: one corresponds to tilts around axes parallel and antiparallel to [100] of the monoclinic cell and is also associated with the Λ_3 irrep; the other involves an inclination of the tilt axis toward [103] and reflects a dominant Λ_2 component to the experimental crystal structure. Both tilt systems couple at **k** = [1/4, 1/4, 1/4]. If the Sr ions are treated as having zero tilt, the result of the 1/4-component **k**-vector is that along the parent perovskite axes of **1**·$2H_2O$, the senses of the tilts in the repeating $(Sr{\cdots}Fe{\cdots})_n$ chains are given by 0 + 0 − 0 + 0 −. In other words, the tilt of each Fe octahedron is opposite to that of the Fe preceding it. This is in contrast to the conventional double perovskite with uniform octahedra and **k** = [1/2, 1/2, 1/2], where these Fe tilts would be in phase with respect to each other [Figure 1(b)].

The hydration-induced distortion of Sr^{2+} coordination geometries is analogous to a second-order Jahn−Teller (SOJT) effect, with the key distinction here being the chemical origin of the distortion and the ability to switch it on and off through (de)sorption.[29] The point symmetry (C_2) of the distorted Sr^{2+} environment allows a finite local polarization in the same way that stereoactive lone-pair formation drives polarization in conventional SOJT perovskites such as $BiFeO_3$.[30] In **1**·$2H_2O$ the polarization direction tends to alternate throughout the Sr sublattice, which requires quadrupling of the parent ABX_3 cell; hence **k** = [1/4, 1/4, 1/4] [Figure 2].

An interesting comparison can be drawn to the Ba-containing analogue $(NH_4)_2BaFe(CN)_6{\cdot}3H_2O$ (**2**·$3H_2O$), first described in ref 21. In this structurally related compound, the larger Ba^{2+} cation coordinates three H_2O molecules to give a total coordination number of nine and a coordination geometry with D_3 point symmetry. Consequently, there is no longer any local polarization at the Ba site, but the Ba coordination is nevertheless axially distorted in a conceptually similar fashion to the first-order Jahn−Teller (FOJT) effect observed in, e.g., $LaMnO_3$.[31] A similar group theoretical analysis of the hydration pattern in **2**·$3H_2O$ reveals it to be described entirely by the Λ_2 irrep at **k** = [1/4, 1/4, 1/4] [Figure 2]. This accounts for the corresponding space group symmetry (here, $R\bar{3}c$) and also explains the activation of the same Λ_2 forbidden tilt system that is dominant in **1**·$2H_2O$. As the Λ_3 irrep is inconsistent with a Λ_2 primary order parameter, in this case the Λ_3 tilt system is *not* activated by hydration. Hence there is scope for chemical control over the particular forbidden tilt systems activated by hydration in these double perovskite analogues.

So we have shown that hydration of molecular perovskite analogues can activate unconventional symmetry-breaking processes that are altogether unrealizable in oxide perovskites. The key implication is that the diversity of distortion mechanisms exploitable in tilt engineering strategies will be substantially greater for molecular perovskites, for which **k** ≠ ⟨1/2, 1/2, ξ⟩ systems are no longer forbidden. Moreover, the ability to switch on and off a specific set of symmetry-lowering distortions via host−guest interactions (here, hydration) offers an extraordinary opportunity to develop, e.g., guest-responsive ferroelectric or piezoelectric devices.

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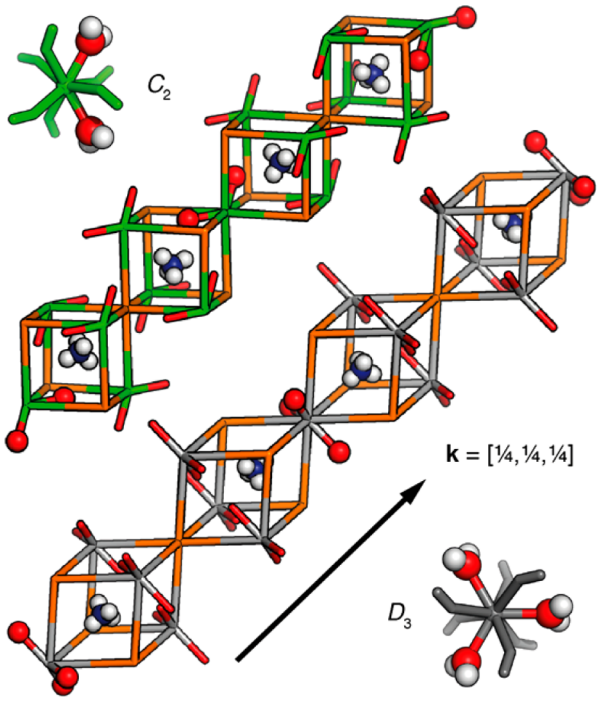

Figure 2. Simplified representations of the **1**·2H_2O (top) and **2**·3H_2O (bottom) structures in terms of the cubic parent perovskite, with Sr shown in green, Ba in gray, and Fe in orange. The ordering of the coordinated H_2O molecules (red) and NH_4^+ ions (blue/white) with 1/4 components along the [111] perovskite direction is evident. The local distortions induced by hydration at Sr and Ba sites are illustrated in the insets.

While we have focused on a small subset of perovskite-like Prussian blue analogues, there is clear opportunity for exploration of a wide range of chemically related systems. For example, the extent to which $NH_4^+\cdots H_2O$ interactions are responsible for controlling hydration patterns may be elucidated by substituting different cavity ions (e.g., $NMeH_3^+$); likewise, the nature of the B-site cations might also be varied to explore effects of charge state, polarizability, and size. Finally, there is scope for investigating the effect of incorporating a range of guests other than H_2O. In all cases, by establishing the phenomenology of unconventional symmetry-breaking mechanisms in molecular perovskite analogues we might now hope to develop increasingly sophisticated design strategies for realizations of new classes of advanced functional materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06785.

Experimental details, additional images showing tilts and polarization, powder diffraction patterns, and thermogravimetric plot (PDF)

Crystal structures of **1** and **1**·2H_2O (CIF)

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Notes

The authors declare no competing financial interest.

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