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Mechanical Tunability via Hydrogen Bonding in Metal−Organic Frameworks with the Perovskite Architecture

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Supporting Information

ABSTRACT: Two analogous metal−organic frameworks (MOFs) with the perovskite architecture, $[C(NH_2)_3][Mn(HCOO)_3]$ (**1**) and $[(CH_2)_3NH_2][Mn(HCOO)_3]$ (**2**), exhibit significantly different mechanical properties. The marked difference is attributed to their distinct modes of hydrogen bonding between the A-site amine cation and the anionic framework. The stronger cross-linking hydrogen bonding in **1** gives rise to Young's moduli and hardnesses that are up to twice those in **2**, while the thermal expansion is substantially smaller. This study presents clear evidence that the mechanical properties of MOF materials can be substantially tuned via hydrogen-bonding interactions.

Perovskite ABO_3 materials have been studied intensively in physics, chemistry, and materials science because of their interesting and technologically important properties, including ferroelectricity, superconductivity, magnetoresistance, and catalysis.[1] The recent emergence of ABX_3-type metal−organic frameworks (MOFs) opens up a new hybrid route toward artificial perovskite structures, which significantly increases the diversity of this intriguing family of materials.[2] For example, Wang et al.[2a] reported a family of MOF perovskites, $[AmineH^+][M(HCOO)_3]$ ($AmineH^+$ = $[CH_3NH_3]^+$, $[CH_3CH_2NH_3]^+$, $[(CH_3)_2NH_2]^+$, $[(CH_2)_3NH_2]^+$, $[(NH_2)_3C]^+$; M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), in which the A, B, and X sites are occupied by the amine cations, metal ions, and formate ligands, respectively. Like the classical perovskite oxides, these MOF perovskites exhibit many fascinating physical properties, such as ferroelectricity,[2e,f] ferroelasticity,[3] and multiferroicity.[4] Compared with the conventional oxides, MOF perovskites offer promising opportunities for tuning and modulation of material properties via diverse structural and chemical variability.[2a] More importantly, this new family of materials can exhibit additional functionalities and structural flexibility that cannot be achieved in perovskite oxides. We have shown that the ferroelectric and ferroelastic phase transitions in MOF perovskites are mainly triggered by the order−disorder of the A-site amine cations via hydrogen bonding rather than tilting of the B-site octahedra and/or A-site displacement as in their oxide counterparts.[2,3,4a,b] The recent report of the large lattice strain (~5%) through an orthorhombic to monoclinic transition in the ferroelastic MOF $[(CH_2)_3NH_2][Mn(HCOO)_3]$ further highlights the potential of these flexible MOF perovskites to undergo large structural changes in response to external stimuli.[3] Herein we analyze the impact of hydrogen bonding on the mechanical properties of two analogous MOF perovskites, $[C(NH_2)_3][Mn(HCOO)_3]$ (**1**) and $[(CH_2)_3NH_2][Mn(HCOO)_3]$ (**2**). The stronger cross-linking hydrogen bonding in **1** gives rise to Young's moduli and hardnesses that are up to twice those in **2**, while the thermal expansion is substantially smaller.

The frameworks in **1** and **2** are charge-balanced by guanidinium ($[(NH_2)_3C]^+$) and azetidium ($[(CH_2)_3NH_2]^+$), respectively, and crystallize in the orthorhombic system with similar cell parameters [*Pnna*, a = 8.5211(3) Å, b = 11.9779(4) Å, and c = 9.0593(3) Å for **1**; *Pnma*, a = 8.688(2) Å, b = 12.303(3) Å, and c = 8.875(2) Å for **2**].[2c,d] As shown in Figure 1, each MnO_6 octahedron within both frameworks is connected to six neighboring metal octahedra via anti−anti bridging $HCOO^-$ ligands, forming a three-dimensional ReO_3-type framework structure. The guanidinium or azetidium cations are situated in the centers of the ReO_3-type cavities, and both structures can be described as ABX_3-type perovskites in which A is the amine cation, B is the manganese ion, and the X is the formate ligand. In **1**, six bridging N−H···O hydrogen bonds from each guanidinium

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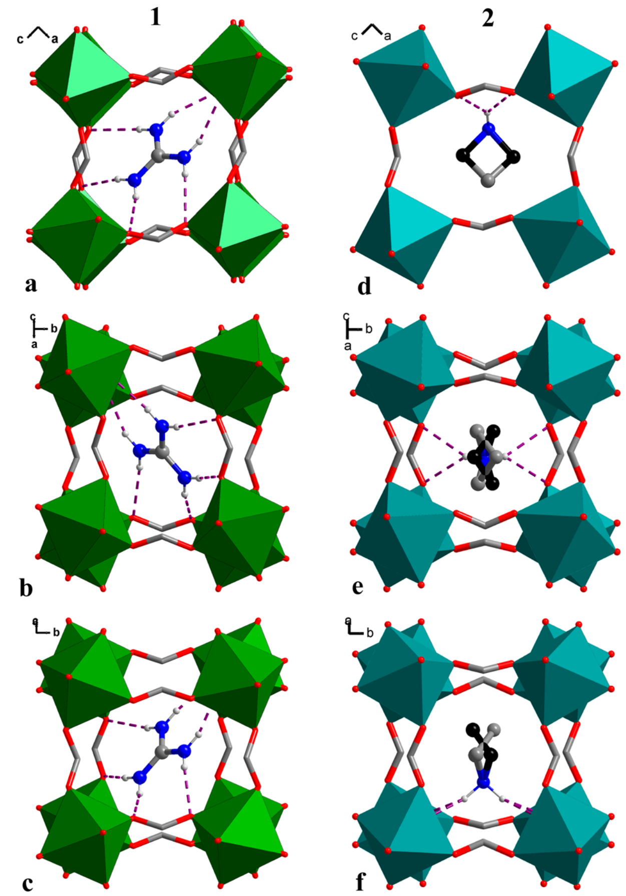

Figure 1. Framework structures of (a−c) $[C(NH_2)_3][Mn(HCOO)_3]$ (**1**) and (d−f) $[(CH_2)_3NH_2][Mn(HCOO)_3]$ (**2**) showing the pseudocubic perovskite unit cell: (a, d) (010); (b, e) (101); (c, f) $(10\bar{1})$. Color scheme: Mn^{2+}, green or teal; O, red; C, gray or black; N, blue. N−H···O bonds are represented as dashed purple lines. H atoms of formate ligands in **1** and **2** and $-CH_2-$ groups of the azetidium in **2** have been omitted for clarity. Note: the azetidium in **2** is equally disordered at two positions, as illustrated in gray and black colors.

cation, with N···O distances of 2.953(2), 2.979(2), and 2.991(2) Å, are formed with the framework [Figure S1a in the Supporting Information (SI)].[2d] For **2**, each azetidium cation is hydrogen-bonded to the anionic framework by four N−H···O hydrogen bonds with N···O distances of 2.961(3) and 3.054(3) Å (Figure S1b).[2c] According to the Glazer notation for conventional ABO_3 perovskites, the octahedral tilting systems of **1** and **2** would be $a^-b^0a^-$ and $a^-b^+a^-$.[5]

Nanoindentation measurements were performed using a three-sided pyramidal Berkovich tip (end radius ∼100 nm) in the continuous stiffness measurement (CSM) mode,[6,7] and the indenter axis was aligned normal to the (010), (101), and $(10\bar{1})$ planes of **1** and **2**. Representative load−penetration (P−h) curves obtained on all three facets of both frameworks are shown in Figure 2a. There are no discontinuity events during unloading and therefore no indications of any phase transitions. All of the P−h plots exhibit large residual depths from unloading, indicating that a significant plastic deformation occurred underneath the Berkovich tip. The loading segments of the P−h curves obtained on all three facets of **1** are smooth, while small discontinuities ("pop-ins") can be clearly observed for all facets of **2**.

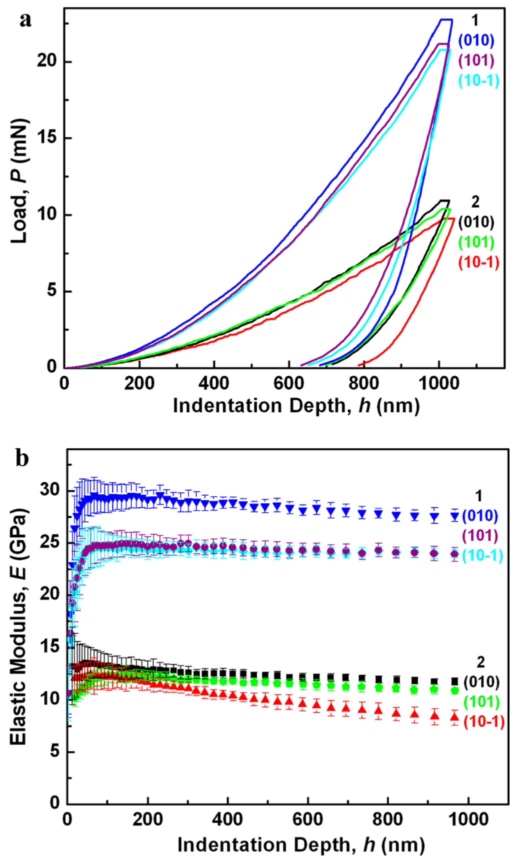

Figure 2. Nanoindentation data normal to the (010), (101), and $(10\bar{1})$ planes of single crystals of **1** and **2** measured with a Berkovich tip: (a) representative P−h curves; (b) elastic moduli as a function of indentation depth. The error bars correspond to the standard deviations of 10−20 measurements that were made on each facet.

These pop-ins, which indicate heterogeneous deformation, occur at several penetration depths ($h_{pop\text{-}in}$) with different magnitudes throughout the whole loading (Figure S2 and Table S1). It is evident that the values of $h_{pop\text{-}in}$ from all three facets of **2** are in multiples of ∼6.2 Å and thus are integral multiples of the d spacing of the pseudocubic unit cell [$d_{(101)}$ = 6.211(1) Å, $d_{(020)}$ = 6.152(2) Å, $d_{(10\bar{1})}$ = 6.211(1) Å]. Similar correlations between the pop-in magnitude and the underlying crystal length scale have been observed in studies of organic crystals.[8] The average values of the elastic moduli (E) and hardnesses (H) normal to the (010), (101), and $(10\bar{1})$ planes of **1** and **2** extracted from the P−h curves are listed in Table 1. The elastic moduli of **1** and **2** lie between those of highly porous MOFs ($E \lesssim 9$ GPa, $\rho \approx 0.9$−1.5

Table 1. Mechanical and DFT-Calculated Data for 1, 2, and $[(CH_3)_2NH_2][Mn(HCOO)_3]$ (3)[9]

MOF	H-bonding energy (eV)[a]	orientation	E (GPa)	H (GPa)
1	−4.63	(010)	28.6(4)	1.25(4)
		(101)	24.5(5)	1.18(4)
		$(10\bar{1})$	23.5(6)	1.11(5)
2	−3.01	(010)	12.6(3)	0.66(3)
		(101)	11.7(3)	0.59(3)
		$(10\bar{1})$	11.5(4)	0.58(3)
3	−3.38	(012)	∼19[b]	∼0.8[b]

[a]The hydrogen-bonding energy is referred to the calculated value of each pseudocubic unit cell. [b]Data were obtained from ref 9.

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g/cm^3) and those of densely packed frameworks ($E \approx 20-100$ GPa, $\rho \gtrsim 2$ g/cm^3).[6] Moreover, they exhibit generally isotropic stiffness, which is different from many other MOF crystals.[6] It is noteworthy that the E values of **1** are about twice those of **2** even though these MOFs have analogous framework structures. The elastic moduli of **1** and **2** are an order of magnitude lower than those of some well-known perovskite oxides,[10] for example, $BaTiO_3$[10a] ($E \approx 170$ GPa, tetragonal phase, $\rho \approx 6.02$ g/cm^3), $LaAlO_3$[10b] ($E \approx 300$ GPa, cubic phase, $\rho \approx 6.52$ g/cm^3), and $SrTiO_3$[10c] ($E \approx 280$ GPa, cubic phase, $\rho \approx 4.88$ g/cm^3). Additionally, the variation of the A-site metal in analogous perovskite oxides does not have such a significant effect on the elastic moduli as the hydrogen-bonding interactions between the A-site cation and the framework in MOF perovskites.[11] For example, the ~22% radius difference of the A-site metals in orthorhombic $GdAlO_3$ and $ScAlO_3$ results in a variation of only ~15% in the Young's modulus.[11c] The great compliance of **1** and **2**, in marked contrast to their oxide counterparts, is understandable in terms of the enhanced flexibility of the much larger and longer formate ligand in comparison to the O^{2-} anion.[3]

The mechanical properties of **1** and **2** can be rationalized by examining the underlying crystal structures. Since **1** and **2** have similar anionic framework structures as well as a trivial density difference (**1** is only ~3.3% denser than **2**),[2c,d] their contributions to the difference between the mechanical properties of **1** and **2** are expected to be minimal. Therefore, the substantial contrast between the mechanical properties of **1** and **2** can be attributed to the disparity in their hydrogen-bonding modes. As shown in Figures 1 and S1b, each azetidium in **2** is aligned within the *ac* plane and hydrogen-bonded to the two opposite edges within the same face of the pseudocubic unit cell by four N−H···O bonds. This adds only a few cross-linked constraints in one face of the pseudocubic unit cell normal to (101). However, each guanidinium in **1** is tilted by 48.7(5)° with respect to the *ac* plane and cross-links two perpendicular edges from two opposite faces of each pseudocubic unit cell. This total of six hydrogen bonds consequently gives more cross-linking constraints to the pseudocubic unit cell along all three orthogonal orientations. As a result of these greater constraints, the amine cation and anionic framework of **1** are bonded more tightly and resist larger mechanical deformation isotropically,[12] leading to a remarkably higher rigidity than for the less constrained structure of **2**.

The measured hardnesses of **1** are about twice those of **2**, revealing the strong structural dependence of framework plasticity (Table 1). Plastic deformation in nontwinned molecular crystals occurs via slip, which is facilitated by the dislocation movements under the influence of applied stress.[8b] High mobility of dislocations within the crystal generally results in more slipping. The larger amount of plastic deformation in **2** indicates that slip develops more easily, which is consistent with the periodic pop-ins observed from the loading segments of the indentation plots. The slip occurs due to the less cross-linked hydrogen bonding between the A-site azetidium and the anionic framework. Upon the accumulation of enough shear stress, slips develop intermittently in multiples of $d_{(101)}$, $d_{(020)}$, $d_{(10\bar{1})}$ (Figure S2.) High-pressure synchrotron single-crystal X-ray studies further support the above conclusion. Both **1** and **2** exhibit pressure-induced phase transitions: **1** transforms from orthorhombic to monoclinic between 1.28−1.68 GPa, while **2** shows a similar transition between only 0.41−0.66 GPa (Table S2).

The thermal expansion of **1** and **2** is also influenced by the different strengths of the hydrogen-bonding interactions in the two structures. As illustrated in Figure 3, the strongly hydrogen-bonded framework, **1**, exhibits significantly less strain compared with the weakly hydrogen-bonded counterpart, **2**. Specifically, the thermal strains of the three orthogonal axes of **2** determined over the temperature range from 293 to 413 K are 1.5−4.9 times those of **1** (Table S3). Furthermore, the equivalent isotropic atomic displacement parameters (U_{iso}) for the manganese atom in **1** are about half those in **2** over the whole temperature range (Figure S4). This suggests that their average positions are more localized, perhaps as a result of the higher framework stiffness. This is a further indication of the effects of the different hydrogen-bonding arrangements in the two frameworks.[13]

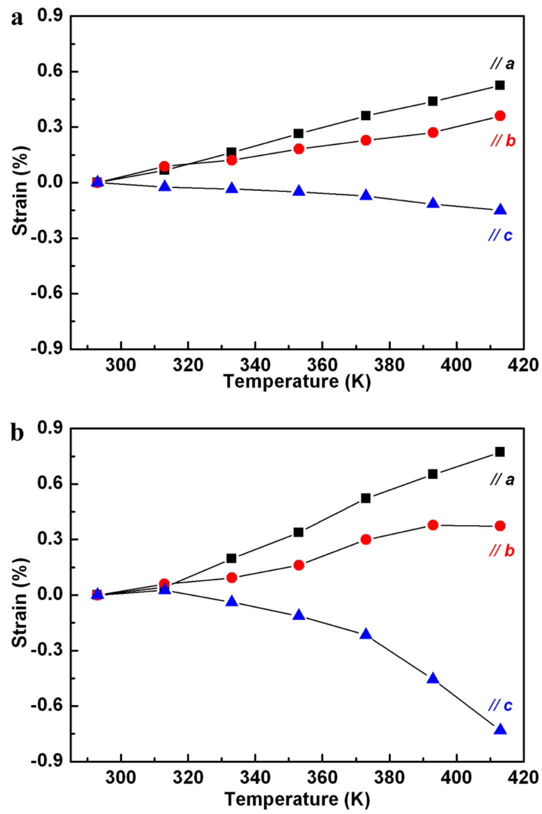

Figure 3. Thermal expansion measured for single crystals of (a) **1** and (b) **2**. The negative thermal expansion along *c* in both structures can be understood in terms of a classical strut and hinge mechanism for this structure type (see the SI for details). The linear thermal strains are referred to the three orthorhombic axes, and the lines drawn between data points are guides to the eye.

In order to quantify the hydrogen-bonding energies in **1** and **2** and correlate them with their different mechanical properties, first-principles calculations were performed by the plane-wave pseudopotential method[14] based on density functional theory (DFT). The energy of hydrogen bonding between the A-site amine cations and the $[Mn(HCOO)_3]^-$ framework was obtained from the total energy of the whole structure by subtracting the contributions of the A-site amine cations and anionic frameworks. Our calculations revealed that the energies of hydrogen bonding are ca. −4.63 and −3.01 eV, respectively, per pseudocubic unit cell of **1** and **2** (ca. −0.77 and −0.75 eV per hydrogen bond, respectively), indicating a substantial energy difference in these two systems: the energy in **1** is about ~55% greater than that in **2**. To further confirm the above results, the hydrogen-bonding energy of another analogous framework,

$[(CH_3)_2NH_2][Mn(HCOO)_3]$ (**3**) [$R\bar{3}c$, $a = 8.3211(3)$ Å and $c = 22.8856(12)$ Å], was also calculated.[9] The dimethylammonium ($[(CH_3)_2NH_2]^+$) in **3** is threefold-disordered and connected to the anionic framework by a three-dimensional arrangement of three hydrogen bonds in each pseudocubic unit cell (Figure S1c). Overall, the disordered cross-linked hydrogen bonding is expected to give intermediate energy and mechanical properties, and the hydrogen-bonding energy of ca. −3.38 eV per pseudocubic unit cell (ca. −0.84 eV per hydrogen bond) and the values $E \approx 19$ GPa and $H \approx 0.8$ GPa confirm this trend.[9]

In summary, the two MOF perovskites $[C(NH_2)_3][Mn(HCOO)_3]$ (**1**) and $[(CH_2)_3NH_2][Mn(HCOO)_3]$ (**2**) show significantly different mechanical properties as a result of their distinct modes of hydrogen bonding between the framework hosts and A-site amine cations. The stronger hydrogen bonding in **1** gives Young's moduli and hardnesses that are up to twice those in **2**, whereas the thermal expansion and atomic displacements are significantly smaller. This study presents clear evidence of the mechanical tunability of MOF materials, enabling scientists to control and direct the physical properties of MOFs via hydrogen-bonding and host−guest interactions.[15]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and supporting cif files, figures, graphs, and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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