Influence of Metal Defects on the Mechanical Properties of ABX$_3$ Perovskite-Type Metal-formate Frameworks

Hanna L. B. Boström* and Gregor Kieslich*

ABSTRACT: Defects are emerging as a key tool for fine-tuning the stimuli-responsive behavior of coordination polymers and metal–organic frameworks. Here, we study the ramifications of defects on the mechanical properties of the molecular perovskite [C(NH$_2$)$_3$]$_2$Mn$^{II}$(HCOO)$_3$ and its defective analogue [C(NH$_2$)$_3$]$_3$Fe$_{2/3}$□$^{1/3}$(HCOO)$_3$, where □ = vacancy. Defects reduce the bulk modulus by 30% and give rise to a temperature-driven phase transition not observed in the nondefective system. The results highlight the opportunities that come with defect-engineering approaches to alter the mechanical properties and underlying thermodynamics, with important implications for the research on stimuli-responsive materials.

INTRODUCTION

Molecular perovskites are dense coordination networks with an ABX$_3$ perovskite-type structure, where A and/or X is a molecular ion. These compounds include a wealth of compositions such as formates,$^{1,2}$ azides,$^{3,4}$ thiocyanates,$^{5,6}$ dicyanamides,$^{7,8}$ dicynanometalates,$^9,10$ and, conceptually related, Prussian blue analogues, covering phenomena of fundamental and technological relevance.$^{11,12}$ Compared to their inorganic counterparts, molecular perovskites show additional degrees of chemical and structural freedom as enabled by the presence of polyatomic species.$^{13,14}$ For instance, the use of polyatomic A-site cations promotes the occurrence of temperature- and pressure-driven phase changes as a result of order–disorder transitions of the molecular A-site cation, opening a variety of functionality to be exploited.$^{5,16}$

Looking at ways to fine-tune material properties, the incorporation of defects have proved to be a tremendously successful approach in porous coordination polymers.$^3$ For example, the archetypical defective metal–organic framework UiO-66 supports both missing linkers and missing clusters,$^{18,19}$ which has implications for e.g. the adsorption properties.$^{20,21}$ However, good mechanical properties are a prerequisite for a material to be practically useful and hence there is a strong need to elucidate the interplay between defects and the nonambient behavior.$^{22}$ Several studies have been focused on this issue, using both experimental and computational techniques,$^{19,22,23,24}$ but further investigation is still required. Concerning molecular perovskites, the incorporation of a large concentration of Schottky-type metal defects has been achieved recently,$^{25}$ and its impact on the stimuli-responsive properties is still unknown.

Here, we study the bulk modulus ($B_0$) and volumetric coefficient of thermal expansion ($\alpha_V$) of the metal-formate framework [C(NH$_2$)$_3$]$_2$Mn$^{II}$(HCOO)$_3$ and its defective analogue [C(NH$_2$)$_3$]$_3$Fe$_{2/3}$□$^{1/3}$(HCOO)$_3$, □ = vacancy and C(NH$_2$)$_3$ = guanidinium) using powder X-ray diffraction (PXRD) under variable temperature and pressure. For simplicity, these will be referred to as GuaMn and GuaFe$_{2/3}$□$^{1/3}$. We note that these quantities also serve as probes of the Gibbs free energy surface through the relationships

\[
B_0 = -\frac{\alpha_V^2}{\beta T} \quad \text{and} \quad \alpha_V = \frac{1}{V} \left( \frac{\beta V}{\beta T} \right)
\]

such that our results provide qualitative insight into the free energy surface of these materials.

METHODS

All chemicals were used as purchased without further purification. The samples were synthesized by previously reported methods.$^{26,27}$ A solution of [C(NH$_2$)$_3$]$_2$CO$_3$ (281.5 mg, 1.56 mmol) and HCOOH (182.5 µL, 4.84 mmol) in methanol (5 mL) was added to a methanolic solution of 0.1 M Mn(NO$_3$)$_2$ or 0.1 M FeCl$_3$ (5 mL). The reaction mixture was stirred overnight at room temperature prior to isolation by filtration in vacuo and washing with methanol.

Variable-temperature PXRD data of GuaFe$_{2/3}$□$^{1/3}$ were collected using a STOE stadi P with Mo K$_\alpha$ radiation and an Oxford diffraction Cryosystem. Variable-pressure PXRD data of both GuaMn and GuaFe$_{2/3}$□$^{1/3}$ were collected using a home-built setup at beamline I15 with $\lambda = 0.4246$ Å, Diamond Light Source, UK.$^{28,29}$

Received: October 30, 2020
Revised: November 25, 2020
Published: January 4, 2021
RESULTS AND DISCUSSION

GuaMn and GuaFe2/3\(\square\)1/3 are topologically identical, but differ in the metal occupancy and symmetry. GuaMn crystallizes in the space group \(Pnma\), driven by R-point octahedral tilting (\(a^b\)–\(b^b\)–\(b^b\) in Glazer notation\(^{35,36}\)) and the orientational X-point order of the guanidinium cations [Figure 1a].\(^{25}\) Allovalent substitution of Mn\(^{II}\) in GuaMn with Fe\(^{III}\) introduces metal vacancies as a charge compensation mechanism, leading to the composition GuaFe2/3\(\square\)1/3 [Figure 1b].\(^{27}\) Despite the large vacancy concentration, structural integrity in GuaFe2/3\(\square\)1/3 is retained with only a small lattice strain, on account of the strong hydrogen bonds between the guanidinium and the formate moieties.\(^{37}\) Given the energy penalty associated with next neighbor vacancy pairs, the vacancies partially order, which reduces the symmetry to the monoclinic space group \(\bar{P}1\) [GuaFe\(\square\)1/3].\(^{26}\) The nonstandard setting of the monoclinic space group allows for direct comparison of lattice parameters between orthorhombic GuaMn and monoclinic GuaFe\(\square\)1/3. Notably, coordination networks are known to harbor a wealth of defects, yet missing ion defects are still relatively rare.\(^{17,20,38,39}\) Variable-pressure diffraction was measured up to 0.4 GPa at 115 K, using equipment dedicated to accurate control of low pressures.\(^{32}\) The bulk moduli were calculated using EoSFit and compressibilities by linear fits [Table 1, Figures S1–S4].\(^{32}\)

The bulk modulus of GuaMn is 20.0(3) GPa, which is in good agreement with the value obtained over a larger pressure range: \(B_0 = 21.3\) GPa.\(^{41}\) Compared to other formate-based perovskites, this value is slightly lower than for dimethylammonium metal formates \(B_0 = 21.3\) GPa for \(M = \text{Mn}^{II}\) and 26.3 GPa for \(M = \text{Co}^{III}\)\(^{16,42,43}\) but similar to that of \([\text{NH}_2\text{NH}_3]\text{Zn(HCOO)}_3\) with \(B_0 = 19\) GPa.\(^{44}\) The defective GuaFe\(\square\)2/3\(\square\)1/3 features a lower bulk modulus of 14.3(2) GPa, which is comparable to the behavior of the heterometallic \([\text{C}_2\text{H}_5\text{NH}_3]K_{0.5}\text{Al}_{1.5}(\text{HCOO})_3\).\(^{35}\)

The difference in bulk moduli of GuaMn and defective GuaFe\(\square\)2/3\(\square\)1/3 highlights how defects increase the mechanical compliance of the framework. Importantly, the impact of defects even overcompensates influence of ion size, which is known to make molecular perovskites more robust.\(^{40}\)

Both systems show an anisotropic pressure response with \(K_a > K_b > K_c\), where \(K_i\) is the compressibility of axis \(i\) [Table 1, Figure 1d]. To compare the compressibilities of the two systems, the mechanical building unit approach was employed.\(^{46}\) The lattice parameters for both systems can be recast as

\[
\bar{r} = \frac{1}{3} \left[ \frac{b}{2} + \sqrt{a^2 + c^2} \right]
\]

and

\[
\theta = 2 \tan^{-1} \left( \frac{c}{a} \right)
\]

where \(\bar{r}\) is the average strut length, that is, the metal–metal distance, and \(\theta\) is the hinging angle, that is, metal–metal–metal angle within the \(ac\) plane [Figure 1c].\(^{46}\) Here, \(\theta > 90^\circ\). This approach represents a physically meaningful parametrization of
the structural changes upon compression, highlighting the behavior of the pseudocubic 3D network. As expected, the strut length $r$ decreases with pressure, which is accompanied by an increase in the hinging of the framework [Figure 1e,f].

The behaviors of $r$ and $θ$ upon compression rationalize the anisotropic compression. As given in eqs 1 and 2, the cell dimensions are linear functions of $r$, but with varying dependence on $θ$. While $c$ is positively correlated with $θ$, $a$ is negatively correlated and $b$ is independent. Thus, $a$ is the most compliant direction, as both the decrease of $r$ and the increase of $θ$ upon compression reduce its length. The reverse scenario appears for $c$: the variations of $r$ and $θ$ operate in tension, which gives a low value of $K_c$. Chemically, the low expansion can be explained by recognizing that the $c$ axis runs along the planes of the incompressible guanidinium cations. In GuaMn, the opposing effects of $r$ and $θ$ on $K_c$ are equal in magnitude and cancel, leading to zero uniaxial compressibility. Further increase of the hinging mechanism may lead to negative linear compressibility. The defects in GuaFe$_{2/3}$ soften $r$, as a result of the larger void space, whereas the pressure-induced increase of $θ$ is unchanged. This does not substantially impact the compressibilities of $a$ and $c$, but $K_c$ increases to a nonzero value.

Furthermore, the thermal behavior of GuaFe$_{2/3}$ was investigated in the range 100–300 K by variable-temperature PXRD. The system remains monoclinic down to 220 K, where additional reflections emerge in the diffraction patterns [Figures S5 and S6]. Because of the low symmetry and lack of high-resolution synchrotron data, the low-temperature phase was not observed and Pawley refinements were only carried out for the ambient phase. The phase transition in defective GuaFe$_{2/3}$ contrasts with the variable-temperature behavior of GuaMn reported by Collings et al., where the system remained in its ambient phase down to 100 K. Hence, the metal defects alter the phase behavior, which may possibly be driven by the underlying free energy surface, which is relatively small.

Defects clearly modify the mechanical properties of GuaFe$_{2/3}$ relative to GuaMn; removing 1/3 of the transition metals reduces the bulk modulus by ~30%. With the emerging understanding of defect chemistry in MOFs and coordination polymers, there is also growing interest in the role of defects on mechanical properties. It can be misleading to compare results between different systems, as the results are likely dependent on the precise topologies and type of defects. Additionally, solvent content strongly impacts the mechanical response, which may complicate comparisons. However, we note that defects reduce the bulk modulus of UiO-66 up to a critical concentration and certain Prussian blue analogues, in line with the results presented here. This likely results from the increased void space, which correlates with greater ease of compression. Comparisons of similar studies may enable the development of general guidelines regarding the influence of defects on the mechanical properties in dense and porous coordination polymers.

### CONCLUSIONS

To conclude, we report the stimuli-responsive behavior of defect-free [C(NH$_2$)$_3$]$^2^+$(HCOO)$_3^−$ and defective [C(NH$_2$)$_3$]$^2^+$(HCOO)$_{10}^−$ and establish how missing-ion vacancies control the structural response to pressure and temperature variation in molecular perovskites for the first time. Upon compression, defects selectively soften the average strut length $r$, without having an effect on the hinging angle $θ$. The defective GuaFe$_{2/3}$ undergoes a thermal phase transition not observed in GuaMn, yet both systems exhibit similar thermal expansion behavior. Placing our results in the context of efforts to manipulate the free energy landscape in coordination polymers, we stress that using defects as a tool to access (stimuli-responsive) properties is an increasingly appealing strategy. For instance, barocaloric behavior has recently been observed in certain molecular perovskites and defects offer intriguing opportunities for controlling the underlying thermodynamics to optimize the barocaloric performance. In particular, defects flatten the underlying free energy surface, which is expected to impact phase transition temperatures. This suggests that defects can be used to enhance the barocaloric properties, for example, by optimizing the temperature of the barocaloric phase transition. More broadly, it will be exciting to see how defects will be exploited to learn about the fundamental interactions in coordination networks. The bulk modulus appears to be an important probe for the impact of defects on the underlying chemical interactions as reflected in the free energy landscape.

### ASSOCIATED CONTENT

* Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c09796. Experimental details, XRD patterns, evolution of lattice parameters as a function of temperature and pressure, and $f$–$F$ plots (PDF).
Complete contact information is available at:

The authors declare no competing financial interest.

REFERENCES

(1) Sletten, E.; Jensen, L. H. The Crystal Structure of Dimethylammonium Copper(II) Formate, NH$_2$(CH$_3$)$_3$Cu(OOCH)$_2$. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1973, 29, 1752–1756.

(2) Wang, X.-Y.; Gan, L.; Zhang, S.-W.; Gao, S. Perovskite-like Metal Formates with Weak Ferromagnetism and as Precursors to Amorphous Materials. Inorg. Chem. 2004, 43, 4615–4625.

(3) Mautner, F. A.; Krischner, H.; Kratky, C. Tetramethylammonium-Calcium-Triazid. Darstellung und Kristallstruktur. Monatsh. Chem. 1988, 119, 1245–1249.

(4) Zhao, X.-H.; Huang, X.-C.; Zhang, S.-L.; Shao, D.; Wei, H.-Y.; Wang, X.-Y. Cation-Dependent Magnetic Ordering and Room-Temperature Bistability in Azido-Bridged Perovskite-Type Compounds. J. Am. Chem. Soc. 2013, 135, 16006–16009.

(5) Thiele, G.; Messer, D. Thiocyanato- and N-Isothiocyanato-Bindungssitomer in den Kristallstrukturen von RbCd(SCN)$_3$ und CaCd(SCN)$_3$. Z. Anorg. Allg. Chem. 1980, 464, 255–267.

(6) Cliffe, M. J.; Keyzer, E. N.; Dunstan, M. T.; Ahmad, S.; De Volder, K. P. Defect-Tolerant Colossal Colossal Negative Thermal Expansion in UiO-66(Al) Metal–Organic Framework. Phys. Chem. Chem. Phys. 2015, 17, 11586–11592.

(7) Dissegna, S.; Epp, K.; Heinz, W. R.; Kieslich, G.; Fischer, R. A. Defective Metal–Organic Frameworks. Adv. Mater. 2018, 30, 1704501.

(8) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guilou, N.; Lambert, C.; Bordiga, S.; Lillerud, K. P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. J. Am. Chem. Soc. 2008, 130, 13850–13851.

(9) Cliffe, M. J.; Hill, J. A.; Murray, C. A.; Coudert, F.-X.; Goodwin, A. L. Defect-dependent colossal negative thermal expansion in UiO-66(Al) metal–organic framework. Phys. Chem. Chem. Phys. 2015, 17, 5125–5128.

(10) Shearer, G. C.; Chavan, S.; Bordiga, S.; Svele, S.; Olsbye, U.; Lillerud, K. P. Defect Engineering: Tuning the Porosity and Composition of the Metal-Organic Framework UiO-66 via Modulated Synthesis. Chem. Mater. 2016, 28, 3749–3761.

(11) Tan, J.; Cheetham, A. K. Mechanical Properties of hybrid inorganic-organic framework materials: Establishing fundamental structure-property relationships. Chem. Soc. Rev. 2011, 40, 1059–1080.

(12) Rogge, S. M. J.; Wieme, J.; Vandyuyhys, L.; Vandendbrande, S.; Maurin, G.; Verstraelen, T.; Waroquier, M.; Van Speybroeck, V. Thermodynamic Insight in the High-Pressure Behavior of UiO-66: Effect of Linker Defects and Linker Expansion. Chem. Mater. 2016, 28, 5721–5732.

(13) Dissegna, S.; Vervoorts, P.; Hobday, C. L.; Düren, T.; Daisenberger, D.; Smith, A. J.; Fischer, R. A.; Kieslich, G. Tuning the Mechanical Response of Metal-O rganic Frameworks by Defect Engineering. J. Am. Chem. Soc. 2018, 140, 11581–11584.

(14) Boström, H. L. B. Tilts and shifts in molecular perovskites. CrystEngComm 2020, 22, 961–968.

(15) Hu, K.-L.; Kurmoo, M.; Wang, Z.; Gao, S. Metal-Orga nic Perovskites: Synthesis, Structures, and Magnetic Properties of [C-C$_2$H$_3$Cu(OOCH)$_2$].Chem. Eur. J. 2009, 15, 12050–12064.

(16) Boström, H. L. B.; Bredesen, J.; Goodwin, A. L. Ordered B-Site Vacancies in an ABX$_3$ Formate Perovskite. Chem. Mater. 2019, 141, 17978–17982.

(17) Brooks, N. J.; Gauthe, B. L. E.; Terrill, N. J.; Rogers, S. E.; Templer, R. H.; Ces, O.; Seddon, J. M. Automated high pressure cell for pressure jump X-ray diffraction. Rev. Sci. Instrum. 2010, 81, 064103.

(18) Vervoorts, P.; Keupp, J.; Schneemann, A.; Hobday, C. L.; Daisenberger, D.; Fischer, R. A.; Schmid, R.; Kieslich, G. Configurational Entropy Driven High-Pressure Behaviour of a Flexible Metal–Organic Framework. Angew. Chem., Int. Ed. 2020, DOI: 10.1002/anie.202011004.

(19) Pawley, G. S. Unit-cell refinement from powder diffraction scans. J. Appl. Cryst. 1989, 14, 357–361.

(20) Coelho, A. A. TOPAS and TOPAS-Academic; an optimization program integrating computer algebra and crystallographic objects written in C++. J. Appl. Cryst. 2018, 51, 210–218.

(21) Angel, R. J.; Alvaro, M.; Gonzalez-Platas, J. EosFit7c and a Fortran module (library) for equation of state calculations. J. Appl. Crystallogr. 2018, 51, 845–849.
(33) Birch, F. Finite elastic strain of cubic crystals. Phys. Rev. 1947, 71, 809–824.
(34) Murnaghan, F. D. The compressibility of media under extreme pressures. Proc. Natl. Acad. Sci. U.S.A. 1944, 30, 244–247.
(35) Glazer, A. M. The Classification of Tilted Octahedra in Perovskites. Acta Crystallogr., Sect. B: Struct. Crystall. Cryst. Chem. 1972, 28, 3384–3392.
(36) Howard, C. J.; Stokes, H. T. Group-Theoretical Analysis of Octahedral Tilting in Perovskites. Acta Crystallogr., Sect. B: Struct. Sci. 1998, 54, 782–789.
(37) Svane, K. L.; Forse, A. C.; Grey, C. P.; Kieslich, G.; Cheetham, A. K.; Walsh, A.; Butler, K. T. How Strong is the Hydrogen Bond in Hybrid Perovskites? J. Phys. Chem. Lett. 2017, 8, 6154–6159.
(38) Sholl, D. S.; Lively, R. P. Defects in Metal–Organic Frameworks: Challenge or Opportunity? J. Phys. Chem. Lett. 2015, 6, 3437–3444.
(39) Bennett, T. D.; Cheetham, A. K.; Fuchs, A. H.; Coudert, F.-X. Interplay between defects, disorder and flexibility in metal-organic frameworks. Nat. Chem. 2017, 9, 11–16.
(40) Collings, I. E.; Hill, J. A.; Cairns, A. B.; Cooper, R. I.; Thompson, A. L.; Parker, J. E.; Tang, C. C.; Goodwin, A. L. Compositional Dependence of Anomalous Thermal Expansion in Perovskite-Like ABX₃ Formates. Dalton Trans. 2016, 45, 4169–4178.
(41) Yang, Z.; Cai, G.; Bull, C. L.; Tinkham, M. A.; Dove, M. T.; Friedrich, A.; Phillips, A. E. Hydrogen-bond-mediated structural variation of metal guanidinium formate hybrid perovskites under pressure. Philos. Trans. R. Soc. A 2019, 377, 20180227.
(42) Sobczak, S.; Chittnis, A.; Andrzejewski, M.; Mącżka, M.; Gohl, S.; Garg, N.; Katusiak, A. Framework and Coordination Strain in Two Isostructural Hybrid Metal-Organic Perovskites. CrystEngComm 2018, 20, 5348–5355.
(43) Collings, I. E.; Saines, P. J.; Mikolasek, M.; Bořka Ballaran, T.; Hanfland, M. Static disorder in a perovskite mixed-valence metal–organic framework. CrystEngComm 2020, 22, 2859–2865.
(44) Kieslich, G.; Forse, A. C.; Sun, S.; Butler, K. T.; Kumagai, S.; Wu, Y.; Warren, M. R.; Walsh, A.; Grey, C. P.; Cheetham, A. K. Role of Amine–Cavity Interactions in Determining the Structure and Mechanical Properties of the Ferroelectric Hybrid Perovskite [NH₃NH₃] Zn(HCOO)₃. Chem. Mater. 2016, 28, 312–317.
(45) Ptak, M.; Svane, K. L.; Collings, I. E.; Paraguassu, W. Effect of Alkali and Trivalent Metal Ions on the High-Pressure Phase Transition of [C₆H₄NH₃] MIO.₃(HCOO)₃ (M⁺ = Na, K and MIII = Cr, Al) Heterometallic Perovskites. J. Phys. Chem. C 2020, 124, 6337–6348.
(46) Ogborn, J. M.; Collings, I. E.; Moggach, S. A.; Thompson, A. L.; Goodwin, A. L. Supramolecular mechanics in a metal–organic framework. Chem. Sci. 2012, 3, 3011–3017.
(47) Cliffe, M. J.; Goodwin, A. L. PASCal: A principal axis strain calculator for thermal expansion and compressibility determination. J. Appl. Crystallogr. 2012, 45, 1321–1329.
(48) Li, W.; Thirumurugan, A.; Barton, P. T.; Lin, Z.; Henke, S.; Yeung, H. H.-M.; Wharmby, M. T.; Bithell, E. G.; Howard, C. J.; Cheetham, A. K. Mechanical tunability via hydrogen bonding in metal-organic frameworks with the perovskite architecture. J. Am. Chem. Soc. 2014, 136, 7801–7804.
(49) Lock, N.; Wu, Y.; Christensen, M.; Cameron, L. J.; Peterson, V. K.; Bridgeman, A. J.; Kepert, C. J.; Iversen, B. B. Elucidating negative thermal expansion in MOF-5. J. Phys. Chem. C 2010, 114, 16181–16186.
(50) Wu, Y.; Kobayashi, A.; Balder, G. J.; Peterson, V. K.; Chapman, K. W.; Lock, N.; Southon, P. D.; Kepert, C. J. Negative thermal expansion in the metal-organic framework material Cu₃(1,3,5-benzenercarboxylate)₂. Angew. Chem., Int. Ed. 2008, 47, 8929–8932.
(51) Bennett, T. D.; Cheetham, A. K.; Fuchs, A. H.; Coudert, F.-X. Interplay between defects, disorder and flexibility in metal-organic frameworks with the perovskite architecture. J. Am. Chem. Soc. 2014, 136, 7801–7804.
(52) Boström, H. L. B.; Collings, I. E.; Cairns, A. B.; Romao, C. P.; Goodwin, A. L. High-pressure behavior of Prussian blue analogues: interplay of hydration, Jahn-Teller distortions and vacancies. Dalton Trans. 2019, 48, 1647–1655.