ELECTRONIC SUPPLEMENTARY INFORMATION

Role of entropic effects in controlling the polymorphism in formate ABX₃ metal-organic frameworks

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ESI-Table1. The enthalpies of formation with respect to constituent atoms at 0 K obtained by DFT calculations for $[NH_3NH_2]Mg(HCOO)_3$ in the perovskite structure (**Mg-1**) and the chiral structure with hexagonal channels (**Mg-2**). The calculated densities for both polymorphs are also given. The Tolerance Factor approach, which only accounts for the relative packing density, correctly predicts the trend in enthalpies; however, entropic effects stabilize the channel structure **Mg-2**, which was experimentally observed as being the stable modification.

Compound	Structure	Name	ρ (g/cm³)	<i>E</i> _{min} (f.u.*) (eV)
[NH ₃ NH ₂]Mg(HCOO) ₃	perovskite	Mg-1	1.60	-124.84
[NH ₃ NH ₂]Mg(HCOO) ₃	channel	Mg- 2	1.53	-124.79
				Δ <i>E</i> = 0.05

*f.u. = formula unit



ESI-Figure 1. Temperature dependence of the Gibbs free energy *G* (a) and entropy *S* (b) of the compounds **Mg-1** (blue) and **Mg-2** (red). With increasing temperature, the entropic contribution becomes more dominant which causes the crossover of *G* at T_c = 300 K. The higher vibrational entropy of the channel structure is caused by a lower density and weaker hydrogen bonding pattern. In comparison to the zinc compound, the weaker hydrogen bonds and in turn the higher vibrational entropy seem to shift the crossover-point of *G* to lower temperatures.

ESI-Table 2. Details of structure solution and crystal data of $[NH_3NH_2]Zn(HCOO)_3$ (polymorph **Zn-2**) at 120 K. Hydrogen atoms were located in the difference Fourier map and refined in a riding model with U_{iso} fixed to the riding atom. For the NH₂-group, N-H bond lengths and H-H distances were manually fixed to standard values, 0.890 Å and 1.453 Å respectively. The *.cif file of the structure is available from the CSD (1414792).

Formula weight (g/mol) 233.48 Temperature (K) 120.00(10) Crystal system orthorhombia Space group $P2_{1}2_{1}2_{1}2_{1}2_{1}2_{1}2_{1}2_{1}$
Temperature (K) 120.00(10) Crystal system orthorhombia Space group $P_{2_12_12_1}$ a (Å) 7.29731(6) b (Å) 7.94804(7) c (Å) 13.82240(12) a (°) 90 β (°) 90 γ (°) 90<
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Space group $P_{2_12_12}$ a (Å) 7.29731(6) b (Å) 7.94804(7) c (Å) 13.82240(12) a (°) 90 β (°) 90 γ (°) 90 Volume (Å3) 801.690(12) Z/Z' 4/1 ρ_{calc} (g cm ⁻³) 1.934 μ (mm ⁻¹) 3.060 F(000) 472 Crystal size (mm ³) 0.6582 × 0.2766 × 0.209 Radiation MoK _a (λ = 0.71073 20 range for data collection (°) 5.004 to 72.029
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-12 ≤ h ≤ 12
Index ranges $-13 \le k \le 13$
Reflections collected 47300
Independent reflections $3869 [R_{int} = 0.0375, R_{sigma} = 0.0151]$
Data/restraints/parameters 3869/5/117
Goodness-of-fit on F ²
Final R indexes $[I \ge 2\sigma (I)]$ R ₁ = 0.0144, wR ₂ = 0.0374
Final R indexes [all data] $R_1 = 0.0150, wR_2 = 0.0377$
Largest diff. peak/hole / (Å ⁻³) 0.31/-0.33
Flack parameter -0.001(3)
Extinction coefficient 0.0205(12



ESI-Figure 2. Image of the crystal used for structure solution at 120 K.

ESI-Table 3. Fractional atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters $(Å^2 x 10^3)$ of the polymorph Zn-2 at 120 K.

Atom	х	У	z	U_{eq}
Zn1	7592.4(2)	7194.3(2)	6645.3(2)	6.36(3)
02	5865.0(12)	9254.0(11)	6629.1(7)	12.69(14)
03	9037.5(12)	8061.8(11)	7885.4(6)	10.59(14)
04	6087.0(13)	6050.2(12)	7720.3(7)	13.88(16)
05	6192.3(12)	6108.1(11)	5468.6(6)	11.36(15)
06	9192.0(12)	8698.2(11)	5734.1(6)	12.60(15)
07	9228.7(12)	5042.4(11)	6437.3(6)	12.65(15)
C3	5086.6(15)	6926.0(13)	4947.4(8)	10.98(18)
C4	5009.7(17)	9845.8(15)	7335.2(8)	10.45(18)
C5	9916.9(16)	9429.1(15)	7864.5(8)	10.64(18)
N2	6845.2(14)	2129.9(14)	5383.0(8)	14.51(17)
N1	7657.2(14)	3174.5(12)	4638.1(7)	11.94(15)
H3	4925	8089	5082	13
H4	5205	9350	7952	13
H5	9929	10037	7273	13
H1A	7231	2849	4049	14
H1B	8898	3061	4654	14
H1C	7353	4269	4744	14
H2A	7222	2522	5952.4	18
H2B	7263	1088	5301	18



ESI-Figure 3. Single crystals of Zn-2 (a) and (b) and Zn-1 (c) and (d).



ESI-Figure 4. Crystals of $[NH_3NH_2]Zn(HCOO)_3$ after transformation from **Zn-2** to **Zn-1**. Whereas the shape of the **Zn-2** crystals is maintained (see ESI-Figur3 (a) and (b)), the single crystals transformed to the thermodynamically more stable **Zn-1**; for PXRD pattern see ESI-Figure 6 c.



ESI-Figure 5. TGA/DTA (**a**) and DSC (**b**) data of **Zn-2**. Small features in (**b**) around 350 K belong to minor **Zn-1** impurities. The decomposition temperature obtained from TGA/DTA is 380 K, similar to **Zn-1**. The most dominant feature in (**b**) around 363K corresponds to a phase transition, similar to $[NH_3NH_2]Co(HCOO)_3$ and $[NH_3NH_2]Mg(HCOO)_3$. Details and results of the analysis of TGA and DSC data is given in ESI-Table 4.

ESI-Table 4. Details of the DSC data analysis of **Zn-2**. The phase transition observed at ~367 K underlines the strong relationship of $[NH_3NH_2]Zn(HCOO)_3$ to $[NH_3NH_2]Co(HCOO)_3$ and $[NH_3NH_2]Mg(HCOO)_3$.

		Cycle 2
T _C (heating) / K	367.3	367.1
T _C (cooling) / K	363.6 <i>,</i> 359.5	363.7, 358.2
∆H (heating) / kJ·mol ⁻¹	2.13	2.28
∆H (cooling) / kJ·mol ⁻¹	2.20	2.30
∆S (heating) / J·mol ⁻¹ ·K ⁻¹	5.80	6.21
ΔS (cooling) / J·mol ⁻¹ ·K ⁻¹	_	_



ESI-Figure 6. Powder X-ray diffraction pattern of the different polymorphs investigated in this study: (a) **Zn-2** and (b) **Zn-1**. The tics shown correspond to the expected peak positions from the simulated pattern of **Zn-1** (black) and **Zn-2** (blue). In (c) the PXRD pattern of **Zn-2** crystals is given which have transformed to the thermodynamically more stable **Zn-1** over time.

Methods

Lattice dynamic calculations. All total energy calculations were performed within the projector augmented wave formalism¹ within using the VASP code.² A plane wave cut-off of 500 eV and a k-point sampling density with a target length cut-off of 10 Å as prescribed by Moreno and Soler was employed.³ For treatment of exchange and correlation we employed the PBESol functional,⁴ dispersion effects were accounted for by applying the Grimme correction⁵ and electron localisation at the transition metal sites were treated using Hubbard U parameters of 2 for both Zn and Mg as shown to successfully reproduce structural factors in a previous study.⁶ For geometry optimisation the forces on the ions were relaxed to extremely strict criteria 10⁻³ eV⁻¹ in order to ensure well converged structures for phonon calculations. The phonon calculations were performed using the finite-difference method, with energy-volume corrections added to obtain the quasi-harmonic approximation of the free energy expansion, all pre- and post- processing for the phonon calculations were performed using the Phonopy package.⁷

Synthesis of [NH₃NH₂]Zn(HCOO)₃. Single crystals of [NH₃NH₂]Zn(HCOO)₃ **Zn-1** were grown using the mild solution approach.⁸ Single crystals of the **Zn-2** were grown by a slight modified approach and in particular, triethylamine (TEA) was used as templating agent. In a typical synthesis, 1 mmol of $Zn(ClO_4)_2$ · GH_2O was dissolved in a mixture of 2 ml of MeOH and 1.5 ml of H2O. In another beaker, 40 mmol of HCOOH, 5 mmol of TEA and 2 mmol of N₂H₅Cl were dissolved in 5ml MeOH. The two solutions were mixed together and kept at room temperature. After several days, transparent, colorless crystals (Figure 1d) were collected and analysed.

X-ray diffraction. Single crystal diffraction experiments were carried out using an Oxford Diffraction Gemini A Ultra X-ray diffractometer with Mo K α radiation (λ = 0.70930 Å) operated at 50 kV and 40 mA. Data were collected at 120 K under nitrogen flow. Data collection, unit cell determination and refinement, absorption correction and data reduction were performed using the CrysAlisPro software from Agilent Technologies. The structures were solved by direct methods and were then refined by the least squares methods using the SHELX program⁹ within the Olex2 interface.¹⁰ All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically.

Hydrogen atoms were added to chemically reasonable positions found in the Fourier difference map, and then refined with constrained N–H distances (0.890 Å). After structure solution, an analytical absorption correction was performed by applying a face-based absorption correction. Details of structure solution are available in the supporting information, SI-Table 1. CIF files are available of the structure described herein, CSD 1414792.

Powder X-ray diffraction experiments of **Zn-1**, **Zn-2** and the transformed crystals were carried out on a Bruker D2 PHASER equipped with Cu tube (λ = 1.5402Å), between 10 and 50° 2Theta and a step size of 0.02°. The grown crystals were ground carefully to a fine powder before experiments, respectively. In particular, crystals of **Zn-2** were carefully ground, since transformation from **Zn-2** to the thermodynamically stable polymorph **Zn-1** was observed upon grinding in early experiments.

Thermal analysis. DSC data was acquired on a Shimadzu DSC-60 Plus under nitrogen atmosphere. The sample sample has been used as previously for powder X-ray diffraction. The 1st cycle was measured between -130°C and 100°C. For the 2nd cycle, a maximum temperature of 105°C was used. TGA/DTA data was acquired on Shimadzu DTG-60H, under nitrogen atmosphere. The same sample as the DSC measurement was used after DSC measurement. Measurement was performed from room temperature to 550 °C at a sweep rate at 3 K min⁻¹.

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