Supporting Information

# Hypophosphite hybrid perovskites: a platform for unconventional tilts and shifts

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## 1 Synthetic methods

During our previously reported synthesis of [A]Mn(H<sub>2</sub>POO)<sub>3</sub> hybrid perovskites,<sup>1</sup> reaction mixtures using azetidine, tetramethylammonium hydroxide, and dimethylamine were found to have formed no solids or binary manganese hypophosphite salts after several days using the vial-in-vial diffusion method where the outer vial contained pure DMF. However, on standing for four months, [DMA]Mn(H<sub>2</sub>POO)<sub>3</sub> perovskite was found in all the above reaction mixtures. We conclude that the amine is generated *in situ* from the hydrolysis of DMF. The perovskite appears to be a thermodynamic product under reaction conditions, although it degrades slowly on exposure to air, i.e. during overnight single-crystal analysis. Exact synthetic details follow below.

Reagents were used as received from standard chemical suppliers (Alfa Aesar and Sigma-Aldrich) without further purification: Hypophosphorous acid (50% w/w aq. soln.), manganese carbonate, azetidine, tetramethylammonium hydroxide solution (25% w/w aq. soln.), and dimethylamine (2.0 M methanol soln.).

In a typical synthesis, manganese carbonate (0.115 g, 1 mmol) was dissolved in excess aqueous hypophosphorous acid solution (50 % w/w; 0.646 mL, 6 mmol) *via* bath sonication followed by magnetic stirring and heating at 50 °C. The alkylamine or alkylammonium salt (1 mmol) was then added and stirred until dissolved (in some cases deionised water was added to aid dissolution). One sixth of this solution (the other aliquots having been reserved for testing under other conditions) was placed into a vapour diffusion chambers containing N,N-dimethylformamide (DMF). Water in the reaction mixture gradually diffused into the DMF, increasing the volume of liquid in the outer vial and possibly encouraging hydrolysis to dimethylamine. The sealed solutions were kept at room temperature (10 °C < *T* < 20 °C, UK autumn temperature), over several months. Eventually, crystals of [DMA]Mn(H<sub>2</sub>POO)<sub>3</sub> were discovered along with crystals of other simple Mn hypophosphite phases.

## 2 Single-crystal X-ray diffraction

Single crystal X-ray diffraction measurements were performed on an Oxford Diffraction Gemini E Ultra diffractometer with an Eos CCD detector using Mo K $\alpha$  radiation ( $\lambda$  = 0.7107 Å). The crystals were mounted on a cryoloop using perfluorinated oil (Paratone-N). Data were collected at room temperature. Data collection and reduction were performed with CrysAlisPro (Version 1.171.34i, Agilent Technologies). The structure was solved with ShelXT and refined with ShelXL-97<sup>2</sup> through the OLEX2 platform.<sup>3</sup> All non-hydrogen atoms were refined anisotropically.

The crystallographic details of  $[DMA]Mn(H_2POO)_3$  are listed in Table S2.1 below.

Compound	[DMA]Mn(H₂POO)₃
Empirical formula	C <sub>6</sub> H <sub>42</sub> Mn <sub>3</sub> N <sub>3</sub> O <sub>18</sub> P <sub>9</sub>
Formula weight	887.97
Temperature/K	298.9(6)
Crystal system	monoclinic
Space group	P21/c
a/Å	14.6139(3)
b/Å	13.3050(3)
c/Å	19.3418(6)
α/°	90
β/°	109.188(3)
γ/°	90
Volume/Å <sup>3</sup>	3551.84(17)
Z	4
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.661
μ/mm <sup>-1</sup>	1.519
F(000)	1812
Crystal size/mm <sup>3</sup>	0.529 × 0.468 × 0.352
Radiation	ΜοΚα (λ = 0.71073)
20 range for data collection/°	2.95 to 56.726
Index ranges	-19 ≤ h ≤ 13, -17 ≤ k ≤ 11, -18 ≤ l ≤ 25
Reflections collected	14768
Independent reflections	7802 [ $R_{int} = 0.0263$ , $R_{sigma} = 0.0365$ ]
Data/restraints/parameters	7802/0/358
Goodness-of-fit on F <sup>2</sup>	1.043
Final R indexes [I>=2σ (I)]	$R_1 = 0.0447$ , $wR_2 = 0.1056$
Final R indexes [all data]	R <sub>1</sub> = 0.0638, wR <sub>2</sub> = 0.1188
Largest diff. peak/hole / e Å <sup>-3</sup>	0.79/-0.69

#### Table S2.1. Crystallographic details of [DMA]Mn(H<sub>2</sub>POO)<sub>3</sub>

#### **3** Calculation of distortion factor

We previously reported<sup>1</sup> a distortion factor,  $\delta$ , as a simple way to gauge the distortion of a perovskite from the ideal cubic perovskite aristotype.

$$\delta = \left[\frac{V_{ideal}}{V_{real}} - 1\right] \times \ 100 \ \%$$

The two parameters are calculated as described below.

$$V_{ideal} = (Average of M - (L) - M distances in unit cell)^3$$
  
 $V_{real} = rac{Volume of unit cell}{Number of perovskite cages in unit cell}$ 

It follows that in a perfectly cubic system  $V_{real} = V_{ideal}$  and therefore  $\delta = 0$  %.

The M-(L)-M distances used from  $V_{ideal}$  were extracted from the CIF using the "Distance Explorer" function of CrystalMaker.<sup>4</sup>

## **4** References

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