Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Stability and flexibility of heterometallic formate perovskites with the dimethylammonium cation: pressure-induced phase transitions

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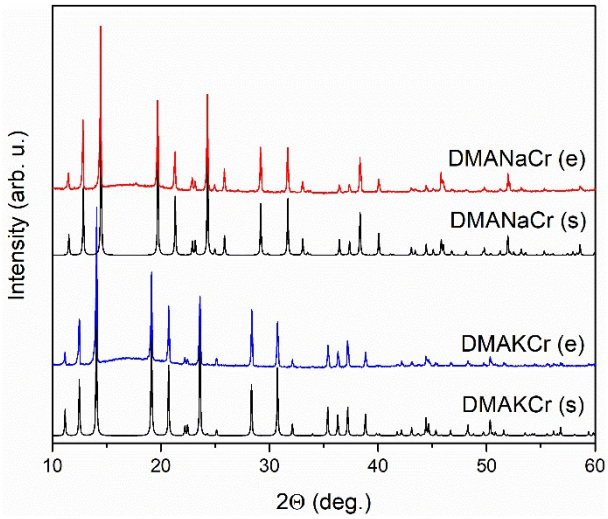
Electronic Supplementary information

Fig. S1. Experimental (e) XRD patterns of DMANaCr (red line) and DMAKCr (blue line) compared to the simulated ones (s) calculated using literature data.[1,2]



Tab. S1. Experimental[1–3] and (DFT/PBEsol+D3) calculated unit cell parameters for DMANaCr and DMAKCr in the LT phase.

	DMANaCr		DMAKCr (LT)		DMAZn	
	Exp. (302 K)[1]	DFT	Exp. (80 K)[2]	DFT	Exp. (180 K)[3]	DFT[4]
Space group	$R\bar{3}$	$P3_2$	$P1$[a]	$P\bar{1}$	$R\bar{3}c$	$P1$[b]
a (Å)	8.328	8.22	8.56	8.33	8.182	8.12
b (Å)	8.328	8.22	15.14	14.94	8.182	8.12
c (Å)	23.012	22.31	9.30	9.30	22.123	21.61
α (°)	90	90	86.0	86.4	90	89.7
β (°)	90	90	90.2	90.4	90	90.2
γ (°)	120	120	56.8	56.6	120	120.0
V (Å^3)	1382.2	1305.5	1004.5	963.0	1282.57	1235.1

[a]A supercell expansion of the reported structure (doubled volume).
[b]The initial structure had imaginary phonon frequencies and when removing these the symmetry was broken. Reducing the tolerance to 0.005 Å the structure belongs to the *C*2/*c* space group.

Tab. S2. Experimental[1,2] and (DFT/PBEsol+D3) calculated geometries (distances, d and angles, ∠) of the N–H···O bonds between DMA^+ cations of the DMANaCr and DMAKCr crystals.

	DMANaCr				DMAKCr (HT)		DMAKCr (LT)			
	d(N···O) (Å)		∠(N–H···O) (°)		d(N···O) (Å)	∠(N–H···O) (°)	d(N···O) (Å)		∠(N–H···O) (°)	
	Exp. (302 K)[1]	DFT	Exp. (302 K)[1]	DFT	Exp. (298 K)[2]	Exp. (298 K)[2]	Exp. (80 K)[2]	DFT	Exp. (80 K)[2]	DFT
$N–H···O_{Cr}$	3.099	2.922	151.5	166.2	3.243	146.9	–	–	–	–
	3.537	3.364	131.7	124.2	3.656	149.0	–	–	–	–
$N–H···O_{Na/K}$	2.877	2.696	170.2	176.5	2.856	155.3	2.841	2.709	148.5	166.2
	3.065	3.042	134.1	125.1	3.008	112.5	2.893	*	142.2	*
							3.013	2.719	170.6	171.1

* For the DFT calculations we use only one of the two molecular position, thus no parameters can be extracted for this H-bond.

Tab. S3. The calculated C–O bond lengths (Å) in the formate units of the DMANaCr, DMAKCr and DMAZn[4] crystals.

	DMANaCr	DMAKCr	DMAZn[4]
C–O (CrO_6/ZnO_6) H-bonded	1.297–1.298	1.297	1.274–1.277
C–O (CrO_6/ZnO_6) not H-bonded	1.281–1.282	1.281–1.283	1.262–1.266
C–O (NaO_6/KO_6/ZnO_6) H-bonded	1.254–1.255	1.253–1.255	1.259–1.261
C–O (NaO_6/KO_6) not H-bonded	1.239–1.241	1.238–1.239	

Tab. S4. The pressure-dependent unit cell parameters calculated for DMANaCr.[a]

	DFT optimised structure	DFT at 96% volume
a=b (Å)	8.22	8.18
c (Å)	22.31	21.64
V ($Å^3$)	1305.5	1253.3
Pressure (GPa)*	-0.012	0.995
$H···O_{Cr}$ (Å)	1.89–1.92	1.85–1.87
$H···O_{Na}$ (Å)	1.62	1.60–1.61

* denotes the calculated value.

1 M. Mączka, B. Bondzior, P. Dereń, A. Sieradzki, J. Trzmiel, A. Pietraszko and J. Hanuza, *Dalt. Trans.*, 2015, **44**, 6871–6879.

2 M. Ptak, A. Gągor, A. Sieradzki, B. Bondzior, P. Dereń, A. Ciupa, M. Trzebiatowska and M. Mączka, *Phys. Chem. Chem. Phys.*, 2017, **19**, 12156–12166.

3 H. F. Clausen, R. D. Poulsen, A. D. Bond, M.-A. S. Chevallier and B. B. Iversen, *J. Solid State Chem.*, 2005, **178**, 3342–3351.

4 K. L. Svane, A. C. Forse, C. P. Grey, G. Kieslich, A. K. Cheetham, A. Walsh and K. T. Butler, *J. Phys. Chem. Lett.*, 2017, **8**, 6154–6159.