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Neutron diffraction studies on the thermal expansion and anomalous mechanics in the perovskite-type $[C(ND_2)_3]Me^{2+}(DCOO)_3$ [Me = Cu, Mn, Co]

Supplementary information

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Additional experimental information

MnGF single-crystals were grown by slow evaporation of the solution containing formic acid, $[C(NH_2)_3]_2\ CO_3$, water and $Mn(ClO_4)_2{\cdot}6H_2O$, as described by Hu *et al.* [15].

The following deuterated materials were prepared by slightly modifying the method in reference [15], due to unavailability of the deuterated analogue of $[C(NH_2)_3]_2\ CO_3$:

CuGF was prepared by dissolving dehydrated $CuSO_4$, $C(ND_2)_3Cl$, K_2CO_3 and DCOOD in D_2O. Single-crystals were grown from slow evaporation of diluted solutions. CoGF/MnGF were synthesised in a similar fashion using the corresponding metal salts such as dehydrated $CoCl_2$ and $MnCl_2{\cdot}H_2O$, respectively.

Table S1: Some experimental details relating to data collection. ^{H} refers to a protonated sample, while the rest are deuterated. To convert proton beam charge to beamtime, the values may be divided by 160 μA, assuming a stable beam throughout the experiment.

Instrument	Sample	Total proton beam charge in μA h (per measurement)	Sample specifications	Additional details
SXD	$MnGF^H$ CuGF	400 200	~ 113 mm^2 ~ 100 mm^2	1 crystal 1 crystal
WISH (powder)	MnGF CoGF CuGF	~ 13 to 14	~ 1.2 to 1.4 gm	Sample contained in 8mm diameter vanadium can

On SXD, the samples were placed in a top loading closed cycle refrigerator. On WISH, vanadium can loaded with sample was placed in an Oxford instruments Variox cryostat.

Rietveld refinement process

Structural parameters from single-crystal neutron diffraction data of CuGF and MnGF were used as the starting model. In the case of CuGF, 30 K data from SXD was used as a starting model for NPD from 40 to 290 K (upward) and 25 to 5 K (downward). For MnGF, 30 K data from SXD was used as a starting model for NPD from 50 to 200 K (upward) and 25 to 9 K (downward). In such cases, subsequent refinements were done with the former refinement as a guide to the next temperature. In the case of CoGF, initial refinement was done for the 275 K data. The structural parameters reported by Hu et. al. (single-crystal X-ray diffraction at 290 K) was used as a starting model. Further refinements were done consecutively, by employing the previous temperature as the starting model.

The following were the free variables in the refinements: (a) the lattice parameters; (b) the atomic coordinates; (c) a polynomial background function, (d) a scale factor; (e) peak shape parameters; and (f) displacement parameters (isotropic).

All the refinements were implemented with a TOF profile function 3 (in GSAS) featuring a convolution of back-to-back exponentials with a pseudo-Voigt function. Backgrounds were modelled using the shifted Chebyshev polynomials. Thermal parameters of like-atoms (except D) were refined with constraints set equal. The deuterium atoms have been divided into two categories “free from disorder” and “with disorder”. With each category treated independently from each other. Initial attempts of Rietveld refinement resulted in negative ADP values for certain atoms. Hence the interpolated values of ADP obtained from the SXD data were used and kept fixed for each temperature. Such a treatment was applied for Cu (CuGF), Mn and C in MnGF (also used in CoGF).

The Following soft restraints were implemented: (i) along the bonds: C-N, N-D, C-O, C-D; (ii) across the bonds: N-N, N-D, D-D, C-D, O-D, O-O. These implementations resulted in meaningful structural features and are comparable with results from single-crystal neutron diffraction.

Table S2: Rietveld refinement results of target compounds.

	Copper guanidinium formate: $[C(ND_2)_3]Cu(DCOO)_3$			
CCDC No.	1839555	1839556	1839557	1839558
T (K)	25	100	190	290
Crystal system	Orthorhombic			
Space group	$Pna2_1$			
a, *b*, *c* (Å)	8.42922(7), 9.03874(10), 11.29341(10)	8.44705(7), 9.03360(10), 11.30470(10)	8.47827(7), 9.03192(10), 11.32571(10)	8.51810(8), 9.03552(11), 11.35385(11)
R_p (%)	4.44	4.16	3.87	3.55
wR_p (%)	4.82	4.55	4.35	4.23

	Manganese guanidinium formate: $[C(ND_2)_3]Mn(DCOO)_3$			
CCDC No.	1839559	1839560	1839561	1839562
T (K)	25	75	125	200
Crystal system	Orthorhombic			
Space group	*Pnna*			
a, *b*, *c* (Å)	8.42957(10), 11.89231(18), 9.09323(15)	8.44100(10), 11.90050(18), 9.08519(15)	8.45544(11), 11.91319(19), 9.07778(16)	8.47995(11), 11.93774(20), 9.06952(18)
R_p (%)	5.25	5.28	5.26	5.53
wR_p (%)	5.63	5.78	5.93	6.14

	Cobalt guanidinium formate: $[C(ND_2)_3]Co(DCOO)_3$			
CCDC No.	1839563	1839564	1839565	1839566
T (K)	30	100	200	275
Crystal system	Orthorhombic			
Space group	*Pnna*			
a, *b*, *c* (Å)	8.26161(20), 11.68198(35), 8.92432(32)	8.27377(19), 11.69313(34), 8.91652(32)	8.29786(19), 11.71840(34), 8.91122(33)	8.31848(19), 11.74230(35), 8.90972(34)
R_p (%)	6.38	6.37	6.25	6.09
wR_p (%)	7.61	7.77	7.91	7.95

Table S3: Variable-temperature lattice parameter data for $[C(ND_2)_3]$ *Cu* $(DCOO)_3$

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Temperature (K)	a (Å)	σ_a	b (Å)	σ_b	c (Å)	σ_c
5	8.42887	0.00007	9.03903	0.00010	11.29293	0.00010
6	8.42884	0.00007	9.03905	0.00010	11.29297	0.00010
7	8.42886	0.00007	9.03910	0.00010	11.29295	0.00010
8	8.42883	0.00007	9.03908	0.00010	11.29297	0.00010
9	8.42888	0.00007	9.03904	0.00010	11.29298	0.00010
10	8.42886	0.00007	9.03906	0.00010	11.29296	0.00010
25	8.42922	0.00007	9.03874	0.00010	11.29341	0.00010
40	8.43082	0.00007	9.03789	0.00010	11.29443	0.00010
55	8.43337	0.00007	9.03691	0.00010	11.29606	0.00010
70	8.43668	0.00007	9.03577	0.00010	11.29819	0.00010
85	8.44070	0.00007	9.03479	0.00010	11.30068	0.00010
100	8.44705	0.00007	9.03360	0.00010	11.30470	0.00010
115	8.45079	0.00007	9.03307	0.00010	11.30707	0.00010
130	8.45544	0.00007	9.03259	0.00010	11.31014	0.00010
145	8.46057	0.00007	9.03216	0.00010	11.31355	0.00010
160	8.46909	0.00007	9.03183	0.00010	11.31922	0.00010
175	8.47342	0.00007	9.03179	0.00010	11.32230	0.00010
190	8.47827	0.00007	9.03192	0.00010	11.32571	0.00010
205	8.48368	0.00007	9.03214	0.00010	11.32955	0.00010
220	8.49119	0.00007	9.03265	0.00010	11.33486	0.00010
230	8.49473	0.00007	9.03287	0.00010	11.33730	0.00010
235	8.49704	0.00007	9.03310	0.00010	11.33896	0.00010
240	8.49927	0.00007	9.03331	0.00010	11.34056	0.00010
245	8.50140	0.00007	9.03351	0.00010	11.34210	0.00010
250	8.50481	0.00007	9.03385	0.00010	11.34452	0.00010
255	8.50631	0.00007	9.03407	0.00011	11.34552	0.00010
260	8.50792	0.00007	9.03424	0.00011	11.34666	0.00010
275	8.51261	0.00007	9.03477	0.00011	11.34997	0.00010
290	8.51810	0.00008	9.03552	0.00011	11.35385	0.00010

Table S4: Variable-temperature lattice parameter data for $[C(ND_2)_3]$ *Mn* $(DCOO)_3$

Temperature (K)	a (Å)	σ_a	b (Å)	σ_b	c (Å)	σ_c
9	8.42810	0.00010	11.89148	0.00017	9.09439	0.00015
9.5	8.42814	0.00010	11.89151	0.00017	9.09439	0.00014
10	8.42816	0.00010	11.89150	0.00017	9.09443	0.00015
20	8.43775	0.00010	11.89777	0.00018	9.08746	0.00015
25	8.42957	0.00010	11.89231	0.00018	9.09323	0.00015
50	8.43503	0.00010	11.89581	0.00018	9.08910	0.00015
75	8.44100	0.00010	11.90050	0.00018	9.08519	0.00015
100	8.44783	0.00010	11.90631	0.00018	9.08134	0.00016
125	8.45544	0.00011	11.91319	0.00019	9.07778	0.00016
150	8.46366	0.00011	11.92118	0.00019	9.07455	0.00017
175	8.47239	0.00011	11.92993	0.00019	9.07167	0.00017
200	8.47995	0.00011	11.93774	0.00020	9.06952	0.00018

Table S5: Variable-temperature lattice parameter data for $[C(ND_2)_3]$ *Co* $(DCOO)_3$

Temperature (K)	a (Å)	σ_a	b (Å)	σ_b	c (Å)	σ_c
14.5	8.26011	0.00020	11.68061	0.00035	8.9259	0.00032
15	8.26016	0.00020	11.68060	0.00035	8.92591	0.00032
30	8.26161	0.00020	11.68198	0.00035	8.92432	0.00032
45	8.26377	0.00020	11.68392	0.00035	8.92238	0.00032
75	8.26913	0.00020	11.68857	0.00034	8.91877	0.00032
100	8.27377	0.00019	11.69313	0.00034	8.91652	0.00032
125	8.27915	0.00019	11.69838	0.00034	8.91463	0.00032
150	8.28572	0.00019	11.70511	0.00034	8.91299	0.00033
175	8.29154	0.00019	11.71147	0.00034	8.91196	0.00033
200	8.29786	0.00019	11.71840	0.00034	8.91122	0.00033
225	8.30439	0.00019	11.72589	0.00034	8.91052	0.00033
250	8.31200	0.00019	11.73465	0.00035	8.90998	0.00034
275	8.31848	0.00019	11.74230	0.00035	8.90972	0.00034