Supporting Information:

Framework and Coordination Strain in Two Isostructural Hybrid Metal-Organic Perovskites

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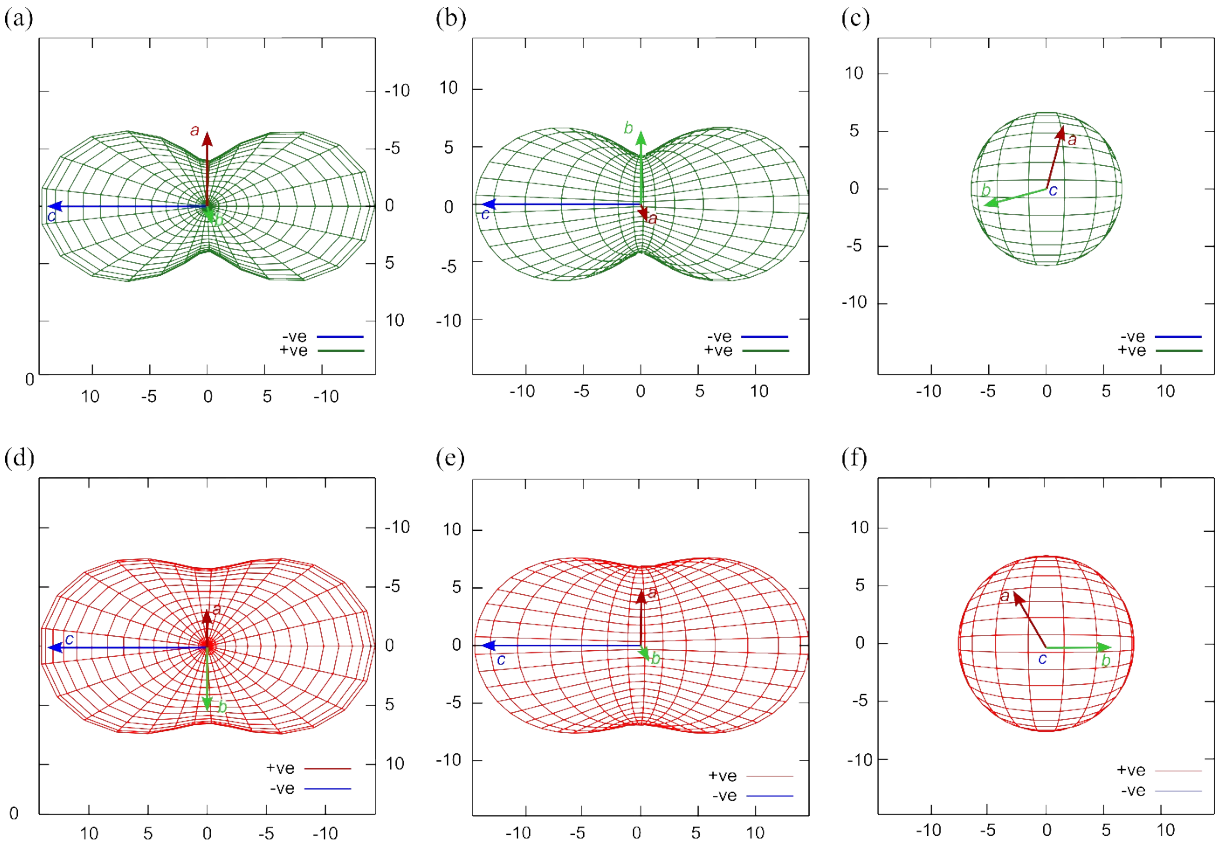

Figure S1. Calculated compressibility (in TPa^{-1}) indicatrices of the formate crystals viewed along the (a) [100] (b) [010] and (c) [010] directions in: (a-c) $DmaNiFor_3$; and (d-f) $DmaCoFor_3$.

Table S1. Compressibility related to crystallographic axes calculated for $DmaNiFor_3$

			Direction			Empirical parameters			
Axes	K(TPa^{-1})	σK(TPa^{-1})	a	b	c	ε_0	λ	P_c	ν
X_1	14.6549	3.8197	0	0	1	-1.36E-03	-8.99E-03	0.001	1.2582
X_2	3.9281	1.5571	-0.966	-0.2586	0	-5.16E-04	-8.61E-03	0.001	0.6492
X_3	4.3124	1.7758	0.259	0.9659	0	6.03E-01	-5.91E-01	-1.7234	0.031
V	23.3374	0.4845							

Birch-Murnaghan Coefficients

	B_0 (GPa)	σB_0 (GPa)	V_0 (Å3)	σV_0 (Å3)	B'	σB'	P_c (GPa)
2nd	34.6697	1.0105	1257.588	1.9358	4	n/a	0
3rd	35.1937	3.8009	1257.343	2.6754	3.6756	2.232	0

Table S2. Compressibility related to crystallographic axes calculated for $DmaCoFor_3$

			Direction			Empirical parameters			
Axes	K(TPa^{-1})	σK(TPa^{-1})	a	b	c	ε_0	λ	P_c	ν
X_1	14.2155	2.0865	0	0	1	8.76E-02	-2.37E-03	-10.1784	1.5619
X_2	6.53	0.5194	-0.0049	1	0	-4.70E-04	-8.08E-03	0.001	0.7726
X_3	6.9044	0.2513	0.8931	0.4498	0	-1.01E-04	-8.27E-03	0.001	0.803
V	27.2583	0.9877							

Birch-Murnaghan Coefficients

	B_0 (GPa)	σB_0 (GPa)	V_0 (Å3)	σV_0 (Å3)	B'	σB'	P_c (GPa)
2nd	30.1052	1.2672	1294.028	1.9115	4	n/a	0
3rd	32.3328	5.1252	1293.149	2.6669	2.1634	3.8814	0

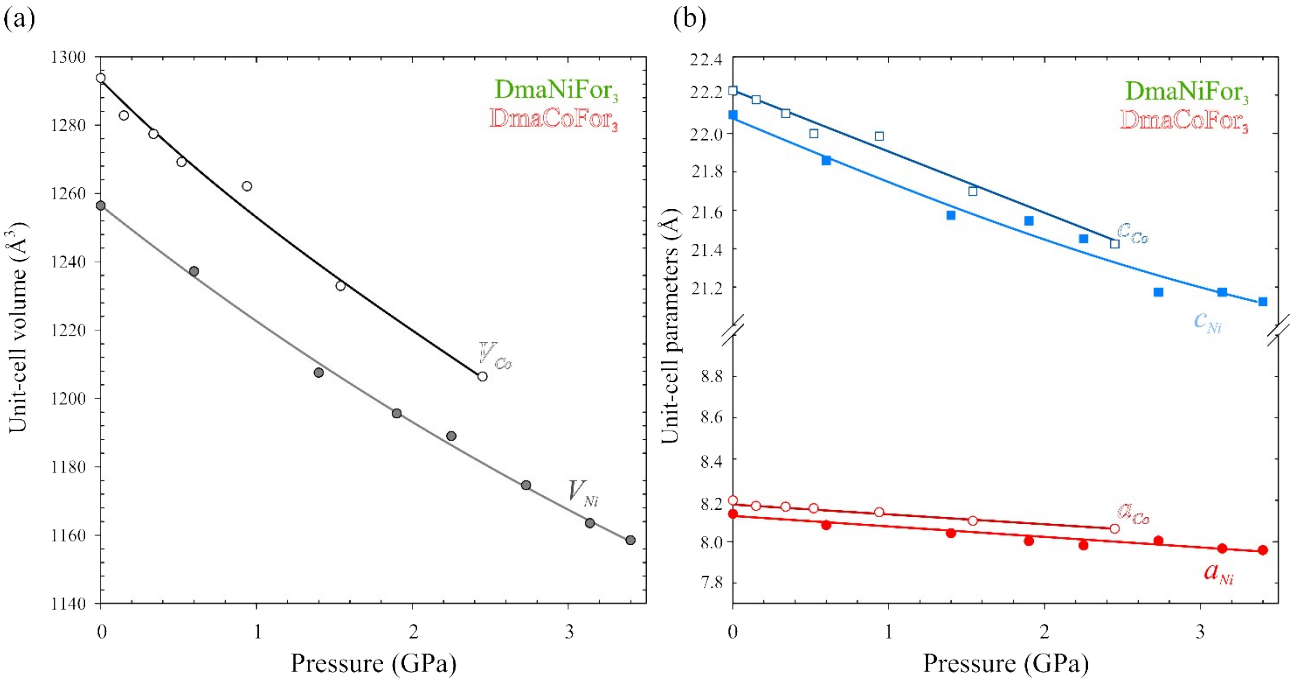

Figure S2. Comparison of the unit-cell dimensions of $DmaCoFor_3$ (open symbols) and $DmaNiFor_3$ (full symbols) as a function of pressure.

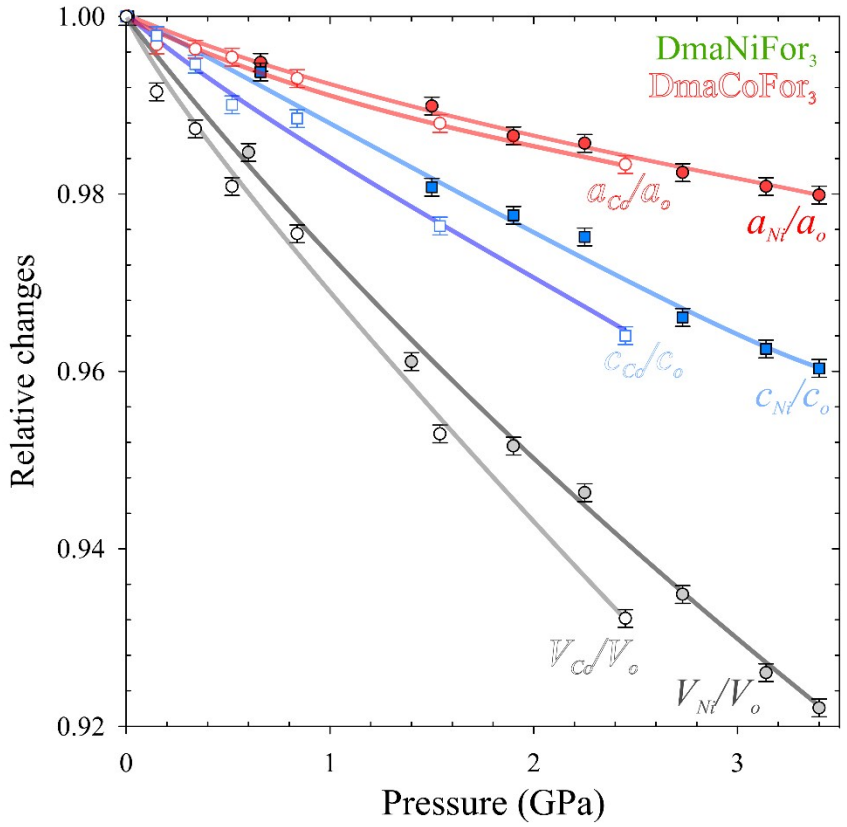

Figure S3. Comparison of relative changes with increasing pressure of parameters *a*, *c* and *V* for $DmaCoFor_3$ (open symbols) and $DmaNiFor_3$ (full symbols).

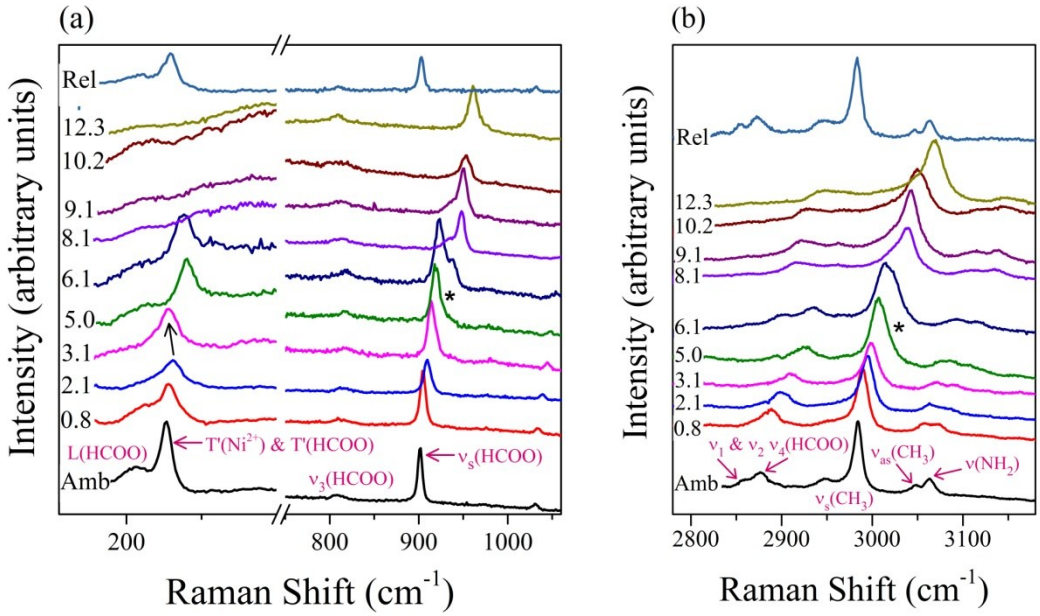

Figure S4. Pressure-dependent Raman spectra of $DmaNiFor_3$ ranging from (a) 170 to 1050 cm^{-1}; and (b) 2800 to 3180 cm^{-1}. The asterisk marks the appearance of a new peak. The arrow shows the softening of mode. All pressure values written against spectra are in GPa. 'Rel' stands for 'released' pressure and collected at ambient conditions.

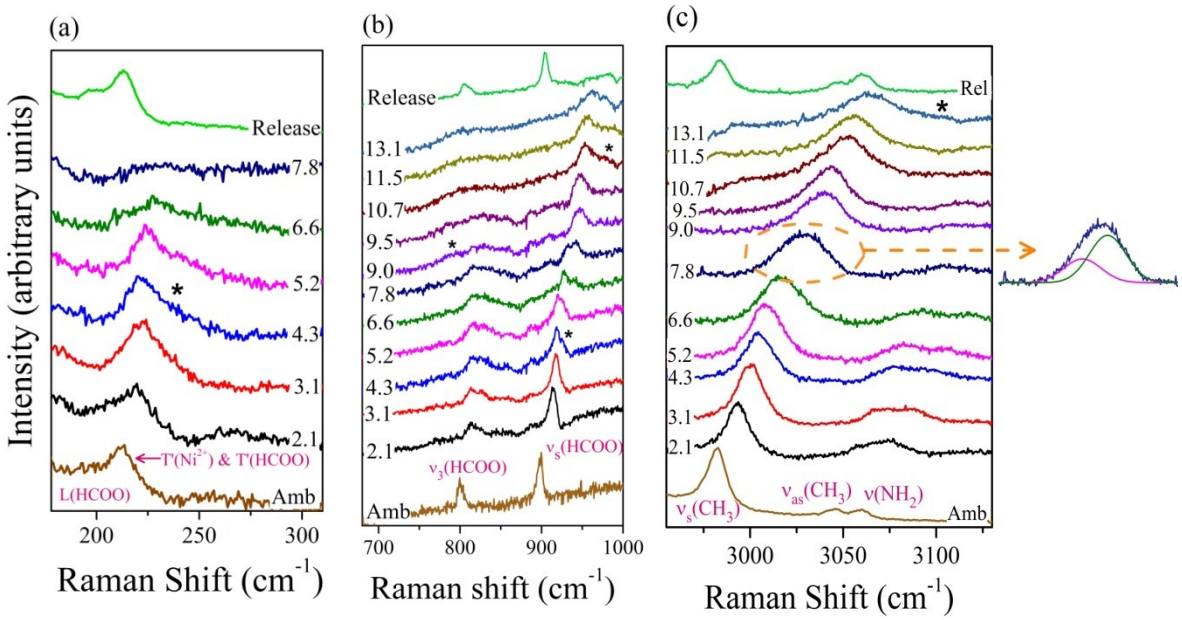

Figure S5. Pressure dependent Raman spectra of $DmaCoFor_3$ ranging from (a) 170 to 300 cm^{-1}; (b) 700 to 1000 cm^{-1}; (c) 2960 to 3120 cm^{-1}. The asterisk marks the appearance of a new peak. All pressure values written against spectra are in GPa.

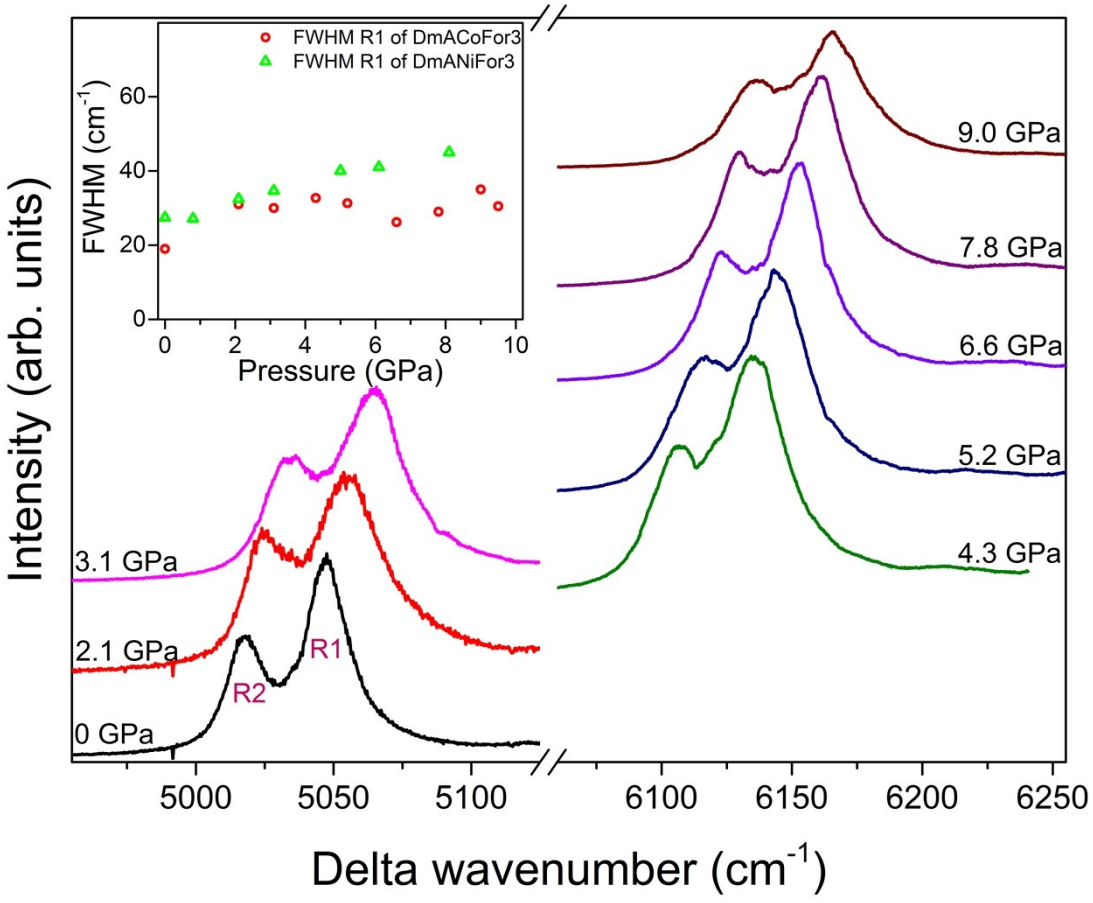

Figure S6. The ruby R1 and R2 line as a function of pressure during high-pressure Raman studies. The FWHM of the ruby peak does not change much with increasing pressure, indicating that the environment is quasi hydrostatic. The first three pressures were measured with the 514 nm and the rest of the pressures were measured with the 488 nm laser wavelength.

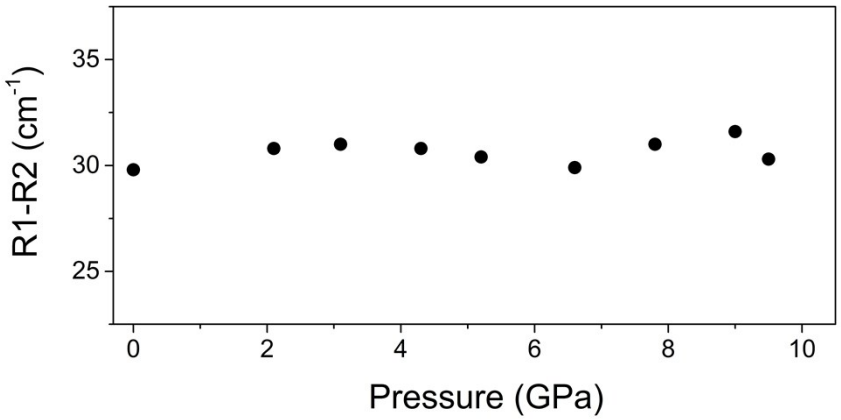

Figure S7. Splitting of the R1 and R2 ruby fluorescence lines with increasing pressure during high-pressure Raman studies.

Pressure	0.1MPa	0.60GPa	1.40GPa	1.90 GPa	2.25 GPa	2.73 GPa	3.14 GPa	3.34 GPa
Formula weight	245.90	245.90	245.90	245.90	245.90	245.90	245.90	737.66
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	trigonal	trigonal	trigonal	trigonal	trigonal	trigonal	triclinic	triclinic
Space group	*R*-3*c*	*R*-3*c*	*R*-3*c*	*R*-3*c*	*R*-3*c*	*R*-3*c*	*R*-3*c*	*R*-3*c*
Unit cell dimensions *a* (Å)	8.12139(16)	8.0690(17)	8.0395(4)	8.0016(16)	7.981(13)	8.0039(15)	7.9659(6)	7.9580(6)
b(Å)	8.12139(16)	8.0690(17)	8.0395(4)	8.0016(16)	7.9955(13)	8.0039(15)	7.9659(6)	7.9580(6)
c (Å)	21.9961(4)	21.941(7)	21.5732(14)	21.563(6)	21.55(3)	21.172(5)	21. 141(3)	21.1236(17)
α (°)	90	90	90	90	90	90	90	90
β (°)	90	90	90	90	90	90	90	90
γ (°)	120	120	120	120	120	120	120	120
Volume (Å^3)	1256.43(6)	1237.2(6)	1207.55(14)	1195.6(6)	1189.0(19)	1174.6(5)	1161.8(2)	1158.52(15)
Z/Z'	6/0. 16667	6/0. 16667	6/0.16667	6/0.16667	6/0.16667	6/0.16667	6/0.16667	6/0.16667
Molecular volume (*V/Z*)	209.405	206.2	201.2583	199.2667	198.1667	195.7667	193.6333	193.0867
Calculated density (g/cm^3)	1.950	1.966	2.012	2.032	2.044	2.069	2.088	2.097
Absorption (mm^{-1})	2.317	2.356	2.411	2.435	2.448	2.478	2.502	2.513
F(000)	780.0	768.0	768.0	768.0	768.0	768.0	768.0	768.0
Crystal size (mm)	0.209×0.231x0.20	0.209×0.231x0.20	0.204×0.196x0.20	0.202×0.1966x0.20	0.202x0.195x 0.20	0.20×0.20x0.195	0.197×0.197×0.195	0.196× 0.196×0.195
2θ-range for data collection (°)	9.41 to 56.716	10.094 to 57.046	11.626 to 56.022	10.192 to 57.148	9.594 to 56.482	11.718 to 56.402	10.238 to 55.666	11.776 to 57.112
Min/max indices: h, k, l	-10/10, -10/10, -28/28	-9/9, -7/7, -22/22	-9/9, -6/6, -22/22	-10/-9, -10/10, 22/20	-10/10, -9/9, -11/11	-10/10, -7/7, -23/24	-7/7, -10/10, -23/24	-10/10, -7/7, -23/24
Reflect. Collected/unique	10214/348	1981/226	1956/216	2305/243	1892/211	2117/230	1825/154	2143/178
R_{int}	0.0985	0.0441	0.0972	0.0983	0.0282	0.1359	0.0363	0.0861
Refinement method;	least-squares	least-squares	least-squares	least-squares	least-squares	least-squares	least-squares	least-squares
Completeness (%)	100	63.84	66.26	71.97	62.20	71.30	53.29	53.29
Data/restrains/parameters	348/4/37	225/0/35	216/0/36	243/0/36	1892/0/28	231/0/36	158/0/36	178/0/36
Goodness-of-fit on F^2	1.122	0.861	1.131	1.163	1.110	1.206	1.135	1.191
Final R1/wR2 (I>2σ(I))	0.0277/ 0.0693	0.0263/0.0869	0.0269/0.0689	0.0391/0.0865	0.0196/0.0471	0.0469/0.1139	0.0181/0.0450	0.0280/0.0627
R1/wR2 (all data)	0.0288/ 0.0707	0.0284/0.0892	0.0286/0.0696	0.0436/0.0926	0.0211/0.0477	0.0521/0.1204	0.0195/0.0453	0.0310/0.0643
Largest diff. peak/hole (e.Å^{-3})	0.71/-0.41	0.35/-0.32	0.31/-0.35	0.46/-0.69	0.30/-0.17	0.79/-0.47	0.34/-0.13	0.23/-0.28

Table S3. Crystallographic data of **DmaNiFor$_3$**

Table S4. Crystallographic data of **DmaCoFor$_3$**

Pressure		0.15 GPa	0.34GPa	0.52GPa	0.82GPa	1.54 GPa	2.45 GPa
Formula weight		779.44	779.44	779.44	779.44	779.44	779.44
Wavelength (Å)		0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system		trigonal	trigonal	trigonal	trigonal	trigonal	trigonal
Space group		*R*-3*c*	*R*-3*c*	*R*-3*c*	*R*-3*c*	*R*-3*c*	*R*-3*c*
Unit cell	*a* (Å)	8.1727(8)	8.1686(14)	8.161(5)	8.142(3)	8.1000(12)	8.0621(10)
dimensions	*b* (Å)	8.1727(8)	8.1686(14)	8.161(5)	8.142(3)	8.1000(12)	8.0621(10)
	c (Å)	22.176(4)	22.105(5)	22.00(2)	21.986(14)	21.699(6)	21.424(6)
	α (°)	90	90	90	90	90	90
	β (°)	90	90	90	90	90	90
	γ (°)	120	120	120	120	120	120
Volume (Å^3)		1282.8(3)	1277.4(4)	1269(2)	1262.1(12)	1232.9(5)	1206.0(4)
Z/Z’		6/0.16667	6/0.16667	6/0.16667	6/0.16667	6/0.16667	6/0.16667
Molecular volume (V/Z)		213.8	212.9	211.5	210.35	205.4833333	201
Calculated density (g/cm^3)		1.873	1.904	1.916	1.903	1.973	2.017
Absorption (mm^{-1})		2.006	2.016	2.029	2.039	2.088	2.135
F(000)		699.0	699.0	699.0	699.0	699.0	699.0
Crystal size (mm)		0.2 x 0.2 x 0.1	0.2 x 0.2 x 0.1	0.2 x 0.2 x 0.1	0.2 x 0.2 x 0.1	0.2 x 0.2 x 0.1	0.2 x 0.2 x 0.1
2θ-range for data collection (°)		9.978 to 52.554	9.982 to 52.892	9.992 to 52.27	10.016 to 52.914	10.068 to 51.944	10.116 to 52.436
Min/max indices: h, k, l		-10/10, -8/8, -22/22	-9/9, -5/5, -26/25	-5/5, -8/9, -26/25	-8/8, -10/9, -22/23	-7/7, -8/8, -22/22	-7/7, -8/8, -22/22
Reflect. Collected/unique		1817/194	1858/236	1176/222	1980/196	1942/188	1917/187
R_{int}		0.0593	0.0852	0.1205	0.1182	0.1383	0.1371
Refinement method;		least-squares	least-squares	least-squares	least-squares	least-squares	least-squares
Completeness (%)		66.4	66.4	77.46	66.9	68.7	68.0
Data/restrains/parameters		194/0/35	236/0/33	222/0/33	196/0/31	188/0/34	187/0/33
Goodness-of-fit on F^2		1.198	1.089	1.155	1.059	1.156	1.130
Final R1/wR2 (I>2σ(I))		0.0376/ 0.0692	0.0504/ 0.1173	0.0777/ 0.1502	0.0407/0.0794	0.0462/0.0718	0.0491/ 0.0611
R1/wR2 (all data)		0.0631/ 0.0788	0.0767/ 0.1364	0.1407/ 0.1887	0.0797/0.0907	0.1024/0.0901	0.0965/ 0.0714
Largest diff. peak/hole (e.Å^{-3})		0.36/-0.32	0.58/-0.52	0.56/-0.66	0.38/-0.40	0.42/-0.48	0.38 / -0.32