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Supporting Information

Structural Insights into a New Family of Three-Dimensional Thiocyanate Bridged Molecular Double Perovskites

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Table S1 Selected inter-atomic distances (Å) and bond angles (°) for **1–5**.

Compound		**1**		**2**	**3**	**4**	**5**
Formula		$A_2[CdM'(SCN)_6]$					
A/M'		NH_4^+/Ni^{2+}		K^+/Ni^{2+}	$Me_2NH_2^+/Ni^{2+}$	$Me_2NH_2^+/Mn^{2+}$	Me_3S^+/Cd^{2+}
Space group		$P2_1/n$		$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Pa\bar{3}$
T / K		298(2)	90(2)	293(2)	293(2)	293(2)	298(2)
∠Cd–S–C / °	Individual	100.0(7) 101.0(7) 102.2(7)	99.0(2) 100.9(2) 103.0(2)	99.3(2) 99.5(2) 100.4(2)	104.7(1) 107.2(1) 116.8(2)	102.7(2) 104.8(2) 112.6(2)	110.5(8)
	Average	101.1	101.0	99.7	109.6	106.7	110.5
∠M'–N–C / °	Individual	173.5(2) 162.6(2) 163.7(2)	173.8(4) 159.8(3) 170.1(4)	172.1(3) 162.0(3) 158.0(3)	166.5(3) 167.7(2) 136.8(3)	166.1(4) 163.2(4) 131.9(4)	148.6(2)
	Average	166.6	167.9	164.0	156.8	153.7	148.6
Cd···M' / Å	Individual	6.071 6.147 6.147	6.009 6.129 6.129	6.075 6.073 6.073	6.306 6.475 6.897	6.416 6.572 6.875	6.874
	Average	6.122	6.089	6.074	6.560	6.621	6.874

Table S2 Crystallographic parameters and selected bond distances (Å) and bond angles (°) for azido-bridged molecular perovskites.

Compound	$(Me_2NH_2)[Cd(N_3)_3]$[s2]		$(Me_3NH)[Cd(N_3)_3]$[s3]		$(Me_4N)[Cd(N_3)_3]$[s4]		
T / K	203(2)	273(2)	283(2)	348(2)	220(2)	300(2)	350(2)
Crystal system	Hexagonal	Hexagonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Cubic
Space group	$R\bar{3}$	$R\bar{3}$	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/m$	$Pm\bar{3}m$
a / Å	8.331(6)	8.337(7)	8.606(5)	8.628(7)	15.692(4)	6.326(3)	6.523(1)
b / Å	8.331(6)	8.337(7)	9.366(5)	9.407(1)	8.834(6)	13.364(6)	6.523(1)
c / Å	11.490(1)	11.554(2)	13.016(8)	13.057(1)	9.529(6)	6.435(3)	6.523(1)
β / °	90	90	105.803(2)	105.504(3)	125.56(6)	90.023(4)	90
V / Å^3	690.56(1)	695.44(1)	1009.5(1)	1021.1(2)	1074.5(7)	544.06(4)	277.53(1)
Cd···Cd / Å	6.148(3) 6.148(3)	6.164(4)	6.398(3) 6.374(3) 6.508(5) 6.354(3) 6.329(3)	6.382(4) 6.528(6)	6.497(3) 6.386(6)	6.682(3) 6.326(3) 6.435(3)	6.523(1)
Cd–N–N / °	118.872(2) 118.878(2) 118.864(2) 118.928(2) 118.858(2) 118.870(1)	119.576(3) 119.518(2) 119.601(3) 119.551(2) 119.561(2) 119.568(3) 119.528(2)	130.417(2) 137.821(2) 126.225(2) 129.318(2) 134.913(2)	129.54(3) 129.298(3) 138.056(3)	131.344(2) 137.760(2) 128.476(2)	147.849(2) 155.935(2) 126.480(3) 130.956(3)	137.384(1)

The calculation of tolerance factor.

According to the modified tolerance factor equation $\alpha = (r_{\mathrm{Aeff}} + \mathrm{r}_{\mathrm{Xeff}})/\sqrt{2}(r_{\mathrm{B}} + 0.5\mathrm{h}_{\mathrm{Xeff}})$ ($r_{\mathrm{B}} = \frac{1}{2}(r_{\mathrm{B'}}+r_{\mathrm{B''}})$) for ABX_3 or $A_2B'B''X_6$ molecular perovskites (ref. S5), the tolerance factors were calculatedfor Cs[Cd(SCN)$_3$], **1**–**5**, and (Me$_4$N)[Cd(SCN)$_3$]. The appropriate values for three-dimensional perovskites are expected between 0.81 and 1.01, and it seems that the present hybrid instances, *i.e.*, **3**–**5**, well obey this regulation. However, for the present inorganic instances adopting three-dimensional perovskite structure, *i.e.*, Cs[Cd(SCN)$_3$], **1**, and **2**, their calculated tolerance factors are much smaller than 0.81. In contrary, (Me$_4$N)[Cd(SCN)$_3$] with a calculated tolerance factor of 0.841 actually adopts a one-dimensional hexagonal perovskite structure but not a three-dimensional perovskite structure. These facts indicate that the calculated tolerance factors did not work well to predict the structure type for these thiocyanate-bridged molecular perovskites. We attribute such exception to the bent Cd−S−C angles, which is far from the ideal 180° that is essentially assumed in the calculation model.

Table S3 Effective radii of molecular cations and anions and tolerance factors for Cs[Cd(SCN)$_3$], **1**–**5**, and (Me$_4$N)[Cd(SCN)$_3$].

Compound	Cs[Cd(SCN)$_3$]	**1**	**2**	**3**	**4**	**5**	(Me$_4$N)[Cd(SCN)$_3$]
A	Cs^+	NH_4^+	K^+	$Me_2NH_2^+$	$Me_2NH_2^+$	Me_3S^+	Me_4N^+
r_{Aeff} / Å	1.67	1.46	1.38	2.72	2.72	2.95	2.92
B'/B"	Cd^{2+}/Cd^{2+}	Ni^{2+}/Cd^{2+}	Ni^{2+}/Cd^{2+}	Ni^{2+}/Cd^{2+}	Mn^{2+}/Cd^{2+}	Cd^{2+}/Cd^{2+}	Cd^{2+}/Cd^{2+}
$r_{\mathrm{B'}}+r_{\mathrm{B''}}$ / Å	1.90	1.64	1.64	1.64	1.79	1.90	1.90
r_{Xeff} / Å	1.84						
h_{Xeff} / Å	6.10						
α	0.620	0.603	0.588	0.833	0.817	0.847	0.841
Exp. result	3D						1D

Note: The ionic radii of divalent metal ions is taken from ref. S5.

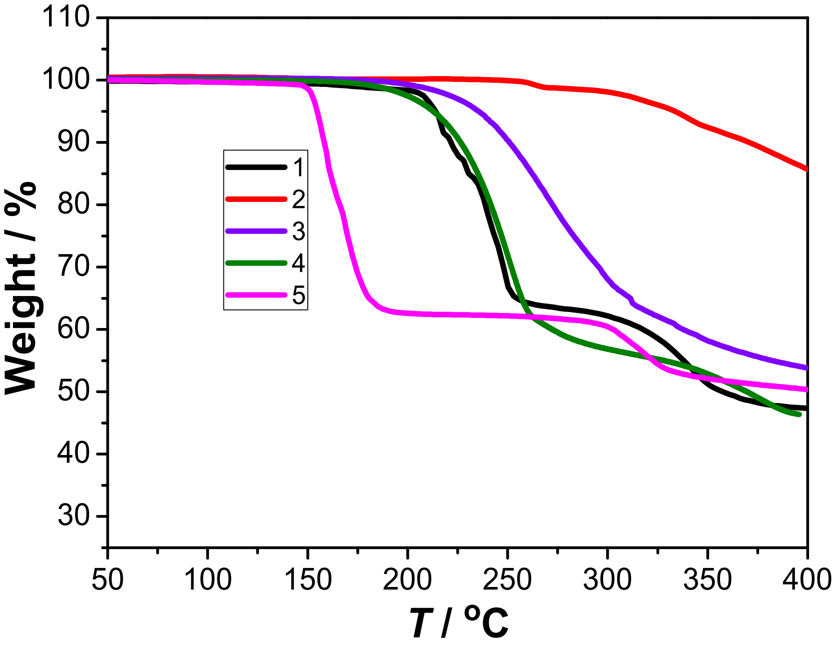

Fig. S1 Thermogravimetric analysis results of **1**–**5.**

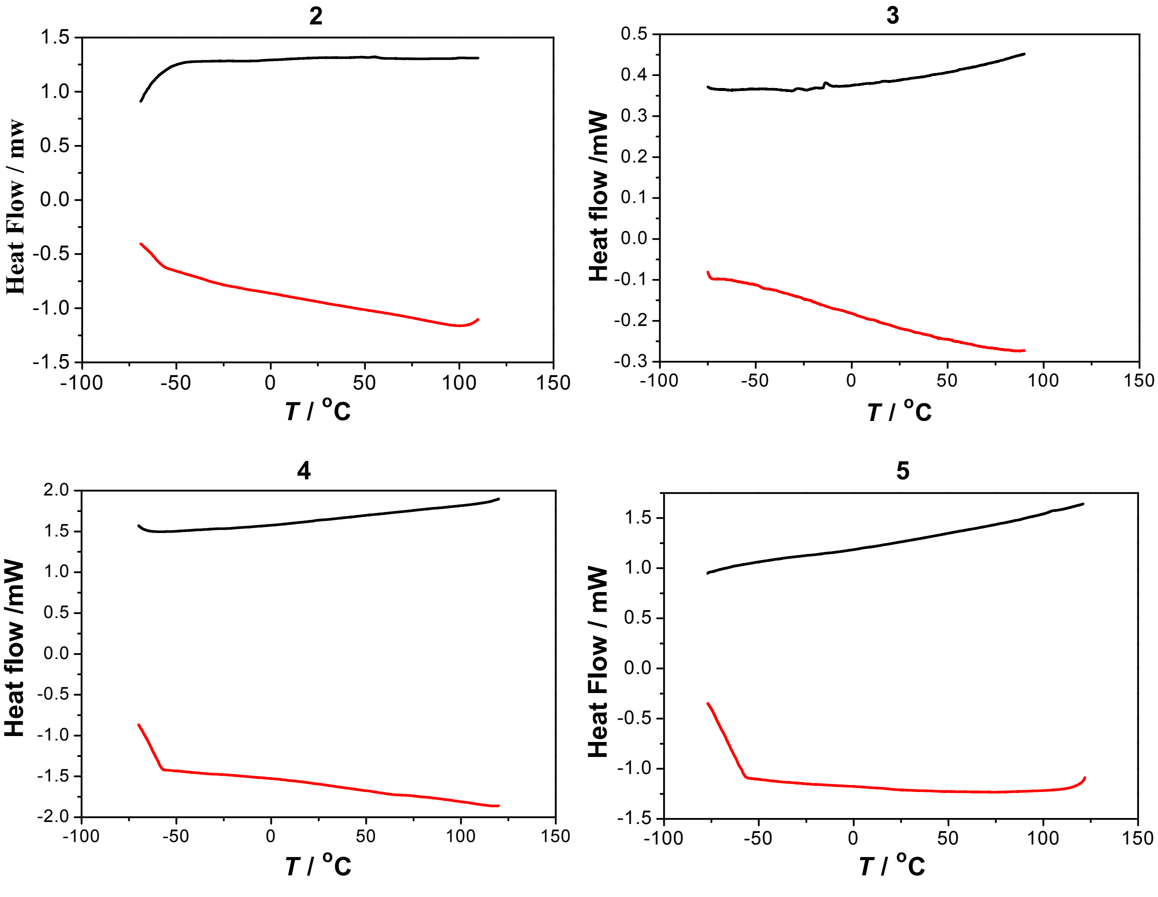

Fig. S2 DSC profiles of **2**–**5.**

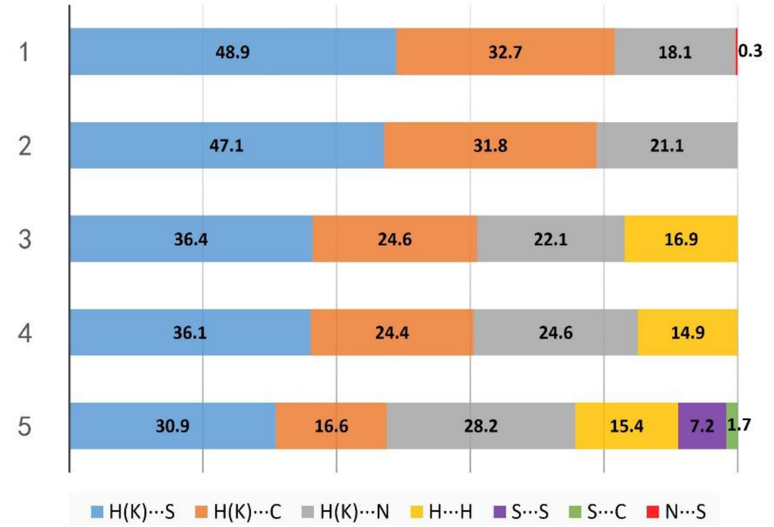

Fig. S3 The percentage of Hirshfeld surface associating with various intermolecular short contacts in **1**–**5**.

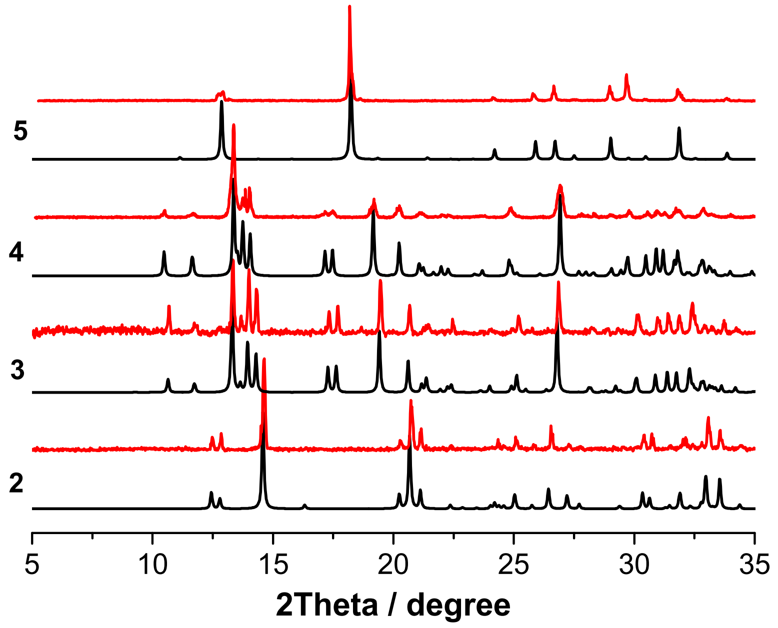

Fig. S4 Simulated (black) and experimental (red) powder XRD patterns of **2**–**5**.

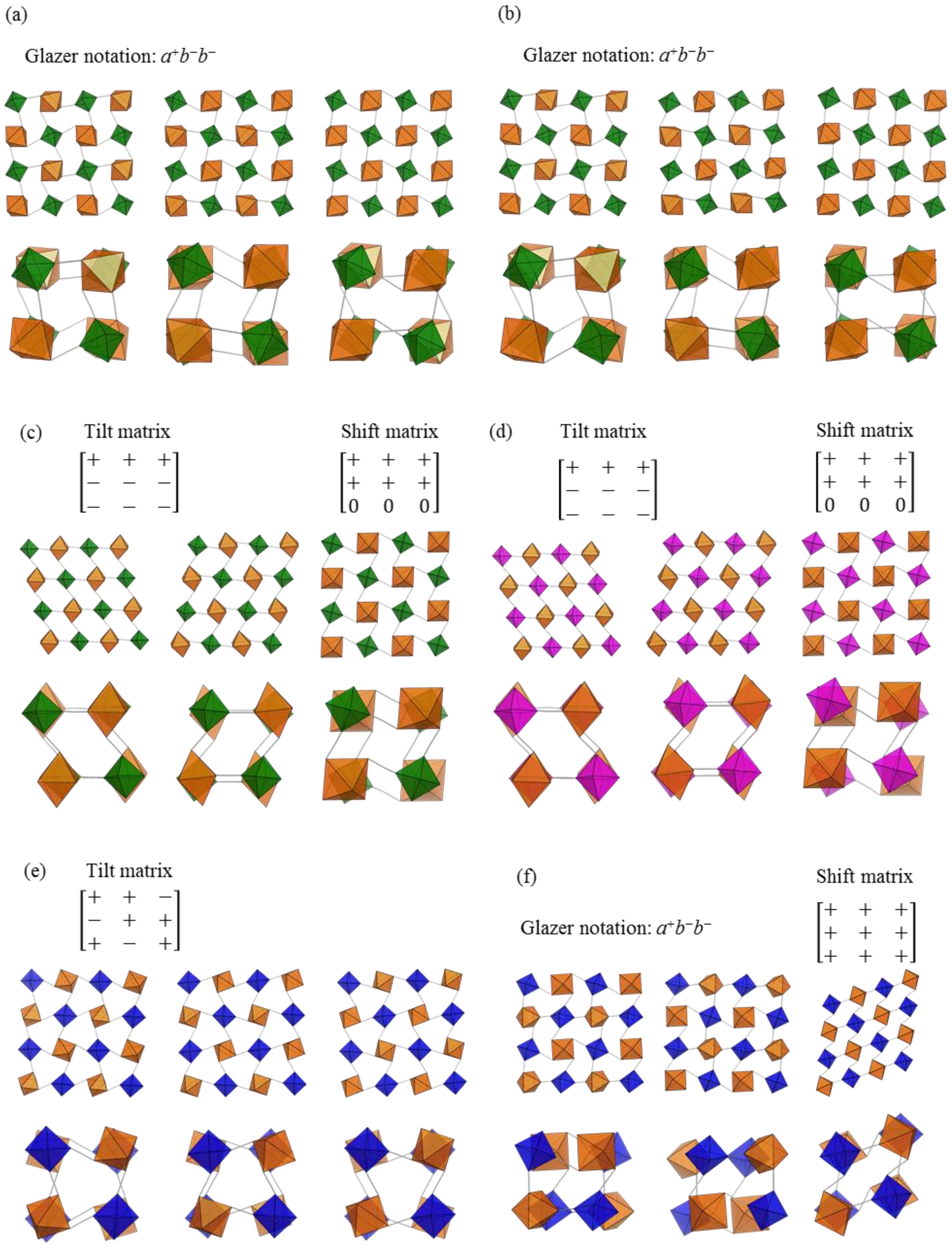

Fig. S5 Tilt and shift matrices of **1** (a), **2** (b), **3** (c), **4** (d) and **5** (e) and Cs[Cd(SCN)$_3$] (f). Single 4×4 octahedral layers and stacked 2×2 layers viewed normal to the three pseudo-cubic perovskite axes. The octahedra are distinguished by different colours: NiN$_6$ in green, CdS$_6$ in orange, MnN$_6$ in pink, and CdN$_6$ in blue.

References

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