## Synthesis, PtS-type structure, and anomalous mechanics of the $Cd(CN)_2$ precursor $Cd(NH_3)_2[Cd(CN)_4]$ Supplementary Information

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x (pre-heating)	x (post-heating)	a (Å)	<i>c</i> (Å)
0.115(11)		5.99036(7)	15.1934(3)
0.268(7)	0.4915(6)	5.98570(4)	15.22927(15)
0.860(15)	0.93766(4)	5.97559(7)	15.4339(2)
0.77(2)	0.92832(12)	5.97158(6)	15.4470(4)

**Table S1:** The variation in lattice parameters as a function of Cd content x in Cd(NH<sub>3</sub>)<sub>2</sub>[Cd<sub>x</sub>Hg<sub>1-x</sub>(CN)<sub>4</sub>] as determined by refinement of weight percentage of Cd(CN)<sub>2</sub> and Hg(CN)<sub>2</sub> after deammination (post-heating) or refinement of Hg occupancy on the pseudotetrahedral site for Cd(NH<sub>3</sub>)<sub>2</sub>[Cd<sub>x</sub>Hg<sub>1-x</sub>(CN)<sub>4</sub>] (pre-heating). The former is treated as the more reliable value because of a high correlation between Hg occupancy and atomic displacement parameters. The data are shown graphically in Figure 4 of the main text.



**Figure S1:** X-ray powder diffraction data for  $Cd(NH_3)_2[Cd_xHg_{1-x}(CN)_4]$  at 300 K. Data are shown in black, with Rietveld fit shown in red and the difference in grey. Green tick marks represent the calculated peak positions of  $Cd(NH_3)_2[Cd_xHg_{1-x}(CN)_4]$ . Refinement of the Hg occupancy on the pseudotetrahedral site reveals the value of *x* to give the formula  $Cd(NH_3)_2[Hg_{0.88}Cd_{0.12}(CN)_4]$ .



**Figure S2:** X-ray powder diffraction data collected (T = 300 K) before (top) and after (bottom) heating a sample of Cd(NH<sub>3</sub>)<sub>2</sub>[Cd<sub>x</sub>Hg<sub>1-x</sub>(CN)<sub>4</sub>] at 80 °C for 24 h. Data are shown in black, with Rietveld fit shown in red and the difference in grey. Green tick marks represent the calculated peak positions of Cd(NH<sub>3</sub>)<sub>2</sub>[Cd<sub>x</sub>Hg<sub>1-x</sub>(CN)<sub>4</sub>], red tick marks those of Cd(CN)<sub>2</sub> and blue tick marks those of Hg(CN)<sub>2</sub>. Refinement of the weight percentage of the Cd(CN)<sub>2</sub> product reveals the amount of Hg in the ammoniated intermediate. The value obtained from refinement of Hg occupancy on the pseudotetrahedral site gives a slightly different value, to give Cd(NH<sub>3</sub>)<sub>2</sub>[Hg<sub>0.73</sub>Cd<sub>0.27</sub>(CN)<sub>4</sub>]. The difference is attributed to the high correlation between the Hg occupancy and atomic displacement parameters on this site. The presence of small amounts of Cd(CN)<sub>2</sub> and Hg(CN)<sub>2</sub> in the top dataset reflects the ability of the Cd(NH<sub>3</sub>)<sub>2</sub>[Cd<sub>x</sub>Hg<sub>1-x</sub>(CN)<sub>4</sub>] structure to lose NH<sub>3</sub> under ambient conditions.



**Figure S3:** X-ray powder diffraction data collected (T = 300 K) before (top) and after (bottom) heating a sample of Cd(NH<sub>3</sub>)<sub>2</sub>[Cd<sub>x</sub>Hg<sub>1-x</sub>(CN)<sub>4</sub>] at 80 °C for 24 h. Data are shown in black, with Rietveld fit shown in red and the difference in grey. Green tick marks represent the calculated peak positions of Cd(NH<sub>3</sub>)<sub>2</sub>[Cd<sub>x</sub>Hg<sub>1-x</sub>(CN)<sub>4</sub>], red tick marks those of Cd(CN)<sub>2</sub> and blue tick marks those of Hg(CN)<sub>2</sub>. Refinement of the weight percentage of the Cd(CN)<sub>2</sub> product reveals the amount of Hg in the ammoniated intermediate. The value obtained from refinement of Hg occupancy on the pseudotetrahedral site gives a slightly different value, to give Cd(NH<sub>3</sub>)<sub>2</sub>[Cd<sub>0.86</sub> Hg<sub>0.14</sub>(CN)<sub>4</sub>]. The difference is attributed to the high correlation between the Hg occupancy and atomic displacement parameters on this site.

T (K)	a (Å)	<i>c</i> (Å)	r (Å)	θ (°)
300	5.97120(6)	15.4404(3)	5.7208	95.1316
290	5.96927(6)	15.4448(4)	5.7206	95.0966
280	5.96683(6)	15.4547(4)	5.7210	95.0370
270	5.96466(6)	15.4606(3)	5.7208	94.9941
260	5.96250(6)	15.4664(4)	5.7207	94.9522
250	5.96056(6)	15.4735(4)	5.7209	94.9075
240	5.95859(6)	15.4786(4)	5.7207	94.8697
230	5.95665(6)	15.4849(4)	5.7208	94.8279
220	5.95464(6)	15.4948(5)	5.7214	94.7723
210	5.95383(6)	15.4962(5)	5.7212	94.7591
200	5.95226(6)	15.5062(5)	5.7221	94.7070
190	5.95025(7)	15.5298(6)	5.7251	94.6010
180	5.95205(8)	15.5243(6)	5.7250	94.6388
170	5.94906(15)	15.5370(7)	5.7256	94.5643
160	5.94689(11)	15.5304(5)	5.7234	94.5666
150	5.94499(8)	15.5245(4)	5.7214	94.5701
140	5.94349(8)	15.5255(3)	5.7208	94.5524
130	5.94142(7)	15.5259(3)	5.7198	94.5306
120	5.93978(8)	15.5378(3)	5.7210	94.4710
110	5.93827(8)	15.5453(3)	5.7215	94.4292
100	5.93667(9)	15.5569(4)	5.7226	94.3713

**Table S2:** Variation in lattice parameters and XBUs with temperature as obtained from Pawley refinements of powder diffraction data for  $Cd(NH_3)_2[Cd(CN)_4]$ . This is shown graphically as the relative change with temperature in Figure 5 of the main text.



**Figure S4:** The relative change in length with temperature for the *a* and *c* lattice parameters of the Hg-rich  $Cd(NH_3)_2[Hg(CN)_4]$  are shown alongside the relative changes in XBU parameters,  $\theta$  and *r*. Their relationship to the lattice parameters is shown inset; the much greater temperature dependence of  $\theta$  relative to *r* is indicative that it is a geometric flexing mechanism that is responsible for the large flexibility and NTE observed in this system.

T (K)	a (Å)	<i>c</i> (Å)	r (Å)	θ (°)
300	5.9810(4)	15.1928(11)	5.6891	96.2318
290	5.98802(11)	15.2001(3)	5.6893	96.1862
280	5.98587(9)	15.2060(3)	5.6892	96.1437
270	5.98381(9)	15.2148(3)	5.6896	96.0912
260	5.98016(9)	15.2248(3)	5.6893	96.019
250	5.97797(8)	15.2333(3)	5.6896	95.9662
240	5.97579(8)	15.2416(3)	5.6898	95.9145
230	5.97385(7)	15.2473(3)	5.6898	95.8746
220	5.97169(7)	15.2558(3)	5.6901	95.822
210	5.97040(12)	15.2606(5)	5.6902	95.7918
200	5.96698(10)	15.2729(4)	5.6905	95.7135
190	5.96469(10)	15.2809(4)	5.6906	95.6616
180	5.96250(9)	15.2886(3)	5.6907	95.6121
170	5.95983(9)	15.2977(3)	5.6909	95.5524
160	5.95832(10)	15.3015(4)	5.6907	95.524
150	5.95578(9)	15.3096(4)	5.6908	95.4693
140	5.95466(10)	15.3130(4)	5.6907	95.4461
140	5.95336(9)	15.3175(4)	5.6908	95.4168
100	5.94865(9)	15.3387(4)	5.6919	95.2927

**Table S3:** Variation in lattice parameters and XBUs with temperature as obtained from Pawley refinements of powder diffraction data for  $Cd(NH_3)_2[Hg(CN)_4]$ . This is shown graphically as the relative change with temperature in Figure S4.