Compositional Dependence of Negative Thermal Expansion in the Prussian Blue Analogues $M^{II}Pt^{IV}(CN)_6$ ($M = Mn, Fe, Co, Ni, Cu, Zn, Cd$)

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Temperature Calibration

Figure S1. Data points (+) used to determine temperature calibration of high energy X-ray diffraction data. The line of equal temperatures is given for reference. The calibrated temperature is given by the relationship $T_c = 0.9127T_n + 23.445$

Structural Refinement

The strongest diffraction peak (and the associated errors) was found to strongly bias the refinements, giving rise to negative values of some carbon and nitrogen atomic displacement parameters. Strong peaks are known to affect the refinements in zeolites and, consequently, the strong peaks are often excluded. Excluding the first two diffraction peaks eliminated the negative U's for the C/N atoms in all but the Cd and Co phases and resulted in lower e.s.d's of the refined parameters. The intensities calculated for the first two peaks based on the refined structural model were in good agreement with the data and provided a comparable fit to that using the complete data (Figure S2, Table S1 and S2). Given the lower e.s.d's and comparable trends with temperature and composition, the reported values are based on the refinements of data in the range 1.7-11.5 2-theta, excluding the two lowest angle reflections.

Figure S2. Powder X-ray diffraction pattern refined for $\text{MnPt}(\text{CN})_6$ at 108 K including (a) and excluding the first two diffraction peaks (11-ID-B, APS). The data points (red crosses), model profile (blue line), reflection markers (vertical black lines) and residual (green lower line) are shown.

Table S1. Representative figures-of-merit for Rietveld refinement of powder X-ray diffraction data including the first two peaks for cubic $M^{II}Pt^{IV}(CN)_6$ (M = Mn, Fe, Co, Ni, Zn, Cd).

M^{II}		Mn	Fe	Co	Ni	Zn	Cd
2 θ range / °		1.1–11.7	1.2–11.5	1.2–11.5	1.1–11.5	1.1–11.5	1.2–11.5
100 K	wR_p	3.42	2.23	2.75	2.92	3.15	3.42
	R_p	2.19	1.67	2.03	2.22	2.12	2.45
	R_{F^2}	2.74	3.71	6.55	7.08	3.07	3.70
400 K	wR_p	2.78	2.31	2.66	2.86	3.15	3.23
	R_p	1.94	1.73	1.97	2.21	2.06	2.36
	R_{F^2}	3.56	4.94	7.57	8.27	3.79	4.41

Table S2. Representative figures-of-merit for Rietveld refinement of powder X-ray diffraction data excluding the first two peaks for cubic $M^{II}Pt^{IV}(CN)_6$ (M = Mn, Fe, Co, Ni, Zn, Cd).

M^{II}		Mn	Fe	Co	Ni	Zn	Cd
2 θ range / °		1.7–11.7	1.7–11.5	1.7–11.5	1.7–11.5	1.7–11.5	1.7–11.5
100 K	wR_p	2.38	1.92	2.26	2.55	1.96	2.08
	R_p	1.72	1.32	1.51	1.8	1.46	1.58
	R_{F^2}	8.52	3.55	11.18	6.16	7.95	8.70
400 K	wR_p	2.13	1.99	2.09	2.53	2.00	2.04
	R_p	1.59	1.36	1.46	1.81	1.42	1.53
	R_{F^2}	11.72	4.65	14.31	7.48	10.99	1.34

Figure S3. Increases in the atomic displacement parameters for MnPt(CN)₆ relative to the values at 100 K. The errors are given as ±1 e.s.d. of the refined parameters for the nitrogen atom (a) and the carbon atom (b and c). The errors for the Mn and Pt atoms are within the size of the data points. The larger errors relative to the scatter in the data trends indicate that the refinement e.s.d's contain a greater contribution from systematic errors than from random errors.

Table S3. Rates of change of atomic displacement parameters from Rietveld refinement of powder X-ray diffraction data excluding the first two peaks for cubic $M^{II}Pt^{IV}(CN)_6$ ($M = Mn, Fe, Co, Ni, Zn, Cd$).

M^{II}	$\frac{dU}{dT}(Pt)$ / $\times 10^6 \text{ \AA}^2 \text{ K}^{-1}$	$\frac{dU}{dT}(C_{\perp})$ / $\times 10^6 \text{ \AA}^2 \text{ K}^{-1}$	$\frac{dU}{dT}(C_{\parallel})$ / $\times 10^6 \text{ \AA}^2 \text{ K}^{-1}$	$\frac{dU}{dT}(N_{\perp})$ / $\times 10^6 \text{ \AA}^2 \text{ K}^{-1}$	$\frac{dU}{dT}(N_{\parallel})$ / $\times 10^6 \text{ \AA}^2 \text{ K}^{-1}$	$\frac{dU}{dT}(M)$ / $\times 10^6 \text{ \AA}^2 \text{ K}^{-1}$
Mn	3.42(2)	4.95(10)	2.95(21)	11.55(11)	2.93(19)	3.71(4)
Fe	3.265(12)	4.68(15)	3.60(31)	9.37(17)	2.74(31)	3.28(4)
Co	3.13(3)	4.16(30)	1.0(4)	8.79(35)	5.2(8)	2.23(6)
Ni	2.64(23)	4.39(30)	3.59(59)	6.93(11)	6.4(8)	2.12(4)
Zn	3.23(1)	5.18(13)	2.39(18)	8.17(9)	5.16(24)	3.58(2)
Cd	3.93(3)	7.57(19)	1.58(78)	13.06(32)	1.92(33)	4.98(5)

Figure S4 (above) and S5. Temperature dependence of the atomic displacement parameters ($\frac{dU}{dT}$'s) from the least-squares linear fits to the data for a) platinum, b) carbon perpendicular and parallel (inner bars) to the $Pt^{IV} \dots M^{II}$ axis, c) nitrogen perpendicular and parallel (inner bars) to the $Pt^{IV} \dots M^{II}$ axis and d) M^{II} , including (S4) and excluding (S5) the first two diffraction peaks.

Table S4. Range of bond lengths from Rietveld refinement of powder X-ray diffraction data excluding the first two peaks for cubic $M^{II}Pt^{IV}(CN)_6$ ($M = Mn, Fe, Co, Ni, Zn, Cd$).

M^{II}	$d_{M-N} / \text{\AA}$	$d_{Pt-C} / \text{\AA}$
Mn	2.215-2.209	2.124-2.092
Fe	2.160-2.163	2.008-2.017
Co	2.146-2.152	2.004-1.999
Ni	2.079-2.089	1.994-2.015
Zn	2.161-2.171	2.010-2.001
Cd	2.199-2.184	2.185-2.209

Figure S6. The coefficients of thermal expansion determined for $MPt(CN)_6$ in order of increasing cation size.

Table S5. Parameters from Rietveld refinement of **MnPt(CN)₆** (11-ID-B, APS).

T /K	a /Å	U _{Mn} /×10 ² Å ²	U _{Pt} /×10 ² Å ²	U _{C⊥} /×10 ² Å ²	U _{C∥} /×10 ² Å ²	U _{N⊥} /×10 ² Å ²	U _{N∥} /×10 ² Å ²	z _C	z _N
107.4	10.83295(20)	0.73(5)	0.342(20)	0.26(25)	2.8(5)	2.10(25)	0.60(32)	0.1887(8)	0.2956(6)
107.6	10.83295(20)	0.70(5)	0.324(19)	0.21(24)	2.8(5)	2.04(25)	0.57(31)	0.1886(8)	0.2955(6)
107.4	10.83285(20)	0.71(5)	0.329(19)	0.22(24)	2.8(5)	2.07(25)	0.61(31)	0.1889(8)	0.2956(6)
109.2	10.83315(20)	0.73(5)	0.342(20)	0.26(25)	2.8(5)	2.11(25)	0.60(32)	0.1887(8)	0.2956(6)
116.4	10.83244(20)	0.73(5)	0.365(20)	0.28(25)	2.8(5)	2.19(26)	0.61(32)	0.1887(8)	0.2955(6)
123.0	10.83210(20)	0.76(5)	0.385(20)	0.35(25)	2.8(5)	2.16(26)	0.61(32)	0.1888(8)	0.2956(6)
129.6	10.83112(20)	0.78(5)	0.412(20)	0.40(25)	2.8(5)	2.26(25)	0.70(31)	0.1887(8)	0.2956(6)
136.5	10.83111(20)	0.80(5)	0.432(20)	0.36(25)	2.9(5)	2.32(26)	0.78(32)	0.1886(8)	0.2955(6)
143.5	10.83050(20)	0.83(5)	0.462(20)	0.45(26)	2.8(5)	2.44(27)	0.70(33)	0.1886(8)	0.2955(6)
150.3	10.82991(20)	0.85(5)	0.478(20)	0.46(26)	3.0(5)	2.60(27)	0.74(33)	0.1885(8)	0.2954(6)
157.1	10.82938(20)	0.88(5)	0.503(21)	0.50(26)	3.0(5)	2.61(27)	0.71(33)	0.1886(8)	0.2957(6)
164.3	10.82891(20)	0.92(5)	0.533(21)	0.58(26)	2.9(5)	2.72(27)	0.77(33)	0.1887(8)	0.2955(6)
171.2	10.82826(20)	0.93(5)	0.556(21)	0.55(26)	3.0(5)	2.76(28)	0.81(33)	0.1887(8)	0.2956(6)
178.1	10.82816(20)	0.95(6)	0.586(22)	0.64(27)	2.9(5)	2.90(29)	0.78(34)	0.1886(9)	0.2955(6)
185.3	10.82725(20)	0.98(5)	0.609(21)	0.66(27)	2.9(5)	2.93(28)	0.88(34)	0.1886(8)	0.2956(6)
192.6	10.82658(20)	1.03(5)	0.636(21)	0.65(26)	3.1(5)	3.01(28)	0.88(34)	0.1886(8)	0.2956(6)
199.7	10.82608(20)	1.05(5)	0.651(21)	0.66(26)	3.0(5)	3.10(28)	0.91(34)	0.1885(8)	0.2955(6)
206.8	10.82602(20)	1.07(6)	0.687(22)	0.78(28)	3.1(5)	3.15(29)	0.81(34)	0.1886(9)	0.2956(6)
213.9	10.82504(20)	1.12(6)	0.709(22)	0.77(27)	3.0(5)	3.24(29)	1.02(34)	0.1883(9)	0.2955(6)
221.4	10.82451(20)	1.15(6)	0.729(22)	0.80(27)	3.1(5)	3.36(29)	0.96(34)	0.1885(9)	0.2957(6)
228.7	10.82391(20)	1.15(6)	0.751(22)	0.85(27)	3.1(5)	3.41(29)	0.98(34)	0.1884(9)	0.2955(6)
235.9	10.82342(20)	1.18(6)	0.780(22)	0.90(27)	3.1(5)	3.54(29)	0.88(34)	0.1884(8)	0.2955(6)
243.2	10.82339(20)	1.20(6)	0.805(22)	1.00(29)	3.2(5)	3.59(30)	0.93(35)	0.1885(9)	0.2956(6)
251.1	10.82254(20)	1.24(6)	0.831(22)	1.00(28)	3.2(5)	3.70(30)	1.12(35)	0.1884(9)	0.2955(6)
258.5	10.82246(20)	1.26(6)	0.858(23)	1.04(29)	3.3(5)	3.81(31)	1.0(4)	0.1884(9)	0.2955(6)
266.0	10.82196(20)	1.27(6)	0.880(23)	1.03(29)	3.2(5)	3.90(32)	1.1(4)	0.1885(9)	0.2956(7)
273.8	10.82157(20)	1.31(6)	0.903(23)	1.06(29)	3.2(5)	3.96(32)	1.0(4)	0.1885(9)	0.2956(7)
281.3	10.82100(20)	1.33(6)	0.926(23)	1.11(29)	3.3(5)	4.06(32)	1.1(4)	0.1885(9)	0.2956(6)
288.9	10.81998(20)	1.38(6)	0.950(23)	1.13(28)	3.4(5)	4.12(31)	1.2(4)	0.1885(9)	0.2955(6)
296.8	10.81945(20)	1.42(6)	0.978(23)	1.19(29)	3.3(5)	4.22(31)	1.2(4)	0.1885(9)	0.2954(6)
304.7	10.81975(20)	1.44(6)	0.997(23)	1.20(29)	3.3(5)	4.28(32)	1.1(4)	0.1886(9)	0.2956(7)
312.4	10.81951(20)	1.45(6)	1.013(24)	1.21(30)	3.2(5)	4.42(33)	1.2(4)	0.1890(9)	0.2957(7)
320.1	10.81936(20)	1.47(6)	1.037(24)	1.22(30)	3.3(5)	4.51(33)	1.1(4)	0.1890(9)	0.2958(7)
328.2	10.81900(20)	1.51(6)	1.067(24)	1.36(31)	3.2(5)	4.52(34)	1.4(4)	0.1887(9)	0.2957(7)
336.0	10.81885(20)	1.52(6)	1.088(24)	1.35(31)	3.4(5)	4.56(34)	1.2(4)	0.1888(9)	0.2959(7)
343.9	10.81871(20)	1.54(6)	1.108(25)	1.36(31)	3.4(5)	4.65(35)	1.3(4)	0.1890(9)	0.2959(7)
351.8	10.81787(20)	1.59(6)	1.134(24)	1.43(31)	3.2(5)	4.73(34)	1.3(4)	0.1886(9)	0.2954(7)
360.0	10.81828(20)	1.60(6)	1.151(25)	1.41(31)	3.5(5)	4.90(35)	1.3(4)	0.1886(9)	0.2956(7)
368.3	10.81790(20)	1.63(6)	1.177(25)	1.48(31)	3.4(5)	4.93(35)	1.5(4)	0.1886(9)	0.2956(7)
376.3	10.81759(20)	1.62(6)	1.198(25)	1.56(31)	3.4(5)	4.92(35)	1.5(4)	0.1885(9)	0.2955(7)
384.4	10.81729(20)	1.69(6)	1.222(25)	1.55(31)	3.4(5)	4.95(34)	1.4(4)	0.1884(9)	0.2954(7)
392.9	10.81742(20)	1.68(6)	1.237(25)	1.65(32)	3.6(5)	5.01(35)	1.5(4)	0.1883(9)	0.2956(7)
396.2	10.81669(20)	1.71(6)	1.245(25)	1.61(31)	3.7(5)	5.13(35)	1.5(4)	0.1886(9)	0.2956(7)

Table S6. Parameters from Rietveld refinement of **FePt(CN)₆** (11-ID-B, APS).

T /K	a /Å	U _{Fe} /×10 ² Å ²	U _{Pt} /×10 ² Å ²	U _{C[⊥]} /×10 ² Å ²	U _C /×10 ² Å ²	U _{N[⊥]} /×10 ² Å ²	U _N /×10 ² Å ²	z _C	z _N
109.7	10.66075(20)	0.50(5)	0.744(22)	0.50(26)	3.0(4)	1.72(24)	2.7(4)	0.1889(8)	0.2976(6)
107.9	10.66027(20)	0.50(5)	0.732(21)	0.53(25)	3.1(4)	1.66(23)	2.74(35)	0.1887(8)	0.2975(6)
107.1	10.66036(20)	0.50(5)	0.732(21)	0.54(26)	3.2(4)	1.64(24)	2.8(4)	0.1885(8)	0.2975(6)
107.3	10.66038(20)	0.50(5)	0.742(21)	0.46(25)	3.0(4)	1.69(24)	2.9(4)	0.1886(8)	0.2974(6)
106.8	10.66052(20)	0.50(5)	0.738(21)	0.42(25)	3.2(4)	1.74(24)	2.8(4)	0.1890(8)	0.2976(6)
107.3	10.66043(20)	0.50(5)	0.736(21)	0.49(25)	3.1(4)	1.69(23)	2.62(34)	0.1887(8)	0.2974(6)
109.8	10.66096(20)	0.51(5)	0.745(21)	0.47(26)	3.2(4)	1.69(24)	2.8(4)	0.1888(8)	0.2977(6)
116.4	10.66035(20)	0.51(5)	0.778(22)	0.47(26)	3.1(4)	1.86(25)	2.9(4)	0.1889(9)	0.2975(7)
122.9	10.66004(20)	0.56(5)	0.788(22)	0.48(26)	3.2(4)	1.91(25)	2.7(4)	0.1888(9)	0.2975(7)
129.6	10.65959(20)	0.57(5)	0.817(22)	0.61(26)	3.1(4)	1.91(25)	2.9(4)	0.1889(9)	0.2975(7)
136.5	10.65958(20)	0.58(5)	0.837(22)	0.60(27)	3.2(4)	1.92(25)	2.8(4)	0.1888(9)	0.2974(7)
143.6	10.65912(20)	0.60(5)	0.864(22)	0.63(27)	3.3(4)	2.04(26)	2.9(4)	0.1889(9)	0.2975(7)
150.3	10.65815(20)	0.63(5)	0.887(23)	0.73(27)	3.2(4)	2.06(25)	2.8(4)	0.1885(9)	0.2972(7)
157.1	10.65840(20)	0.66(5)	0.908(23)	0.68(28)	3.3(5)	2.12(26)	2.8(4)	0.1886(9)	0.2974(7)
164.3	10.65816(20)	0.68(5)	0.933(23)	0.79(28)	3.1(4)	2.15(26)	3.0(4)	0.1890(9)	0.2977(7)
171.1	10.65781(20)	0.70(5)	0.950(23)	0.81(28)	3.3(5)	2.25(26)	2.9(4)	0.1890(9)	0.2975(7)
178.1	10.65752(20)	0.74(5)	0.984(23)	0.80(28)	3.3(5)	2.41(27)	3.0(4)	0.1890(9)	0.2975(7)
185.3	10.65777(20)	0.74(5)	0.998(23)	0.74(28)	3.3(5)	2.41(27)	3.0(4)	0.1885(9)	0.2973(7)
192.6	10.65746(21)	0.77(5)	1.034(24)	0.91(29)	3.4(5)	2.49(28)	3.0(4)	0.1887(9)	0.2975(7)
199.7	10.65649(20)	0.80(5)	1.041(24)	0.83(29)	3.5(5)	2.54(28)	3.1(4)	0.1886(9)	0.2975(7)
206.8	10.65673(20)	0.82(5)	1.072(24)	0.92(29)	3.4(5)	2.57(28)	3.1(4)	0.1888(9)	0.2975(7)
213.9	10.65583(20)	0.85(5)	1.094(24)	0.91(29)	3.4(5)	2.65(28)	3.1(4)	0.1888(9)	0.2976(7)
221.4	10.65549(20)	0.87(5)	1.117(24)	1.01(29)	3.4(5)	2.75(28)	3.1(4)	0.1887(9)	0.2974(7)
228.6	10.65565(20)	0.88(5)	1.125(24)	1.01(29)	3.5(5)	2.80(28)	3.2(4)	0.1885(9)	0.2973(7)
235.9	10.65534(20)	0.91(5)	1.163(25)	1.06(30)	3.6(5)	2.96(29)	3.3(4)	0.1886(9)	0.2972(7)
243.5	10.65445(20)	0.95(5)	1.196(25)	1.21(30)	3.3(5)	2.81(28)	3.2(4)	0.1884(9)	0.2971(7)
251.2	10.65468(21)	0.96(6)	1.204(25)	1.19(31)	3.5(5)	3.00(30)	3.2(4)	0.1889(9)	0.2974(7)
258.6	10.65442(20)	0.98(5)	1.236(25)	1.15(30)	3.6(5)	3.12(30)	3.2(4)	0.1886(9)	0.2973(7)
266.0	10.65359(21)	1.01(5)	1.256(25)	1.23(30)	3.6(5)	3.20(30)	3.3(4)	0.1885(9)	0.2972(7)
273.8	10.65321(20)	1.02(5)	1.277(25)	1.20(30)	3.6(5)	3.27(30)	3.4(4)	0.1888(9)	0.2974(7)
281.3	10.65298(21)	1.07(6)	1.305(25)	1.34(31)	3.6(5)	3.20(30)	3.5(4)	0.1883(9)	0.2971(7)
288.8	10.65334(21)	1.09(6)	1.333(26)	1.31(31)	3.5(5)	3.42(31)	3.4(4)	0.1883(9)	0.2969(7)
296.4	10.65245(21)	1.13(6)	1.350(26)	1.42(32)	3.7(5)	3.49(31)	3.4(4)	0.1888(10)	0.2973(7)
304.7	10.65211(20)	1.15(6)	1.369(25)	1.41(31)	3.8(5)	3.43(30)	3.5(4)	0.1883(10)	0.2970(7)
312.4	10.65198(21)	1.16(6)	1.392(26)	1.41(32)	3.7(5)	3.61(31)	3.5(4)	0.1887(10)	0.2972(7)
320.1	10.65293(21)	1.18(6)	1.411(26)	1.45(32)	3.5(5)	3.74(32)	3.3(4)	0.1890(10)	0.2973(7)
328.2	10.65289(21)	1.19(6)	1.414(27)	1.41(33)	3.9(5)	3.68(33)	3.3(4)	0.1893(10)	0.2977(8)
336	10.65333(21)	1.20(6)	1.431(27)	1.50(33)	3.7(5)	3.72(33)	3.4(4)	0.1890(10)	0.2974(8)
343.9	10.65418(21)	1.19(6)	1.454(27)	1.58(34)	3.7(5)	3.71(33)	3.4(4)	0.1893(10)	0.2976(8)
351.7	10.65431(21)	1.24(6)	1.465(27)	1.52(33)	3.7(5)	3.92(34)	3.3(4)	0.1895(10)	0.2977(8)
360.0	10.65434(21)	1.26(6)	1.502(27)	1.58(34)	3.6(5)	4.06(34)	3.2(4)	0.1892(10)	0.2972(8)
368.3	10.65405(21)	1.27(6)	1.515(27)	1.70(34)	3.7(5)	3.92(33)	3.4(4)	0.1888(10)	0.2972(8)
376.3	10.65414(21)	1.28(6)	1.531(27)	1.57(33)	3.8(5)	4.09(34)	3.4(4)	0.1890(10)	0.2973(8)

Table S7. Parameters from Rietveld refinement of $\text{CoPt}(\text{CN})_6$ (11-ID-B, APS).

T /K	a /Å	U_{Co} / $\times 10^2 \text{Å}^2$	U_{Pt} / $\times 10^2 \text{Å}^2$	$U_{\text{C}\perp}$ / $\times 10^2 \text{Å}^2$	$U_{\text{C}\parallel}$ / $\times 10^2 \text{Å}^2$	$U_{\text{N}\perp}$ / $\times 10^2 \text{Å}^2$	$U_{\text{N}\parallel}$ / $\times 10^2 \text{Å}^2$	z_{C}	z_{N}
106.5	10.56885(21)	-0.54(5)	0.842(24)	2.28(33)	-0.9(4)	0.79(23)	3.5(4)	0.1880(8)	0.2955(7)
107.3	10.56769(21)	-0.53(5)	0.845(23)	2.32(32)	-0.8(4)	0.78(22)	3.4(4)	0.1876(7)	0.2951(6)
107.1	10.56763(21)	-0.50(5)	0.842(23)	2.20(31)	-0.8(4)	0.89(22)	3.5(4)	0.1880(7)	0.2953(6)
109.8	10.56811(21)	-0.52(5)	0.849(24)	2.11(32)	-0.6(4)	0.91(23)	3.6(4)	0.1879(8)	0.2953(7)
116.4	10.56751(21)	-0.49(5)	0.886(24)	2.22(32)	-0.6(4)	1.00(23)	3.5(4)	0.1879(8)	0.2951(7)
123.5	10.56730(21)	-0.48(5)	0.906(24)	2.26(32)	-0.7(4)	0.90(23)	3.7(4)	0.1877(8)	0.2953(7)
130.1	10.56711(21)	-0.46(5)	0.924(24)	2.40(32)	-0.7(4)	0.95(23)	3.6(4)	0.1878(8)	0.2954(7)
136.8	10.56722(22)	-0.45(5)	0.951(24)	2.34(33)	-0.7(4)	1.06(23)	3.8(4)	0.1877(8)	0.2951(7)
143.8	10.56695(22)	-0.43(5)	0.969(24)	2.45(33)	-0.7(4)	1.03(23)	3.9(4)	0.1877(8)	0.2955(7)
150.6	10.56722(22)	-0.42(5)	0.994(25)	2.47(34)	-0.6(4)	1.18(24)	3.8(4)	0.1878(8)	0.2953(7)
157.4	10.56693(21)	-0.39(5)	1.026(25)	2.59(34)	-0.7(4)	1.15(24)	3.8(4)	0.1877(8)	0.2953(7)
164.5	10.56662(21)	-0.38(5)	1.042(25)	2.49(34)	-0.7(4)	1.28(25)	3.9(5)	0.1877(8)	0.2952(7)
171.7	10.56693(21)	-0.37(5)	1.074(26)	2.6(4)	-0.6(4)	1.28(25)	4.0(5)	0.1877(8)	0.2954(7)
178.7	10.56694(22)	-0.36(5)	1.095(26)	2.7(4)	-0.6(4)	1.31(25)	3.9(5)	0.1877(8)	0.2952(7)
185.6	10.56598(22)	-0.33(5)	1.117(26)	2.7(4)	-0.5(4)	1.41(25)	4.1(5)	0.1877(8)	0.2952(7)
192.9	10.56525(22)	-0.31(5)	1.142(26)	2.6(4)	-0.4(4)	1.56(26)	4.2(5)	0.1878(8)	0.2954(7)
200.0	10.56436(22)	-0.30(5)	1.165(26)	2.8(4)	-0.4(4)	1.49(25)	3.9(5)	0.1873(8)	0.2950(7)
207.1	10.56466(22)	-0.28(5)	1.186(26)	2.9(4)	-0.6(4)	1.51(26)	4.2(5)	0.1874(8)	0.2950(7)
214.2	10.56443(22)	-0.29(5)	1.194(26)	2.9(4)	-0.6(4)	1.61(26)	4.0(5)	0.1872(8)	0.2948(7)
222.0	10.56379(23)	-0.26(5)	1.217(26)	2.9(4)	-0.4(4)	1.64(26)	4.0(5)	0.1874(8)	0.2950(7)
229.2	10.56358(23)	-0.23(5)	1.251(26)	2.9(4)	-0.4(4)	1.72(26)	4.1(5)	0.1874(8)	0.2949(7)
236.8	10.56381(23)	-0.22(5)	1.287(27)	3.1(4)	-0.5(4)	1.75(26)	4.0(5)	0.1870(8)	0.2946(7)
244.1	10.56379(23)	-0.19(5)	1.304(27)	3.1(4)	-0.6(4)	1.83(27)	4.4(5)	0.1873(8)	0.2949(7)
252.1	10.56353(23)	-0.19(5)	1.334(27)	3.2(4)	-0.4(4)	1.89(27)	4.2(5)	0.1871(9)	0.2948(7)
259.5	10.56341(23)	-0.17(5)	1.353(27)	3.1(4)	-0.4(4)	1.95(27)	4.6(5)	0.1873(9)	0.2947(8)
267.2	10.56337(23)	-0.15(5)	1.371(27)	3.2(4)	-0.3(4)	2.06(28)	4.4(5)	0.1874(9)	0.2947(8)
274.7	10.56310(23)	-0.13(5)	1.401(28)	3.4(4)	-0.4(4)	2.05(27)	4.1(5)	0.1872(9)	0.2948(7)
282.5	10.56288(23)	-0.09(5)	1.421(28)	3.4(4)	-0.5(4)	2.08(28)	4.6(5)	0.1874(9)	0.2947(8)
290.4	10.56302(23)	-0.09(5)	1.444(28)	3.4(4)	-0.5(4)	2.18(28)	4.5(5)	0.1869(9)	0.2943(8)
298.3	10.56287(23)	-0.08(5)	1.471(28)	3.6(4)	-0.4(4)	2.16(28)	4.5(5)	0.1871(9)	0.2946(8)
306.0	10.56267(23)	-0.04(5)	1.495(28)	3.5(4)	-0.3(4)	2.27(28)	4.5(5)	0.1870(9)	0.2946(8)
314.0	10.56260(23)	-0.04(5)	1.516(29)	3.7(4)	-0.3(5)	2.34(29)	4.4(5)	0.1869(9)	0.2943(8)
322.1	10.56251(23)	-0.03(5)	1.540(29)	3.6(4)	-0.4(4)	2.34(29)	4.4(5)	0.1868(9)	0.2945(8)
329.8	10.56222(23)	0.00(5)	1.569(29)	3.9(4)	-0.4(4)	2.35(29)	4.4(5)	0.1868(9)	0.2942(8)
338.0	10.56211(23)	0.02(5)	1.594(29)	3.7(4)	-0.4(4)	2.43(29)	4.5(5)	0.1869(9)	0.2943(8)
345.8	10.56188(23)	0.03(5)	1.614(29)	3.9(4)	-0.4(5)	2.36(29)	4.6(5)	0.1865(9)	0.2941(8)
353.7	10.56286(23)	0.03(6)	1.632(30)	3.8(4)	-0.5(5)	2.49(30)	4.6(5)	0.1868(9)	0.2941(8)
361.7	10.56334(23)	0.05(6)	1.635(30)	3.9(4)	-0.3(5)	2.51(30)	4.7(5)	0.1869(9)	0.2943(8)
370.3	10.56377(23)	0.05(6)	1.646(30)	4.1(4)	-0.5(5)	2.56(30)	4.3(5)	0.1869(9)	0.2940(8)
378.3	10.56403(23)	0.06(6)	1.669(30)	4.1(4)	-0.4(5)	2.57(30)	4.1(5)	0.1866(9)	0.2942(8)
386.4	10.56468(23)	0.05(6)	1.688(30)	4.2(4)	-0.4(5)	2.63(30)	4.3(5)	0.1867(9)	0.2941(8)
394.2	10.56410(23)	0.08(6)	1.709(30)	4.2(4)	-0.5(5)	2.66(30)	4.5(5)	0.1865(9)	0.2937(8)
395.9	10.56391(23)	0.09(6)	1.725(31)	4.2(4)	-0.5(5)	2.66(30)	4.6(5)	0.1868(9)	0.2939(8)

Table S8. Parameters from Rietveld refinement of **NiPt(CN)₆** (11-ID-B, APS).

T /K	<i>a</i> /Å	U _{Ni} /×10 ² Å ²	U _{Pt} /×10 ² Å ²	U _{C⊥} /×10 ² Å ²	U _{C∥} /×10 ² Å ²	U _{N⊥} /×10 ² Å ²	U _{N∥} /×10 ² Å ²	z _C	z _N
107.4	10.46329(27)	-0.92(7)	1.23(4)	1.0(5)	2.0(6)	1.7(4)	5.0(6)	0.1923(15)	0.3005(13)
107.4	10.46343(26)	-0.92(7)	1.24(4)	1.0(5)	1.9(6)	1.7(4)	5.1(6)	0.1921(15)	0.3004(13)
107.4	10.46736(26)	-0.97(7)	1.25(4)	0.9(5)	2.2(7)	1.4(4)	6.1(7)	0.1905(16)	0.3007(14)
110.1	10.46872(26)	-0.98(7)	1.28(4)	0.9(5)	2.2(7)	1.3(5)	6.8(7)	0.1902(17)	0.3014(15)
116.9	10.47020(26)	-0.98(7)	1.29(4)	0.9(5)	2.2(7)	1.2(5)	7.2(7)	0.1900(17)	0.3019(15)
123.5	10.47084(27)	-0.98(8)	1.32(4)	0.9(6)	2.2(7)	1.2(5)	7.4(8)	0.1893(18)	0.3017(16)
130.1	10.47150(27)	-1.00(8)	1.35(4)	0.5(6)	2.6(7)	1.4(5)	8.5(8)	0.1905(18)	0.3036(17)
137.1	10.47196(28)	-0.97(8)	1.37(4)	0.1(6)	3.3(8)	1.7(4)	8.6(9)	0.1914(18)	0.3048(17)
143.9	10.47204(28)	-0.96(8)	1.39(4)	0.2(6)	3.2(8)	1.7(5)	9.0(9)	0.1912(18)	0.3050(17)
151.7	10.47220(28)	-0.98(8)	1.40(4)	0.2(6)	3.3(8)	1.6(4)	8.7(9)	0.1913(18)	0.3051(17)
159.0	10.47220(27)	-0.95(8)	1.43(4)	0.2(6)	3.3(8)	1.9(5)	8.4(9)	0.1913(18)	0.3043(17)
164.8	10.47130(27)	-0.93(8)	1.45(4)	0.4(6)	3.1(8)	1.9(5)	8.2(8)	0.1912(18)	0.3038(17)
171.7	10.46984(26)	-0.86(8)	1.48(4)	1.1(6)	2.3(7)	1.6(5)	7.9(8)	0.1901(18)	0.3017(16)
179.0	10.46856(26)	-0.86(7)	1.48(4)	1.2(6)	2.1(7)	1.6(5)	7.5(7)	0.1906(17)	0.3017(16)
186.0	10.46807(25)	-0.82(7)	1.51(4)	1.3(6)	2.2(7)	1.8(5)	6.9(7)	0.1910(17)	0.3013(15)
193.0	10.46692(26)	-0.80(7)	1.53(4)	1.4(6)	1.9(6)	1.9(5)	6.7(7)	0.1915(16)	0.3009(15)
200.3	10.46519(26)	-0.76(7)	1.53(4)	1.4(5)	2.1(6)	2.1(5)	6.2(7)	0.1918(16)	0.3009(14)
207.4	10.46500(26)	-0.74(7)	1.57(4)	1.4(5)	2.3(7)	2.2(5)	5.8(7)	0.1917(16)	0.3005(14)
214.8	10.46439(26)	-0.74(7)	1.59(4)	1.4(5)	2.1(6)	2.3(5)	6.1(7)	0.1925(16)	0.3010(14)
222.0	10.46373(27)	-0.71(7)	1.62(4)	1.5(6)	2.3(6)	2.4(5)	6.0(7)	0.1918(17)	0.3005(14)
229.2	10.46334(27)	-0.70(7)	1.64(4)	1.5(6)	2.5(7)	2.4(5)	6.1(7)	0.1921(17)	0.3005(15)
236.8	10.46307(27)	-0.66(7)	1.66(4)	1.5(6)	2.5(7)	2.6(5)	5.8(7)	0.1920(17)	0.3002(14)
244.2	10.46274(27)	-0.65(7)	1.68(4)	1.6(6)	2.3(6)	2.6(5)	6.5(7)	0.1927(17)	0.3009(15)
251.5	10.46239(27)	-0.61(7)	1.72(4)	1.7(6)	2.4(7)	2.6(5)	5.9(7)	0.1921(17)	0.3005(14)
259.2	10.46234(27)	-0.61(7)	1.74(4)	1.8(6)	2.6(7)	2.7(5)	6.1(7)	0.1919(17)	0.3002(14)
266.9	10.46213(27)	-0.60(7)	1.76(4)	1.7(6)	2.5(7)	2.8(5)	6.2(7)	0.1924(17)	0.3008(15)
274.4	10.46205(27)	-0.57(7)	1.78(4)	1.7(6)	2.9(7)	2.9(5)	6.0(7)	0.1926(17)	0.3006(15)
281.9	10.46192(27)	-0.55(7)	1.81(4)	1.8(6)	2.6(7)	2.9(5)	6.4(7)	0.1923(17)	0.3005(15)
289.8	10.46197(27)	-0.55(7)	1.84(4)	1.8(6)	2.7(7)	3.0(5)	5.8(7)	0.1921(17)	0.3005(15)
297.4	10.46179(27)	-0.51(8)	1.85(4)	1.9(6)	2.5(7)	3.0(5)	6.5(7)	0.1926(17)	0.3007(15)
305.1	10.46166(27)	-0.51(7)	1.86(4)	1.7(6)	2.8(7)	3.1(6)	6.3(7)	0.1923(17)	0.3003(15)
312.8	10.46157(27)	-0.47(8)	1.91(4)	2.0(6)	2.6(7)	3.1(6)	6.4(7)	0.1923(17)	0.3004(15)
320.8	10.46154(27)	-0.47(8)	1.90(4)	1.9(6)	2.7(7)	3.2(6)	6.5(7)	0.1925(17)	0.3007(15)
328.8	10.46150(27)	-0.45(8)	1.93(4)	2.0(6)	2.7(7)	3.2(6)	6.4(7)	0.1926(17)	0.3006(15)
336.6	10.46084(27)	-0.43(8)	1.96(4)	2.0(6)	2.7(7)	3.3(6)	6.8(7)	0.1927(17)	0.3007(15)
344.5	10.46091(27)	-0.40(8)	1.98(4)	2.0(6)	2.6(7)	3.3(6)	6.5(7)	0.1923(17)	0.3004(15)
352.8	10.46060(27)	-0.39(8)	2.01(4)	2.1(6)	2.9(7)	3.3(6)	6.7(7)	0.1929(18)	0.3009(15)
360.7	10.46144(27)	-0.39(8)	2.04(4)	2.1(6)	2.8(7)	3.4(6)	6.6(7)	0.1924(18)	0.3007(15)
368.7	10.46188(27)	-0.36(8)	2.06(4)	2.2(6)	2.8(7)	3.4(6)	6.3(7)	0.1920(18)	0.3003(15)
377.0	10.46138(27)	-0.36(8)	2.09(4)	2.2(6)	2.8(7)	3.4(6)	6.8(7)	0.1928(18)	0.3006(16)
385.1	10.46234(27)	-0.38(8)	2.10(4)	2.2(6)	2.8(7)	3.5(6)	6.7(7)	0.1926(18)	0.3003(15)
393.5	10.46352(27)	-0.37(8)	2.09(4)	2.3(6)	2.7(7)	3.5(6)	6.1(7)	0.1917(18)	0.2995(15)
395.9	10.46438(27)	-0.39(8)	2.08(4)	2.6(6)	2.3(7)	3.3(6)	6.2(7)	0.1921(17)	0.2997(15)

Table S9. Parameters from Rietveld refinement of **CuPt(CN)₆** (11-ID-B, APS).

T /K	a /Å	c /Å	V /Å ³	U_{Cu} /×10 ² Å ²	U_{Pt} /×10 ² Å ²	U_{Cl/C2} /×10 ² Å ²	U_{N1/N2} /×10 ² Å ²	z_{Cl}	z_{N1}	x_{C2}/y_{C2} at (x,y,0)	x_{N2}/y_{N2} at (x,y,0)
106.8	7.3389(17)	11.052(4)	595.27(30)	−0.7	0.9	0.25	0.25	0.21	0.28	0.21	0.30
107.1	7.3388(17)	11.053(4)	595.28(30)								
109.8	7.3386(17)	11.053(4)	595.25(30)								
116.4	7.3385(17)	11.053(4)	595.25(30)								
122.9	7.3381(17)	11.054(4)	595.20(30)								
129.9	7.3379(17)	11.054(4)	595.20(31)								
136.8	7.3376(17)	11.054(4)	595.17(31)								
143.6	7.3374(17)	11.054(4)	595.14(31)								
150.3	7.3371(17)	11.055(4)	595.12(31)								
157.4	7.3367(17)	11.055(4)	595.08(31)								
164.3	7.3369(17)	11.056(4)	595.14(31)								
171.1	7.3362(17)	11.056(4)	595.02(31)								
178.4	7.3364(17)	11.057(4)	595.09(31)								
185.6	7.3362(17)	11.057(4)	595.06(31)								
192.6	7.3360(17)	11.057(4)	595.06(31)								
200.0	7.3356(17)	11.057(4)	595.01(31)								
207.1	7.3353(17)	11.058(5)	594.98(31)								
214.2	7.3350(17)	11.058(5)	594.93(31)								
221.4	7.3347(17)	11.058(5)	594.92(31)								
228.9	7.3344(18)	11.058(5)	594.87(32)								
236.5	7.3339(18)	11.058(5)	594.79(32)								
243.8	7.3338(18)	11.059(5)	594.81(32)								
251.5	7.3334(18)	11.059(5)	594.74(32)								
258.9	7.3333(18)	11.060(5)	594.76(32)								
266.3	7.3328(18)	11.060(5)	594.68(32)								
274.1	7.3327(18)	11.061(5)	594.75(32)								
281.9	7.3323(18)	11.063(5)	594.77(32)								
289.5	7.3320(18)	11.064(5)	594.79(32)								
297.1	7.3314(18)	11.065(5)	594.74(32)								
305.0	7.3312(18)	11.066(5)	594.75(32)								
312.7	7.3308(18)	11.067(5)	594.72(32)								
320.4	7.3305(18)	11.067(5)	594.69(32)								
328.5	7.3303(18)	11.067(5)	594.68(32)								
336.7	7.3299(18)	11.067(5)	594.60(32)								
344.5	7.3298(18)	11.068(5)	594.62(32)								
352.4	7.3292(18)	11.067(5)	594.48(32)								
360.7	7.3293(18)	11.067(5)	594.52(32)								
368.6	7.3291(18)	11.068(5)	594.50(32)								
376.7	7.3290(18)	11.068(5)	594.50(32)								
385.1	7.3289(18)	11.068(5)	594.48(32)								
393.5	7.3287(18)	11.068(5)	594.45(32)								
395.2	7.3286(18)	11.068(5)	594.44(32)								
395.2	7.3287(18)	11.068(5)	594.44(33)								

NB. For the tetragonal CuPt(CN)₆ phase full unconstrained refinement of the structure as a function of temperature was not possible. The parameters obtained from careful refinement at 106.8 K were used in subsequent refinements.

Table S10. Parameters from Rietveld refinement of **ZnPt(CN)₆** (11-ID-B, APS).

T /K	a /Å	U _{Zn} /×10 ² Å ²	U _{Pt} /×10 ² Å ²	U _{C[⊥]} /×10 ² Å ²	U _C /×10 ² Å ²	U _{N[⊥]} /×10 ² Å ²	U _N /×10 ² Å ²	z _C	z _N
107.4	10.65436(14)	-0.133(30)	0.171(14)	0.77(20)	0.27(31)	0.95(17)	1.34(26)	0.1886(6)	0.2972(5)
107.4	10.65373(14)	-0.117(29)	0.175(14)	0.76(19)	0.25(30)	0.98(17)	1.42(25)	0.1886(6)	0.2971(5)
107.4	10.65382(14)	-0.120(29)	0.180(14)	0.83(19)	0.24(30)	0.93(16)	1.41(25)	0.1885(6)	0.2972(5)
109.8	10.65376(14)	-0.103(29)	0.186(14)	0.82(19)	0.34(30)	0.99(17)	1.39(25)	0.1885(6)	0.2971(5)
116.4	10.65340(15)	-0.082(29)	0.210(14)	0.84(19)	0.26(30)	1.01(17)	1.42(25)	0.1885(6)	0.2971(5)
123.2	10.65321(15)	-0.059(29)	0.228(14)	0.89(19)	0.26(30)	1.08(17)	1.49(25)	0.1886(6)	0.2971(5)
130.1	10.65290(15)	-0.030(29)	0.253(14)	0.92(20)	0.31(30)	1.12(17)	1.54(26)	0.1885(6)	0.2971(5)
136.8	10.65263(15)	-0.001(29)	0.272(14)	0.94(19)	0.37(30)	1.20(17)	1.43(25)	0.1885(6)	0.2970(5)
143.5	10.65271(15)	0.007(30)	0.294(14)	1.00(20)	0.37(31)	1.24(18)	1.53(27)	0.1885(6)	0.2971(5)
150.6	10.65299(15)	0.027(30)	0.315(14)	0.95(21)	0.41(31)	1.34(18)	1.47(27)	0.1885(6)	0.2971(5)
157.4	10.65233(15)	0.058(31)	0.341(15)	1.00(21)	0.33(31)	1.37(18)	1.59(27)	0.1885(6)	0.2970(5)
164.3	10.65184(15)	0.094(31)	0.368(15)	1.01(21)	0.35(31)	1.46(18)	1.60(27)	0.1887(6)	0.2971(5)
171.4	10.65154(15)	0.116(31)	0.389(15)	1.07(21)	0.49(31)	1.52(19)	1.67(27)	0.1885(6)	0.2970(5)
178.6	10.65160(15)	0.142(31)	0.409(15)	1.15(21)	0.42(31)	1.54(19)	1.71(27)	0.1885(6)	0.2970(5)
185.6	10.65087(15)	0.166(31)	0.434(15)	1.15(21)	0.50(31)	1.63(19)	1.78(28)	0.1884(6)	0.2972(5)
192.6	10.65056(15)	0.194(32)	0.454(15)	1.18(22)	0.52(32)	1.71(19)	1.81(28)	0.1885(6)	0.2970(5)
200.0	10.65048(16)	0.218(32)	0.479(15)	1.18(22)	0.58(32)	1.74(19)	1.74(28)	0.1883(6)	0.2970(5)
207.1	10.65002(16)	0.243(32)	0.504(15)	1.23(22)	0.65(32)	1.83(20)	1.66(28)	0.1882(6)	0.2969(5)
214.3	10.64983(16)	0.263(32)	0.524(15)	1.29(22)	0.53(32)	1.83(20)	1.81(28)	0.1881(6)	0.2969(5)
221.4	10.64934(16)	0.293(32)	0.549(15)	1.37(22)	0.55(32)	1.86(19)	1.93(28)	0.1882(6)	0.2970(5)
229.2	10.64904(16)	0.326(32)	0.576(15)	1.42(22)	0.56(32)	1.92(20)	1.95(28)	0.1882(6)	0.2969(5)
236.5	10.64916(16)	0.345(33)	0.604(16)	1.43(23)	0.61(33)	2.04(21)	2.10(30)	0.1882(6)	0.2970(5)
243.8	10.64838(16)	0.377(32)	0.628(15)	1.51(22)	0.64(32)	2.09(20)	2.14(29)	0.1880(6)	0.2967(5)
251.5	10.64815(16)	0.400(32)	0.642(16)	1.56(23)	0.62(32)	2.13(20)	2.17(29)	0.1880(6)	0.2970(5)
258.9	10.64824(16)	0.422(34)	0.673(16)	1.56(24)	0.60(33)	2.18(21)	2.16(30)	0.1881(7)	0.2970(5)
266.3	10.64760(16)	0.457(33)	0.690(16)	1.61(23)	0.63(32)	2.28(21)	2.19(30)	0.1880(6)	0.2969(5)
273.8	10.64722(16)	0.487(33)	0.715(16)	1.70(23)	0.63(32)	2.30(21)	2.19(30)	0.1879(6)	0.2968(5)
281.6	10.64696(16)	0.507(33)	0.736(16)	1.69(24)	0.73(33)	2.37(21)	2.18(30)	0.1879(6)	0.2968(5)
289.4	10.64651(16)	0.529(34)	0.759(16)	1.73(24)	0.64(33)	2.44(21)	2.35(31)	0.1879(7)	0.2966(5)
297.0	10.64716(16)	0.55(4)	0.776(17)	1.76(25)	0.74(34)	2.46(22)	2.19(31)	0.1877(7)	0.2966(5)
304.7	10.64659(16)	0.58(4)	0.801(17)	1.75(25)	0.64(34)	2.65(23)	2.20(31)	0.1881(7)	0.2966(6)
312.8	10.64627(16)	0.60(4)	0.820(17)	1.75(25)	0.76(34)	2.74(23)	2.11(31)	0.1881(7)	0.2964(6)
320.5	10.64596(16)	0.63(4)	0.852(17)	1.74(25)	0.84(35)	2.81(23)	1.99(31)	0.1880(7)	0.2965(6)
328.2	10.64566(16)	0.67(4)	0.870(18)	1.80(25)	0.78(34)	2.89(24)	2.05(31)	0.1881(7)	0.2964(6)
336.3	10.64552(17)	0.69(4)	0.897(18)	1.85(26)	0.90(35)	2.99(24)	2.01(31)	0.1881(7)	0.2963(6)
344.5	10.64462(17)	0.72(4)	0.917(17)	1.89(25)	0.89(34)	3.03(23)	2.12(31)	0.1882(7)	0.2962(5)
352.4	10.64436(17)	0.76(4)	0.949(17)	1.96(25)	0.88(34)	3.08(23)	2.10(31)	0.1880(7)	0.2960(5)
361.7	10.64461(17)	0.78(4)	0.977(18)	2.11(26)	0.79(34)	3.05(24)	2.30(32)	0.1880(7)	0.2960(6)
368.7	10.64381(17)	0.83(4)	1.003(18)	2.20(26)	0.76(34)	3.07(23)	2.39(32)	0.1880(7)	0.2960(6)
377.0	10.64405(17)	0.85(4)	1.029(18)	2.08(27)	0.79(35)	3.25(25)	2.42(33)	0.1881(7)	0.2960(6)
385.4	10.64365(17)	0.87(4)	1.051(18)	2.26(27)	0.83(35)	3.26(25)	2.36(33)	0.1879(7)	0.2959(6)
393.5	10.64345(17)	0.90(4)	1.072(18)	2.29(27)	0.78(35)	3.26(24)	2.47(33)	0.1880(7)	0.2959(6)
395.9	10.64331(17)	0.91(4)	1.086(19)	2.21(27)	0.9(4)	3.37(25)	2.41(33)	0.1881(7)	0.2961(6)

Table S11. Parameters from Rietveld refinement of $\text{CdPt}(\text{CN})_6$ (11-ID-B, APS).

T /K	a /Å	U_{Cd} / $\times 10^2 \text{Å}^2$	U_{Pt} / $\times 10^2 \text{Å}^2$	$U_{\text{C}\perp}$ / $\times 10^2 \text{Å}^2$	$U_{\text{C}\parallel}$ / $\times 10^2 \text{Å}^2$	$U_{\text{N}\perp}$ / $\times 10^2 \text{Å}^2$	$U_{\text{N}\parallel}$ / $\times 10^2 \text{Å}^2$	z_{C}	z_{N}
108.4	11.02069(21)	1.01(4)	0.221(22)	-1.00(26)	11.9(11)	3.4(4)	-0.7(4)	0.1988(13)	0.3005(7)
107.1	11.02069(21)	1.02(4)	0.228(22)	-0.95(26)	12.5(11)	3.4(4)	-0.8(4)	0.1992(13)	0.3008(7)
107.3	11.02046(21)	1.02(4)	0.232(22)	-0.98(26)	12.2(11)	3.4(4)	-0.7(4)	0.1992(13)	0.3006(7)
109.5	11.01974(21)	1.05(4)	0.265(22)	-0.89(27)	11.8(11)	3.5(4)	-0.7(4)	0.1987(13)	0.3005(7)
116.4	11.01910(21)	1.08(4)	0.290(22)	-0.86(27)	12.0(11)	3.6(4)	-0.7(4)	0.1988(13)	0.3007(7)
122.9	11.01831(21)	1.13(4)	0.314(22)	-0.78(28)	11.7(11)	3.6(4)	-0.6(4)	0.1984(13)	0.3006(7)
129.6	11.01758(21)	1.16(4)	0.343(22)	-0.75(28)	11.8(11)	3.6(4)	-0.5(4)	0.1983(13)	0.3007(7)
136.5	11.01685(21)	1.19(4)	0.364(22)	-0.72(28)	12.3(11)	3.8(4)	-0.7(4)	0.1989(13)	0.3009(7)
143.6	11.01598(21)	1.24(4)	0.390(22)	-0.61(28)	11.8(11)	3.9(4)	-0.5(4)	0.1981(13)	0.3006(8)
150.3	11.01531(21)	1.27(4)	0.416(23)	-0.56(29)	11.9(11)	4.0(4)	-0.6(4)	0.1987(13)	0.3008(8)
157.1	11.01453(21)	1.29(4)	0.448(23)	-0.48(29)	12.0(11)	4.1(4)	-0.5(4)	0.1990(13)	0.3008(8)
164.3	11.01377(22)	1.33(4)	0.478(23)	-0.43(30)	11.8(11)	4.2(4)	-0.6(4)	0.1986(13)	0.3007(8)
171.1	11.01294(22)	1.35(4)	0.495(23)	-0.43(29)	12.4(11)	4.3(4)	-0.6(4)	0.1989(13)	0.3008(8)
178.1	11.01216(22)	1.39(4)	0.526(23)	-0.34(30)	11.7(11)	4.3(4)	-0.5(4)	0.1989(13)	0.3008(8)
185.3	11.01196(22)	1.42(4)	0.556(24)	-0.35(30)	12.1(11)	4.6(4)	-0.6(4)	0.1989(14)	0.3007(8)
192.6	11.01059(22)	1.46(4)	0.581(24)	-0.22(31)	11.9(11)	4.5(4)	-0.5(4)	0.1991(14)	0.3010(8)
199.7	11.01024(22)	1.50(4)	0.615(24)	-0.20(31)	11.9(11)	4.7(4)	-0.6(4)	0.1990(14)	0.3009(8)
207.1	11.00907(22)	1.54(4)	0.644(24)	-0.16(31)	12.0(11)	4.7(4)	-0.4(4)	0.1994(14)	0.3011(8)
214.2	11.00870(22)	1.57(4)	0.675(24)	-0.14(31)	12.1(11)	4.8(4)	-0.5(4)	0.1987(14)	0.3007(8)
221.4	11.00712(22)	1.62(4)	0.696(24)	-0.08(32)	11.7(11)	4.9(4)	-0.5(4)	0.1990(14)	0.3009(8)
228.9	11.00644(22)	1.65(4)	0.730(25)	0.03(32)	11.9(11)	5.0(4)	-0.4(4)	0.1992(14)	0.3011(8)
236.5	11.00568(22)	1.68(4)	0.752(25)	0.03(32)	12.0(11)	5.1(4)	-0.4(4)	0.1993(14)	0.3012(8)
243.8	11.00494(23)	1.71(4)	0.778(25)	0.15(33)	11.8(11)	5.3(5)	-0.5(4)	0.1998(14)	0.3014(8)
251.2	11.00556(23)	1.70(4)	0.777(26)	0.13(33)	12.1(12)	5.4(5)	-0.7(4)	0.2011(14)	0.3019(8)
258.9	11.00578(23)	1.71(4)	0.784(26)	0.12(33)	12.3(12)	5.6(5)	-0.8(4)	0.2011(14)	0.3021(8)
266.3	11.00612(23)	1.72(4)	0.801(26)	0.16(33)	12.4(12)	5.5(5)	-0.8(4)	0.2011(14)	0.3020(8)
273.8	11.00566(23)	1.76(4)	0.837(27)	0.33(35)	12.3(12)	5.5(5)	-0.7(4)	0.2014(14)	0.3021(8)
281.6	11.00523(23)	1.79(4)	0.852(27)	0.27(34)	12.3(12)	5.8(5)	-0.8(4)	0.2013(14)	0.3020(8)
289.5	11.00452(23)	1.81(4)	0.879(27)	0.4(4)	11.8(12)	5.7(5)	-0.7(4)	0.2011(14)	0.3018(8)
297.1	11.00413(23)	1.84(5)	0.905(27)	0.38(35)	12.2(12)	5.8(5)	-0.7(4)	0.2012(15)	0.3020(8)
304.7	11.00288(23)	1.88(5)	0.923(27)	0.4(4)	12.0(12)	5.8(5)	-0.5(4)	0.2006(15)	0.3018(8)
312.7	11.00284(23)	1.90(5)	0.953(27)	0.5(4)	11.7(12)	5.9(5)	-0.6(4)	0.2007(15)	0.3019(8)
320.4	11.00199(23)	1.95(5)	0.984(27)	0.5(4)	12.2(12)	6.0(5)	-0.6(4)	0.2008(15)	0.3018(8)
329.5	11.00130(23)	2.00(5)	1.013(27)	0.7(4)	11.9(12)	6.0(5)	-0.5(4)	0.2007(15)	0.3018(8)
336.3	11.00041(23)	2.03(5)	1.046(27)	0.7(4)	11.7(12)	6.2(5)	-0.5(4)	0.2002(15)	0.3016(8)
344.5	10.99944(23)	2.06(5)	1.070(28)	0.8(4)	11.8(12)	6.3(5)	-0.4(4)	0.2001(15)	0.3015(9)
352.4	10.99862(23)	2.11(5)	1.112(28)	0.9(4)	12.0(12)	6.4(5)	-0.5(4)	0.2001(15)	0.3014(8)
360.3	10.99753(23)	2.16(5)	1.138(28)	1.0(4)	11.1(11)	6.5(5)	-0.3(5)	0.2000(15)	0.3016(9)
368.6	10.99661(23)	2.20(5)	1.179(28)	1.0(4)	11.6(12)	6.7(5)	-0.5(4)	0.2002(15)	0.3017(9)
376.7	10.99557(23)	2.24(5)	1.197(28)	1.0(4)	11.5(12)	6.8(5)	-0.4(5)	0.2001(15)	0.3016(9)
384.7	10.99471(23)	2.28(5)	1.232(28)	1.1(4)	11.5(12)	6.8(5)	-0.4(5)	0.1999(15)	0.3015(9)
392.8	10.99463(23)	2.29(5)	1.252(29)	1.1(4)	11.5(12)	6.8(5)	-0.3(5)	0.1998(15)	0.3014(9)
396.2	10.99390(24)	2.31(5)	1.265(29)	1.3(4)	11.6(12)	6.6(5)	-0.4(5)	0.2001(15)	0.3015(9)

Figure S7. Powder X-ray diffraction pattern from careful Rietveld refinement of CuPt(CN)_6 at 107 K. The data points (red crosses), model profile (blue line), reflection markers (vertical black lines) and residual (green lower line) are shown.

Spectroscopic Studies

Figure S8. Raman spectra collected for the as-synthesized samples of $M^{II}Pt^{IV}(CN)_6$ ($M = Mn, Fe, Co, Cu, Zn, Cd$).

Figure S9. The low energy δ_{NMN} mode in the Raman spectra collected for $M^{II}Pt^{IV}(CN)_6$ and the corresponding linear coefficients of thermal expansion. For $CuPt(CN)_6$: $\alpha_a = -5.01(6) \times 10^{-6} K^{-1}$, $\alpha_c = +5.26(17) \times 10^{-6} K^{-1}$.