# The Impact of Metallophilicity on "Colossal" Positive and Negative Thermal Expansion in a Series of Isostructural Dicyanometallate Coordination Polymers

Supporting Information

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***Table S1.*** Lattice parameters, coefficients of thermal expansion ($\alpha_i$) and volumes of $KNi[Au(CN)_2]_3$, determined by powder X-ray diffraction from 100 to 395 K.

| $T$ / K | $a$ / Å | $\alpha_a$ / x10$^{-6}$ K$^{-1}$ | $c$ / Å | $\alpha_c$ / x10$^{-6}$ K$^{-1}$ | $V$ / Å$^3$ |
|---|---|---|---|---|---|
| 100 | 6.7531(5) | 59.7(6) | 7.7517(5) | -42.2(4) | 306.15(3) |
| 115 | 6.7567(5) | 59.7(6) | 7.7459(5) | -42.2(4) | 306.25(3) |
| 130 | 6.7647(5) | 59.6(6) | 7.7440(5) | -42.2(4) | 306.90(3) |
| 145 | 6.7674(5) | 59.5(6) | 7.7377(5) | -42.3(4) | 306.90(3) |
| 160 | 6.7736(5) | 59.5(6) | 7.7325(5) | -42.3(4) | 307.25(3) |
| 175 | 6.7786(5) | 59.4(6) | 7.7303(5) | -42.3(4) | 307.62(3) |
| 190 | 6.7832(5) | 59.4(6) | 7.7265(5) | -42.3(4) | 307.88(3) |
| 205 | 6.7905(5) | 59.3(6) | 7.7184(5) | -42.4(4) | 308.22(3) |
| 220 | 6.7969(5) | 59.3(6) | 7.7155(5) | -42.4(4) | 308.69(3) |
| 235 | 6.8034(5) | 59.2(6) | 7.7126(5) | -42.4(4) | 309.16(3) |
| 250 | 6.8085(5) | 59.2(6) | 7.7077(5) | -42.4(4) | 309.43(3) |
| 265 | 6.8151(5) | 59.1(6) | 7.6999(5) | -42.5(4) | 309.71(3) |
| 280 | 6.8205(5) | 59.1(6) | 7.6986(5) | -42.5(4) | 310.15(3) |
| 295 | 6.8283(5) | 59.0(6) | 7.6932(5) | -42.5(4) | 310.64(3) |
| 310 | 6.8346(5) | 59.0(6) | 7.6865(5) | -42.5(4) | 310.95(3) |
| 325 | 6.8401(5) | 58.9(6) | 7.6832(5) | -42.6(4) | 311.31(3) |
| 340 | 6.8455(5) | 58.9(6) | 7.6751(5) | -42.6(4) | 311.48(3) |
| 355 | 6.8546(5) | 58.8(6) | 7.6687(5) | -42.6(4) | 312.05(3) |
| 375 | 6.8636(5) | 58.7(6) | 7.6602(5) | -42.7(4) | 312.52(3) |
| 395 | 6.8689(5) | 58.7(6) | 7.6529(5) | -42.7(4) | 312.70(3) |

***Table S2.*** Lattice parameters, coefficients of thermal expansion ($\alpha_i$) and volumes of $KCd[Ag(CN)_2]_3$, determined by powder X-ray diffraction from 100 to 395 K.

| $T$ / K | $a$ / Å | $\alpha_a$ / x10$^{-6}$ K$^{-1}$ | $c$ / Å | $\alpha_c$ / x10$^{-6}$ K$^{-1}$ | $V$ / Å$^3$ |
|---|---|---|---|---|---|
| 100 | 6.8439(5) | 76.6(8) | 8.4206(8) | -64.3(6) | 341.57(3) |
| 115 | 6.8494(5) | 76.5(8) | 8.4124(8) | -64.4(6) | 341.79(3) |
| 130 | 6.8574(5) | 76.4(8) | 8.4059(8) | -64.5(6) | 342.32(3) |
| 145 | 6.8641(5) | 76.3(8) | 8.3983(8) | -64.5(6) | 342.68(3) |
| 160 | 6.8721(5) | 76.3(8) | 8.3916(8) | -64.6(6) | 343.21(3) |
| 175 | 6.8786(5) | 76.2(8) | 8.3824(8) | -64.7(6) | 343.48(3) |
| 190 | 6.8870(5) | 76.1(8) | 8.3754(8) | -64.7(6) | 344.03(3) |
| 205 | 6.8946(5) | 76.0(8) | 8.3661(8) | -64.8(6) | 344.41(3) |
| 220 | 6.9025(5) | 75.9(8) | 8.3584(8) | -64.8(6) | 344.88(3) |
| 235 | 6.9103(5) | 75.8(8) | 8.3500(8) | -64.9(6) | 345.31(3) |
| 250 | 6.9187(5) | 75.7(8) | 8.3442(8) | -65.0(6) | 345.91(3) |
| 265 | 6.9262(5) | 75.6(8) | 8.3353(8) | -65.0(7) | 346.29(3) |
| 280 | 6.9334(5) | 75.6(8) | 8.3275(8) | -65.1(7) | 346.69(3) |
| 295 | 6.9417(5) | 75.5(8) | 8.3192(8) | -65.2(7) | 347.17(3) |
| 310 | 6.9494(5) | 75.4(8) | 8.3114(8) | -65.2(7) | 347.62(3) |
| 325 | 6.9581(5) | 75.3(8) | 8.3016(8) | -65.3(7) | 348.08(3) |
| 340 | 6.9666(5) | 75.2(8) | 8.2926(8) | -65.4(7) | 348.55(3) |
| 355 | 6.9749(5) | 75.1(8) | 8.2828(8) | -65.4(7) | 348.97(3) |
| 375 | 6.9862(5) | 75.0(8) | 8.2707(8) | -65.5(7) | 349.59(3) |
| 395 | 6.9980(5) | 74.9(7) | 8.2608(8) | -65.6(7) | 350.35(3) |

***Table S3.*** Lattice parameters, coefficients of thermal expansion ($\alpha_i$) and volumes of $KCd[Au(CN)_2]_3$, determined by powder X-ray diffraction from 100 to 395 K.

| $T$ / K | $a$ / Å | $\alpha_a$ / x10$^{-6}$ K$^{-1}$ | $c$ / Å | $\alpha_c$ / x10$^{-6}$ K$^{-1}$ | $V$ / Å$^3$ |
|---|---|---|---|---|---|
| 100 | 6.7656(7) | 72.9(7) | 8.2965(10) | -56.1(6) | 328.88(7) |
| 115 | 6.7714(7) | 72.8(7) | 8.2915(10) | -56.2(6) | 329.25(7) |
| 130 | 6.7771(7) | 72.8(7) | 8.2857(10) | -56.2(6) | 329.57(7) |
| 145 | 6.7837(7) | 72.7(7) | 8.2804(10) | -56.3(6) | 330.00(7) |
| 160 | 6.7896(7) | 72.6(7) | 8.2696(10) | -56.3(6) | 330.14(7) |
| 175 | 6.7962(7) | 72.5(7) | 8.2641(10) | -56.4(6) | 330.57(7) |
| 190 | 6.8021(7) | 72.4(7) | 8.2592(10) | -56.4(6) | 330.94(7) |
| 205 | 6.8116(7) | 72.4(7) | 8.2539(10) | -56.5(6) | 331.66(7) |
| 220 | 6.8179(7) | 72.3(7) | 8.2431(10) | -56.5(6) | 331.84(7) |
| 235 | 6.8249(7) | 72.2(7) | 8.2391(10) | -56.6(6) | 332.36(7) |
| 250 | 6.8332(7) | 72.1(7) | 8.2339(10) | -56.6(6) | 332.95(7) |
| 265 | 6.8398(7) | 72.1(7) | 8.2298(10) | -56.7(6) | 333.43(7) |
| 280 | 6.8471(7) | 72.0(7) | 8.2159(10) | -56.7(6) | 333.58(7) |
| 295 | 6.8545(7) | 71.9(7) | 8.2109(10) | -56.8(6) | 334.10(7) |
| 310 | 6.8625(7) | 71.8(7) | 8.2030(10) | -56.8(6) | 334.56(7) |
| 325 | 6.8725(7) | 71.7(7) | 8.1965(10) | -56.9(6) | 335.27(7) |
| 340 | 6.8795(7) | 71.7(7) | 8.1901(10) | -56.9(6) | 335.69(7) |
| 355 | 6.8882(7) | 71.6(7) | 8.1779(10) | -57.0(6) | 336.04(7) |
| 375 | 6.8995(7) | 71.5(7) | 8.1722(10) | -57.0(6) | 336.90(7) |
| 395 | 6.9098(7) | 71.4(7) | 8.1564(10) | -57.1(6) | 337.26(7) |

***Table S4.*** Lattice parameters, coefficients of thermal expansion ($\alpha_i$) and volumes of $In[Au(CN)_2]_3$, determined by powder X-ray diffraction from 100 to 395 K.

| $T$ / K | $a$ / Å | $\alpha_a$ / x10$^{-6}$ K$^{-1}$ | $c$ / Å | $\alpha_c$ / x10$^{-6}$ K$^{-1}$ | $V$ / Å$^3$ |
|---|---|---|---|---|---|
| 100 | 6.5223(8) | 86.1(9) | 8.1323(14) | -62.2(9) | 299.60(6) |
| 115 | 6.5274(8) | 86.0(9) | 8.1242(14) | -62.2(9) | 299.77(6) |
| 130 | 6.5358(8) | 85.9(9) | 8.1217(14) | -62.3(9) | 300.45(6) |
| 145 | 6.5421(8) | 85.7(9) | 8.1150(14) | -62.4(9) | 300.78(6) |
| 160 | 6.5514(8) | 85.6(9) | 8.1104(14) | -62.4(9) | 301.47(6) |
| 175 | 6.5588(8) | 85.5(9) | 8.1019(14) | -62.5(9) | 301.83(6) |
| 190 | 6.5659(8) | 85.4(9) | 8.0955(14) | -62.5(9) | 302.25(6) |
| 205 | 6.5744(8) | 85.3(9) | 8.0878(14) | -62.6(9) | 302.74(6) |
| 220 | 6.5834(8) | 85.2(9) | 8.0795(14) | -62.6(9) | 303.26(6) |
| 235 | 6.5906(8) | 85.1(9) | 8.0726(14) | -62.7(9) | 303.66(6) |
| 250 | 6.5996(8) | 85.0(8) | 8.0634(14) | -62.8(9) | 304.15(6) |
| 265 | 6.6082(8) | 84.9(8) | 8.0554(14) | -62.8(9) | 304.64(6) |
| 280 | 6.6171(8) | 84.8(8) | 8.0484(14) | -62.9(9) | 305.19(6) |
| 295 | 6.6272(8) | 84.7(8) | 8.0427(14) | -62.9(9) | 305.91(6) |
| 310 | 6.6370(8) | 84.5(8) | 8.0331(14) | -63.0(9) | 306.45(6) |
| 325 | 6.6449(8) | 84.4(8) | 8.0230(14) | -63.1(9) | 306.79(6) |
| 340 | 6.6543(8) | 84.3(8) | 8.0139(14) | -63.1(9) | 307.31(6) |
| 355 | 6.6634(8) | 84.2(8) | 8.0061(14) | -63.2(9) | 307.85(6) |
| 375 | 6.6715(8) | 84.1(8) | 7.9949(14) | -63.3(9) | 308.17(6) |
| 395 | 6.6832(8) | 83.9(8) | 7.9870(14) | -63.3(9) | 308.95(6) |

***Table S5.*** Lattice parameters, coefficients of thermal expansion ($\alpha_l$) and volumes of $In[Ag(CN)_2]_3 \cdot xH_2O$, determined by powder X-ray diffraction from 100 to 325 K.[a]

| *T* / K | *a* / Å | $\alpha_a$ / x10$^{-6}$ K$^{-1}$ | *c* / Å | $\alpha_c$ / x10$^{-6}$ K$^{-1}$ | *V* / Å$^3$ |
|---|---|---|---|---|---|
| 100 | 6.7761(17) | 98(2) | 8.1294(17) | -73(1) | 323.25(15) |
| 115 | 6.7884(17) | 97(2) | 8.1219(17) | -73(1) | 324.13(15) |
| 130 | 6.7977(17) | 97(2) | 8.1157(17) | -74(1) | 324.77(15) |
| 145 | 6.8065(17) | 97(2) | 8.1055(17) | -74(1) | 325.21(15) |
| 160 | 6.8161(17) | 97(2) | 8.0975(17) | -74(1) | 325.80(15) |
| 175 | 6.8255(17) | 97(2) | 8.0888(17) | -74(1) | 326.35(15) |
| 190 | 6.8352(17) | 97(2) | 8.0788(17) | -74(1) | 326.87(15) |
| 205 | 6.8455(17) | 97(2) | 8.0708(17) | -74(1) | 327.54(15) |
| 220 | 6.8552(17) | 96(2) | 8.0589(17) | -74(1) | 327.98(15) |
| 235 | 6.8657(17) | 96(2) | 8.0517(17) | -74(1) | 328.69(15) |
| 250 | 6.8754(17) | 96(2) | 8.0421(17) | -74(1) | 329.23(15) |
| 265 | 6.8840(17) | 96(2) | 8.0289(17) | -74(1) | 329.51(15) |
| 280 | 6.8970(17) | 96(2) | 8.0235(17) | -74(1) | 330.53(16) |
| 295 | 6.9060(17) | 96(2) | 8.0171(17) | -74(1) | 331.13(16) |
| 310 | 6.9168(17) | 96(2) | 8.0084(17) | -75(1) | 331.81(16) |
| 325 | 6.9252(17) | 95(2) | 7.9968(17) | -75(1) | 332.13(16) |

[a] Compound dehydrates at 340 K.

***Table S6.*** Lattice parameters, coefficients of thermal expansion ($\alpha_l$) and volumes of $In[Ag(CN)_2]_3$, determined by powder X-ray diffraction from 395 to 100 K.[a]

| *T* / K | *a* / Å | $\alpha_a$ / x10$^{-6}$ K$^{-1}$ | *c* / Å | $\alpha_c$ / x10$^{-6}$ K$^{-1}$ | *V* / Å$^3$ |
|---|---|---|---|---|---|
| 395 | 6.9832(14) | 104(2) | 7.9252(14) | -85(2) | 334.70(15) |
| 375 | 6.9735(14) | 105(2) | 7.9396(14) | -84(2) | 334.37(15) |
| 355 | 6.9577(14) | 105(2) | 7.9540(14) | -84(2) | 333.46(15) |
| 340 | 6.9447(14) | 105(2) | 7.9634(14) | -84(2) | 332.61(15) |
| 325 | 6.9337(14) | 105(2) | 7.9752(14) | -84(2) | 332.05(15) |
| 310 | 6.9235(14) | 105(2) | 7.9845(14) | -84(2) | 331.46(15) |
| 295 | 6.9132(14) | 105(2) | 7.9950(14) | -84(2) | 330.91(15) |
| 280 | 6.9010(14) | 106(2) | 8.0052(14) | -84(2) | 330.16(15) |
| 265 | 6.8892(14) | 106(2) | 8.0138(14) | -84(2) | 329.39(14) |
| 250 | 6.8799(14) | 106(2) | 8.0264(14) | -83(2) | 329.02(14) |
| 235 | 6.8681(14) | 106(2) | 8.0331(14) | -83(2) | 328.16(14) |
| 220 | 6.8578(14) | 106(2) | 8.0433(14) | -83(2) | 327.59(14) |
| 205 | 6.8482(14) | 106(2) | 8.0524(14) | -83(2) | 327.05(14) |
| 190 | 6.8405(14) | -- | 8.0659(14) | -- | 326.86(14) |
| 175 | 6.8318(14) | -- | 8.0762(14) | -- | 326.44(14) |
| 160 | 6.8186(14) | -- | 8.0805(14) | -- | 325.36(14) |
| 145 | 6.8105(14) | -- | 8.0895(14) | -- | 324.95(14) |
| 130 | 6.8008(14) | -- | 8.0966(14) | -- | 324.30(14) |
| 115 | 6.7915(14) | -- | 8.1042(14) | -- | 323.72(14) |
| 100 | 6.7833(14) | -- | 8.1112(14) | -- | 323.22(14) |

[a] Thermal expansion coefficients not fit to data below 205 K since there appeared to be a small amount of nitrogen sorption from the cryostream.

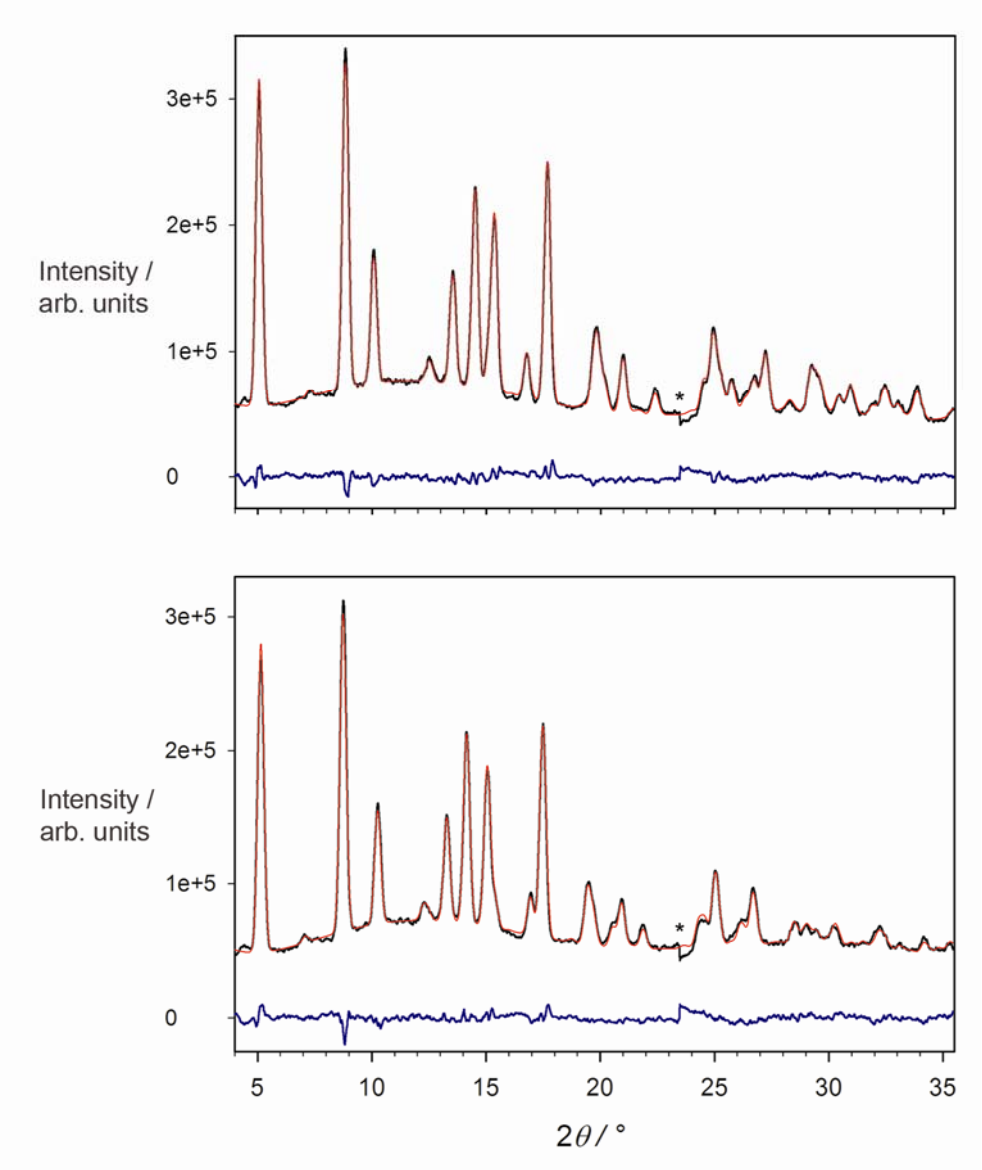


***Figure S1.*** Experimental powder pattern of $In[Au(CN)_2]_3$ (*black*) with simulated fit (*red*) at *(top)* 100 K, and *(bottom)* 395 K. Calculated difference is shown beneath in blue. * indicates the angle at which the detector images overlap.

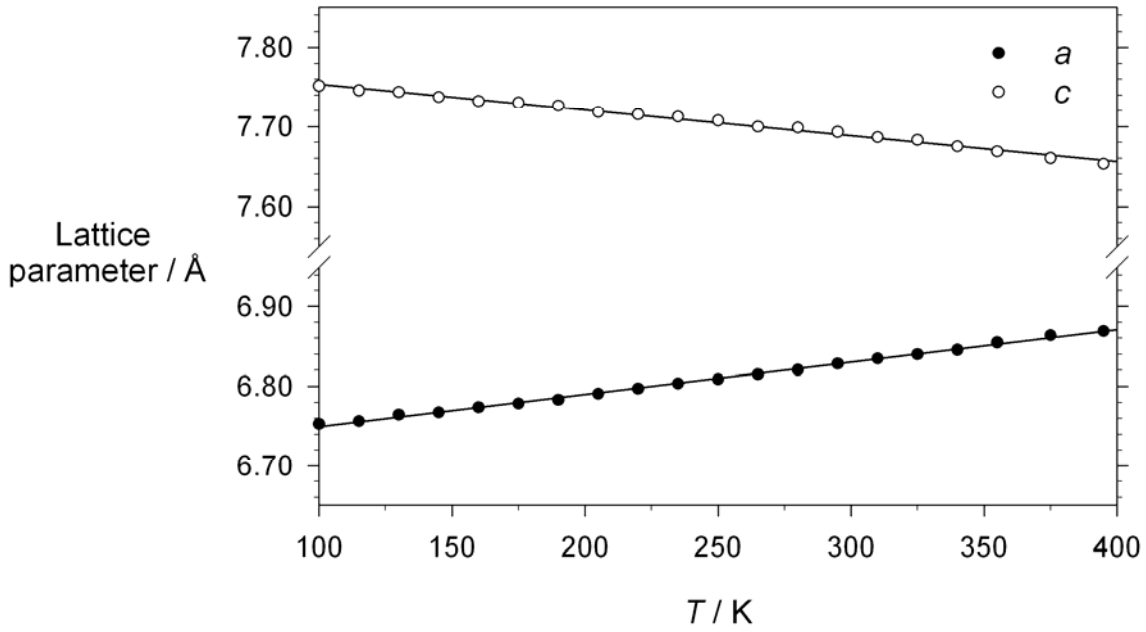


***Figure S2.*** Lattice parameters (Å) as a function of temperature (K) for $KNi[Au(CN)_2]_3$ from 100 K to 395 K. Closed circles: ***a***; open circles: ***c***. Errors are within the points.

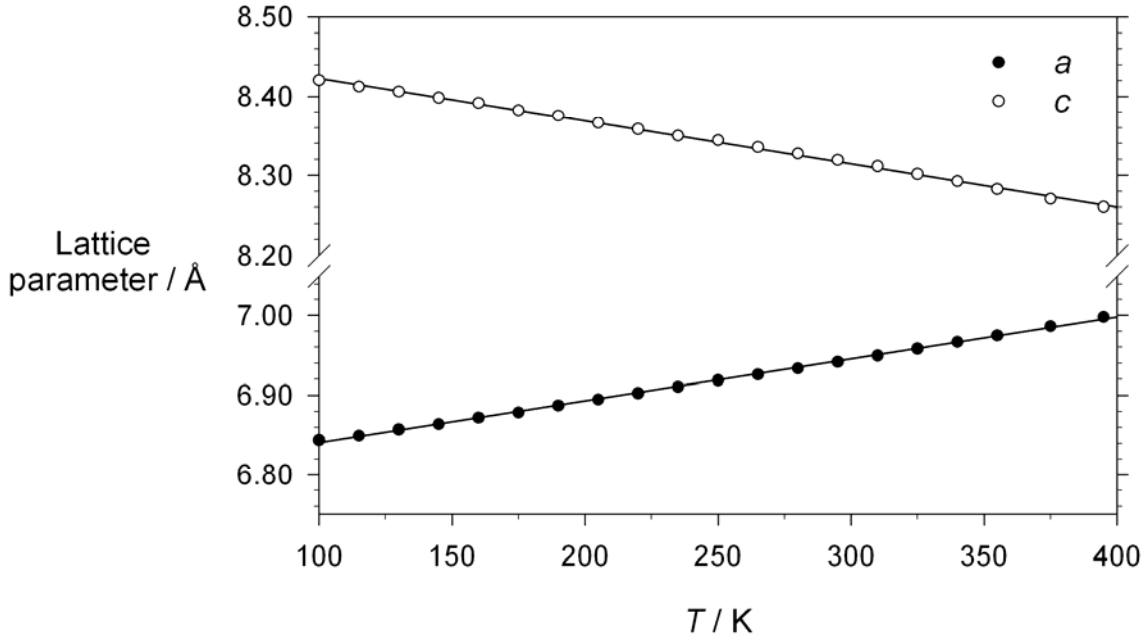


***Figure S3.*** Lattice parameters (Å) as a function of temperature (K) for $KCd[Ag(CN)_2]_3$ from 100 K to 395 K. Closed circles: ***a***; open circles: ***c***. Errors are within the points.

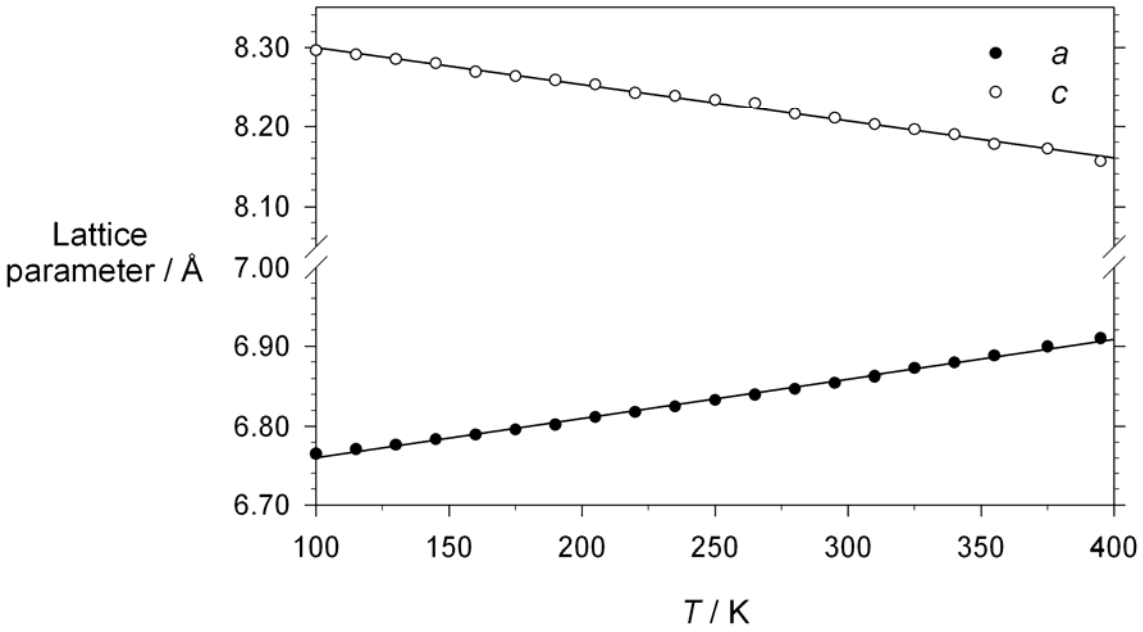


***Figure S4.*** Lattice parameters (Å) as a function of temperature (K) for $KCd[Au(CN)_2]_3$ from 100 K to 395 K. Closed circles: ***a***; open circles: ***c***. Errors are within the points.

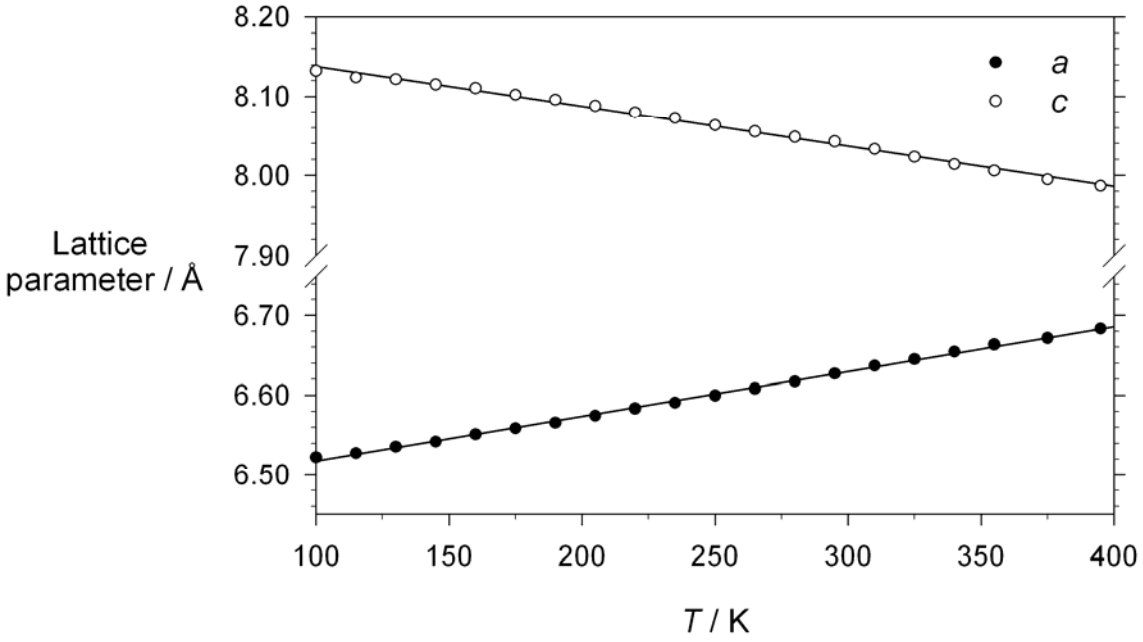


***Figure S5.*** Lattice parameters (Å) as a function of temperature (K) for $In[Au(CN)_2]_3$ from 100 K to 395 K. Closed circles: ***a***; open circles: ***c***. Errors are within the points.

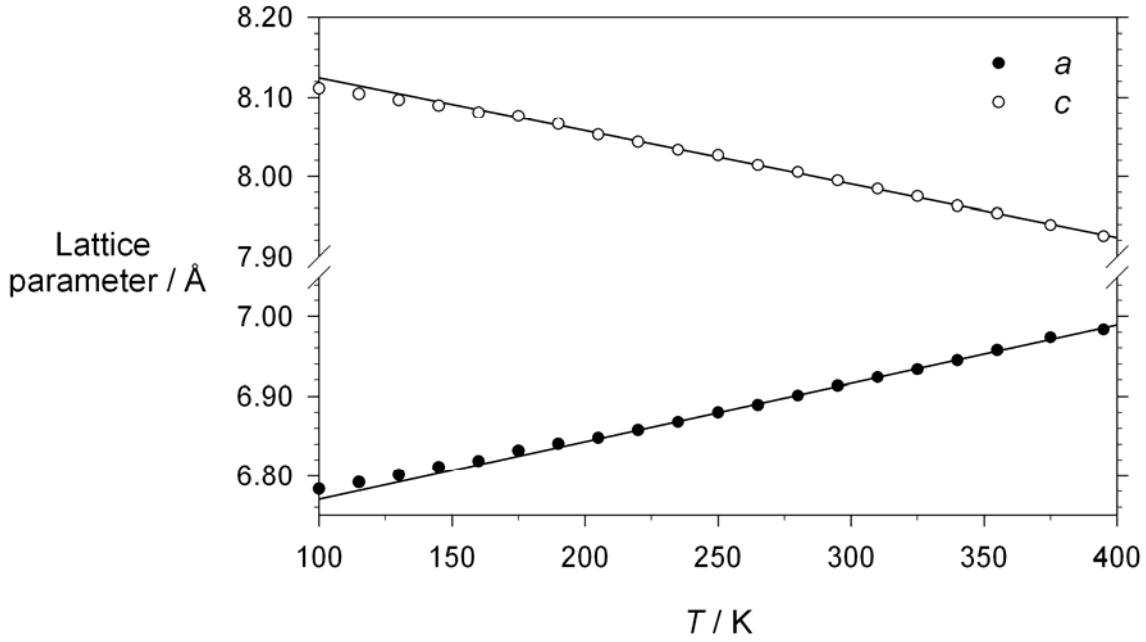


***Figure S6.*** Lattice parameters (Å) as a function of temperature (K) for $In[Ag(CN)_2]_3$ from 395 K to 100 K. Closed circles: ***a***; open circles: ***c***. Regression is fit to data points in the region between 395 and 205 K; below this temperature, it is believed that a small amount of nitrogen sorption from the cryostream occurs. Errors are within the points.