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Supporting Information

Linear Negative Thermal Expansion in $Pd(acac)_2$

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Variable Temperature Powder X-Ray Diffraction (VTPXRD)

Variable temperature powder X-ray diffraction measurements were performed at the P02.1 beamline at the storage ring PETRAIII (DESY, Hamburg, Germany) with high-brilliance synchrotron light sources[1] and a Habcryo-X Cryostream from Oxford Cryosystems Plus for temperature regulation. For sample preparation, borosilicate glass capillaries (0.8 mm in diameter) were used. The beamline operates at a fixed photon energy of 60 keV (λ = 0.20679 Å) equipped with a high-resolution monochromator and a Perkin Elmer 1621EN detector with a collecting step size of 0.0029118 in 2θ. The temperature dependent diffraction data were collected in the temperature range of 100 to 400 K and back to 115 K in steps of 15 K with 100 seconds exposure per temperature step.

Pawley profile fit analysis[2] was carried out for all patterns by using TOPAS v6. Standard deviations of all parameters were calculated and the use of "randomize_on_errors" ensured that the minimum of refinement was achieved.[3]

Table S1: Results of the Pawley profile fits of the VTPXRD measurements for $Cu(acac)_2$.

T / K	r_wp	a / Å	b / Å	c / Å	β / °	V / Å³
100	1.51	10.2749(3)	4.6304(1)	11.2928(4)	92.371(1)	536.82(3)
115	1.48	10.2755(3)	4.6389(1)	11.2902(4)	92.368(1)	537.72(3)
130	1.49	10.2762(3)	4.6470(1)	11.2889(4)	92.355(1)	538.63(3)
145	1.46	10.2794(3)	4.6537(1)	11.2916(4)	92.335(1)	539.71(3)
160	1.34	10.2812(3)	4.6607(1)	11.2929(4)	92.304(1)	540.70(3)
175	1.38	10.2833(3)	4.6667(1)	11.2959(3)	92.273(1)	541.65(2)
190	1.36	10.2886(3)	4.6727(1)	11.3029(4)	92.222(1)	542.98(3)
205	1.29	10.2929(3)	4.6782(1)	11.3094(3)	92.187(1)	544.18(2)
220	1.28	10.2962(3)	4.6834(1)	11.3141(3)	92.119(1)	545.20(2)
235	1.22	10.3008(3)	4.6883(1)	11.3219(3)	92.082(1)	546.40(2)
250	1.22	10.3076(3)	4.6928(1)	11.3336(3)	92.005(1)	547.89(3)
265	1.22	10.3129(3)	4.6975(1)	11.3404(3)	91.973(1)	549.05(2)
280	1.26	10.3192(3)	4.7018(1)	11.3516(3)	91.888(1)	550.46(2)
295	1.20	10.3274(3)	4.7059(1)	11.3618(3)	91.859(1)	551.89(2)
310	1.20	10.3354(3)	4.7099(1)	11.3759(3)	91.768(1)	553.50(2)
325	1.10	10.3402(3)	4.7138(1)	11.3831(3)	91.738(1)	554.57(2)
340	1.12	10.3488(3)	4.7174(1)	11.3982(3)	91.653(1)	556.23(2)
355	1.05	10.3555(3)	4.7219(1)	11.4078(3)	91.601(1)	557.60(2)
370	1.09	10.3640(3)	4.7255(1)	11.4227(3)	91.516(1)	559.24(2)
385	1.08	10.3708(3)	4.7292(1)	11.4336(3)	91.475(1)	560.58(2)
400	1.09	10.3793(3)	4.7324(1)	11.4480(3)	91.400(1)	562.15(2)

Table S2: Results of the Pawley profile fits of the VTPXRD measurements for $Pd(acac)_2$.

T / K	r_wp	a / Å	b / Å	c / Å	β / °	V / Å³
100	3.18	9.9486(6)	5.2315(2)	10.4425(7)	95.677(2)	540.83(5)
115	3.08	9.9647(5)	5.2258(2)	10.4684(6)	95.484(2)	542.63(5)
130	3.30	9.9801(5)	5.2176(2)	10.5000(6)	95.264(2)	544.46(5)
145	2.96	9.9941(5)	5.2140(2)	10.5267(5)	95.111(2)	546.36(4)
160	3.45	10.0088(6)	5.2040(3)	10.5620(7)	94.881(3)	548.13(6)
175	2.95	10.0220(5)	5.2008(2)	10.5897(6)	94.755(2)	550.06(5)
190	3.45	10.0382(6)	5.1892(3)	10.6277(8)	94.536(3)	551.87(6)
205	2.77	10.0488(5)	5.1874(2)	10.6545(6)	94.408(2)	553.75(4)
220	3.26	10.0636(6)	5.1741(3)	10.6938(7)	94.190(2)	555.34(6)
235	2.65	10.0713(4)	5.1745(2)	10.7148(5)	94.094(2)	556.97(4)
250	3.10	10.0858(5)	5.1617(2)	10.7551(6)	93.879(2)	558.63(5)
265	2.57	10.0985(4)	5.1624(2)	10.7819(5)	93.809(2)	560.85(4)
280	2.83	10.1095(5)	5.1512(2)	10.8179(6)	93.602(2)	562.24(5)
295	2.54	10.1197(4)	5.1519(2)	10.8389(5)	93.535(2)	564.03(4)
310	2.54	10.1331(5)	5.1420(2)	10.8765(5)	93.340(2)	565.76(4)
325	2.53	10.1439(5)	5.1419(2)	10.8972(5)	93.269(2)	567.46(4)
340	2.41	10.1579(5)	5.1331(2)	10.9350(5)	93.095(2)	569.33(4)
355	2.63	10.1690(6)	5.1316(3)	10.9594(6)	93.002(2)	571.11(5)
370	2.44	10.1821(5)	5.1248(2)	10.9921(5)	92.849(2)	572.87(4)
385	2.56	10.1936(5)	5.1227(3)	11.0181(6)	92.748(2)	574.69(5)
400	2.51	10.2039(5)	5.1193(2)	11.0426(6)	92.636(2)	576.21(5)

Rietveld Refinements

Rietveld refinements for each temperature point of the VTPXRD measurements were performed using TOPAS v6. The lattice parameters from Pawley profile fits were used, see Table S1 and Table S2, and structural information as provided by reported crystallographic information files[4,5] were used as starting points for the refinements, respectively. The positions of the H atoms were not refined. Below are the atomic coordinates of $Cu(acac)_2$ and $Pd(acac)_2$ for each temperature point. To obtain a feeling for the stability of the refinements, various ways of treating temperature factors were tested e.g. B values were openly refined, constrained, and fixed. When starting from B values around 1, only a negligible difference on atomic positions and refinement parameters within std. deviations were observed. To minimize the number of refined parameters, final xyz coordinates were obtained with B_{iso} fixed to one, with $B_{iso} = 8\times\pi^2\times U_{iso}$. Furthermore, knowing about the potential impact of preferred orientation due to a preferred growth of $Cu(acac)_2$ and $Pd(acac)_2$ along [010], we have analysed the impact of preferred orientation on our analytical outcomes as implemented in TOPAS v6. The change of r_wp value was neglible, e.g. change from 2.15 to 2.12 for $Cu(acac)_2$ and from 3.98 to 3.97 for $Pd(acac)_2$ at 295K respectively. We therefore conclude that preferred orientation has no impact in our structure refinement.

$Cu(acac)_2$

Table S3: Results of Rietveld refinements of the VTPXRD measurements of $Cu(acac)_2$.

T / K	r_wp
100	2.31
115	2.34
130	2.32
145	2.31
160	2.13
175	2.23
190	2.20
205	2.21
220	2.12
235	2.15
250	2.11
265	2.52
280	2.15
295	2.15
310	2.12
325	2.02
340	2.07
355	2.51
370	2.12
385	2.03
400	2.12

Representative Rietveld plots for $Cu(acac)_2$

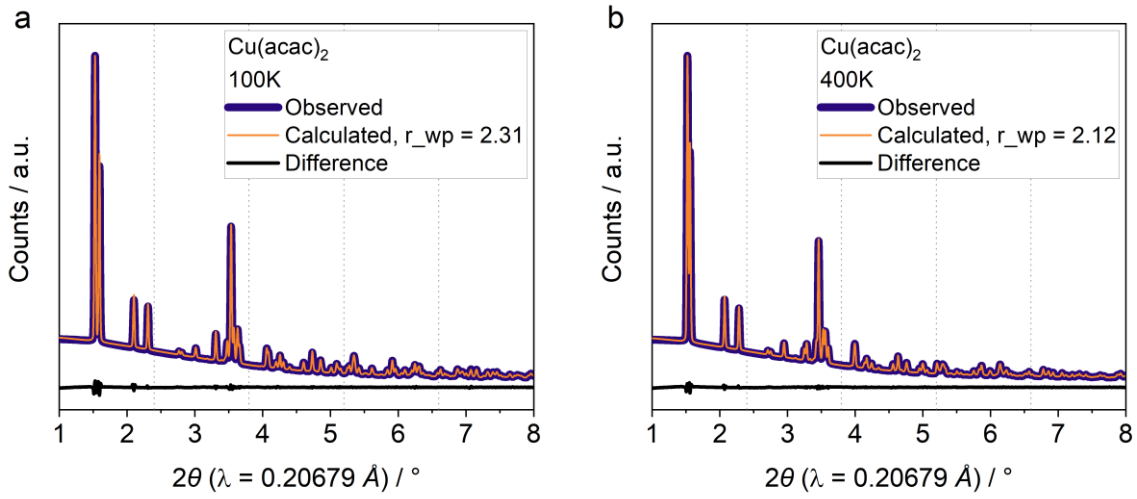

Figure S1: Visualisation of the Rietveld refinements of $Cu(acac)_2$ at 100K (**a**) and at 400K (**b**). The experimental Powder X-ray diffraction pattern of $Cu(acac)_2$ is shown in blue, the calculated data from Rietveld refinements in orange and the difference curve of the Rietveld refinements in black.

Temperature dependent atomic coordinates for $Cu(acac)_2$ as obtained from Rietveld Refinements

Table S4: Atom coordinates of $Cu(acac)_2$ at 100K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.339(1)	0.216(3)	0.498(1)
O	O3	0.568(4)	0.213(5)	0.369(4)
C	C4	0.510(3)	0.418(5)	0.314(5)
C	C5	0.309(3)	0.421(4)	0.427(1)
C	C6	0.387(5)	0.526(5)	0.337(2)
C	C7	0.177(4)	0.557(6)	0.443(5)
C	C8	0.584(5)	0.552(6)	0.215(4)

Table S5: Atom coordinates of $Cu(acac)_2$ at 115K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.339(1)	0.216(3)	0.498(1)
O	O3	0.569(5)	0.212(6)	0.370(6)
C	C4	0.512(4)	0.418(6)	0.314(5)
C	C5	0.309(3)	0.421(4)	0.426(2)
C	C6	0.388(5)	0.525(5)	0.337(2)
C	C7	0.178(4)	0.558(6)	0.442(5)
C	C8	0.585(6)	0.550(5)	0.215(6)

Table S6: Atom coordinates of $Cu(acac)_2$ at 130K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.339(1)	0.214(3)	0.497(1)
O	O3	0.569(6)	0.213(6)	0.370(5)
C	C4	0.511(6)	0.417(6)	0.314(6)
C	C5	0.309(3)	0.419(4)	0.426(2)
C	C6	0.387(6)	0.524(5)	0.337(2)
C	C7	0.177(4)	0.553(6)	0.441(6)
C	C8	0.585(6)	0.551(7)	0.215(5)

Table S7: Atom coordinates of $Cu(acac)_2$ at 145K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.339(1)	0.215(3)	0.498(1)
O	O3	0.569(6)	0.211(7)	0.370(6)
C	C4	0.511(6)	0.416(6)	0.314(6)
C	C5	0.309(3)	0.419(4)	0.427(2)
C	C6	0.387(6)	0.523(6)	0.337(2)
C	C7	0.178(4)	0.553(5)	0.443(5)
C	C8	0.585(7)	0.547(7)	0.215(5)

Table S8: Atom coordinates of $Cu(acac)_2$ at 160K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.340(1)	0.215(3)	0.498(1)
O	O3	0.568(6)	0.212(8)	0.370(7)
C	C4	0.511(6)	0.416(7)	0.314(6)
C	C5	0.309(3)	0.419(4)	0.427(2)
C	C6	0.387(6)	0.523(7)	0.338(2)
C	C7	0.178(4)	0.555(7)	0.443(5)
C	C8	0.584(8)	0.549(8)	0.215(6)

Table S9: Atom coordinates of $Cu(acac)_2$ at 175K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.340(1)	0.215(3)	0.498(1)
O	O3	0.569(6)	0.211(8)	0.370(7)
C	C4	0.511(6)	0.416(8)	0.314(6)
C	C5	0.310(3)	0.419(4)	0.427(2)
C	C6	0.388(6)	0.523(8)	0.338(2)
C	C7	0.179(4)	0.555(8)	0.443(6)
C	C8	0.585(7)	0.548(9)	0.215(7)

Table S10: Atom coordinates of $Cu(acac)_2$ at 190K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.340(1)	0.215(3)	0.498(1)
O	O3	0.569(6)	0.210(8)	0.370(7)
C	C4	0.512(6)	0.414(7)	0.314(5)
C	C5	0.310(3)	0.418(4)	0.426(2)
C	C6	0.389(6)	0.521(8)	0.337(2)
C	C7	0.179(4)	0.554(7)	0.442(6)
C	C8	0.586(7)	0.545(9)	0.215(6)

Table S11: Atom coordinates of $Cu(acac)_2$ at 205K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.340(1)	0.214(3)	0.498(1)
O	O3	0.569(6)	0.210(8)	0.370(7)
C	C4	0.512(6)	0.413(8)	0.314(6)
C	C5	0.310(3)	0.417(4)	0.427(2)
C	C6	0.388(6)	0.520(8)	0.337(2)
C	C7	0.179(4)	0.552(8)	0.442(6)
C	C8	0.585(6)	0.544(9)	0.215(7)

Table S12: Atom coordinates of $Cu(acac)_2$ at 220K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.340(1)	0.214(3)	0.497(1)
O	O3	0.570(7)	0.209(8)	0.370(8)
C	C4	0.513(6)	0.412(8)	0.314(6)
C	C5	0.310(3)	0.417(4)	0.426(2)
C	C6	0.389(6)	0.519(7)	0.337(2)
C	C7	0.180(4)	0.552(8)	0.440(6)
C	C8	0.587(7)	0.543(9)	0.215(7)

Table S13: Atom coordinates of $Cu(acac)_2$ at 235K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.340(1)	0.214(3)	0.498(1)
O	O3	0.570(7)	0.208(8)	0.370(8)
C	C4	0.512(6)	0.411(8)	0.313(6)
C	C5	0.310(3)	0.417(4)	0.426(2)
C	C6	0.389(6)	0.518(7)	0.337(2)
C	C7	0.179(4)	0.551(8)	0.442(6)
C	C8	0.587(7)	0.540(9)	0.215(7)

Table S14: Atom coordinates of $Cu(acac)_2$ at 250K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.340(1)	0.214(3)	0.499(1)
O	O3	0.569(7)	0.208(8)	0.369(8)
C	C4	0.511(6)	0.411(7)	0.314(6)
C	C5	0.310(3)	0.416(4)	0.428(2)
C	C6	0.388(6)	0.518(8)	0.338(2)
C	C7	0.180(4)	0.552(8)	0.444(6)
C	C8	0.584(7)	0.541(9)	0.215(7)

Table S15: Atom coordinates of $Cu(acac)_2$ at 265K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.340(1)	0.212(3)	0.498(1)
O	O3	0.569(6)	0.209(8)	0.370(8)
C	C4	0.512(6)	0.411(9)	0.314(6)
C	C5	0.310(3)	0.414(4)	0.427(1)
C	C6	0.388(6)	0.516(8)	0.337(2)
C	C7	0.179(4)	0.547(8)	0.442(5)
C	C8	0.585(8)	0.541(9)	0.215(7)

Table S16: Atom coordinates of $Cu(acac)_2$ at 280K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.340(1)	0.213(2)	0.498(1)
O	O3	0.569(6)	0.207(8)	0.370(8)
C	C4	0.512(6)	0.409(9)	0.314(6)
C	C5	0.311(3)	0.415(4)	0.426(1)
C	C6	0.389(6)	0.516(8)	0.337(2)
C	C7	0.180(4)	0.549(8)	0.442(5)
C	C8	0.586(8)	0.537(9)	0.215(7)

Table S17: Atom coordinates of $Cu(acac)_2$ at 295K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.341(1)	0.214(2)	0.497(1)
O	O3	0.570(6)	0.207(8)	0.370(8)
C	C4	0.513(6)	0.409(9)	0.314(6)
C	C5	0.312(3)	0.415(4)	0.426(1)
C	C6	0.391(6)	0.516(8)	0.337(2)
C	C7	0.181(4)	0.551(8)	0.440(5)
C	C8	0.588(8)	0.538(9)	0.216(7)

Table S18: Atom coordinates of $Cu(acac)_2$ at 310K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.341(1)	0.213(2)	0.497(1)
O	O3	0.570(6)	0.207(8)	0.370(8)
C	C4	0.514(6)	0.409(9)	0.314(6)
C	C5	0.312(4)	0.415(4)	0.426(2)
C	C6	0.391(6)	0.515(8)	0.337(2)
C	C7	0.182(4)	0.549(8)	0.441(5)
C	C8	0.588(8)	0.537(9)	0.217(7)

Table S19: Atom coordinates of $Cu(acac)_2$ at 325K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.341(1)	0.213(1)	0.497(1)
O	O3	0.570(7)	0.206(9)	0.370(6)
C	C4	0.513(5)	0.407(8)	0.314(4)
C	C5	0.311(5)	0.413(5)	0.426(3)
C	C6	0.390(3)	0.514(7)	0.337(3)
C	C7	0.181(5)	0.548(8)	0.441(6)
C	C8	0.587(6)	0.536(9)	0.215(6)

Table S20: Atom coordinates of $Cu(acac)_2$ at 340K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.341(1)	0.213(3)	0.497(1)
O	O3	0.570(7)	0.205(8)	0.370(7)
C	C4	0.514(6)	0.407(9)	0.314(6)
C	C5	0.312(6)	0.414(4)	0.426(2)
C	C6	0.391(3)	0.514(8)	0.337(2)
C	C7	0.182(4)	0.549(9)	0.441(6)
C	C8	0.588(7)	0.534(9)	0.216(7)

Table S21: Atom coordinates of $Cu(acac)_2$ at 355K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.342(1)	0.210(3)	0.497(1)
O	O3	0.570(6)	0.203(8)	0.371(7)
C	C4	0.514(5)	0.403(9)	0.314(6)
C	C5	0.312(5)	0.409(5)	0.425(2)
C	C6	0.391(3)	0.509(7)	0.337(2)
C	C7	0.182(5)	0.541(8)	0.440(5)
C	C8	0.589(8)	0.529(9)	0.216(7)

Table S22: Atom coordinates of $Cu(acac)_2$ at 370K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.341(1)	0.213(2)	0.497(1)
O	O3	0.570(6)	0.205(8)	0.370(8)
C	C4	0.514(6)	0.405(9)	0.314(5)
C	C5	0.312(4)	0.412(4)	0.426(2)
C	C6	0.391(6)	0.512(8)	0.337(2)
C	C7	0.182(4)	0.547(8)	0.440(2)
C	C8	0.589(8)	0.533(9)	0.216(8)

Table S23: Atom coordinates of $Cu(acac)_2$ at 385K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.341(1)	0.211(3)	0.497(1)
O	O3	0.569(7)	0.204(9)	0.371(8)
C	C4	0.512(6)	0.404(9)	0.315(6)
C	C5	0.311(3)	0.410(4)	0.426(1)
C	C6	0.390(6)	0.510(8)	0.338(2)
C	C7	0.181(4)	0.543(9)	0.441(6)
C	C8	0.586(8)	0.532(9)	0.217(7)

Table S24: Atom coordinates of $Cu(acac)_2$ at 400K.

Atom	Label	x	y	z
Cu	Cu	0.500(0)	0.000(0)	0.500(0)
O	O2	0.340(1)	0.210(3)	0.497(1)
O	O3	0.569(7)	0.203(9)	0.371(8)
C	C4	0.512(6)	0.402(9)	0.315(6)
C	C5	0.311(4)	0.408(4)	0.426(2)
C	C6	0.390(6)	0.508(8)	0.338(2)
C	C7	0.182(4)	0.539(9)	0.441(6)
C	C8	0.587(8)	0.527(9)	0.217(8)

$Pd(acac)_2$

Table S25: Results of the Rietveld refinements of the VTPXRD measurements of $Pd(acac)_2$.

T / K	r_wp
100	4.60
115	4.45
130	4.71
145	4.43
160	4.69
175	4.03
190	4.52
205	3.88
220	4.75
235	4.07
250	4.68
265	4.13
280	4.39
295	3.98
310	3.96
325	3.93
340	3.78
355	3.87
370	3.82
385	3.70
400	3.54

Representative Rietveld plots for $Pd(acac)_2$

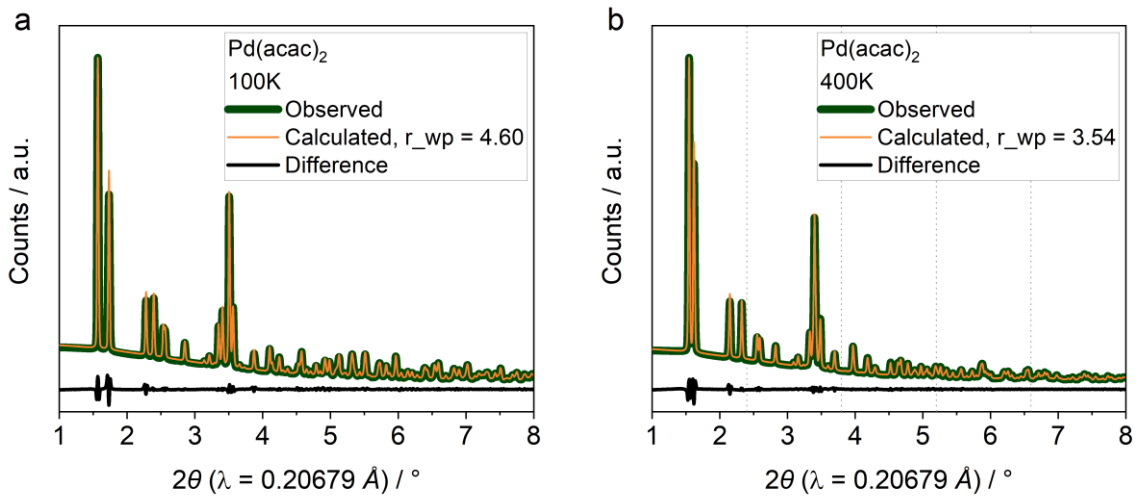

Figure S2: Visualisation of the Rietveld refinements of $Pd(acac)_2$ at 100K (**a**) and at 400K (**b**). The experimental Powder X-ray diffraction pattern of $Pd(acac)_2$ is shown in green, the calculated data from Rietveld refinements in orange and the difference curve of the Rietveld refinements in black.

Temperature dependent atomic coordinates of $Pd(acac)_2$ as obtained through Rietveld Refinements

Table S26: Atom coordinates of $Pd(acac)_2$ at 100K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.332(2)	0.206(5)	0.503(1)
O	O3	0.573(8)	0.199(9)	0.358(9)
C	C4	0.509(8)	0.391(9)	0.305(8)
C	C5	0.305(5)	0.396(7)	0.428(3)
C	C6	0.385(8)	0.488(8)	0.335(4)
C	C7	0.174(7)	0.528(8)	0.445(8)
C	C8	0.579(8)	0.517(9)	0.201(8)

Table S27: Atom coordinates of $Pd(acac)_2$ at 115K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.332(2)	0.206(5)	0.503(1)
O	O3	0.574(8)	0.201(9)	0.358(9)
C	C4	0.510(8)	0.392(9)	0.305(8)
C	C5	0.306(6)	0.396(8)	0.427(3)
C	C6	0.386(8)	0.488(8)	0.334(4)
C	C7	0.174(7)	0.527(8)	0.444(8)
C	C8	0.581(9)	0.519(9)	0.201(8)

Table S28: Atom coordinates of $Pd(acac)_2$ at 130K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.332(3)	0.206(5)	0.501(1)
O	O3	0.575(8)	0.199(9)	0.359(9)
C	C4	0.512(8)	0.390(9)	0.305(8)
C	C5	0.307(5)	0.396(8)	0.425(3)
C	C6	0.388(8)	0.487(9)	0.333(4)
C	C7	0.175(8)	0.528(9)	0.440(8)
C	C8	0.583(9)	0.517(8)	0.201(8)

Table S29: Atom coordinates of $Pd(acac)_2$ at 145K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.332(3)	0.205(5)	0.503(1)
O	O3	0.574(8)	0.200(9)	0.360(9)
C	C4	0.511(9)	0.391(9)	0.306(8)
C	C5	0.306(6)	0.395(8)	0.427(3)
C	C6	0.386(8)	0.487(9)	0.335(4)
C	C7	0.175(7)	0.526(8)	0.443(8)
C	C8	0.581(9)	0.517(9)	0.203(9)

Table S30: Atom coordinates of $Pd(acac)_2$ at 160K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.333(3)	0.205(5)	0.503(1)
O	O3	0.574(8)	0.202(9)	0.359(9)
C	C4	0.510(9)	0.393(9)	0.306(8)
C	C5	0.306(5)	0.396(8)	0.428(3)
C	C6	0.386(8)	0.488(9)	0.336(4)
C	C7	0.175(8)	0.526(8)	0.445(8)
C	C8	0.580(9)	0.520(9)	0.203(9)

Table S31: Atom coordinates of $Pd(acac)_2$ at 175K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.330(2)	0.205(4)	0.504(1)
O	O3	0.572(9)	0.201(9)	0.361(8)
C	C4	0.509(8)	0.392(9)	0.308(9)
C	C5	0.303(5)	0.395(8)	0.429(4)
C	C6	0.384(7)	0.487(8)	0.336(4)
C	C7	0.172(9)	0.525(8)	0.445(8)
C	C8	0.580(9)	0.520(9)	0.205(9)

Table S32: Atom coordinates of $Pd(acac)_2$ at 190K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.330(3)	0.204(3)	0.503(2)
O	O3	0.572(9)	0.201(9)	0.361(8)
C	C4	0.509(8)	0.391(9)	0.308(8)
C	C5	0.303(5)	0.393(7)	0.428(3)
C	C6	0.384(6)	0.486(8)	0.336(4)
C	C7	0.173(9)	0.522(9)	0.444(8)
C	C8	0.579(9)	0.518(9)	0.205(8)

Table S33: Atom coordinates of $Pd(acac)_2$ at 205K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.330(2)	0.205(3)	0.504(2)
O	O3	0.572(9)	0.200(9)	0.361(7)
C	C4	0.509(8)	0.390(8)	0.308(8)
C	C5	0.304(4)	0.395(6)	0.429(3)
C	C6	0.385(5)	0.486(8)	0.337(4)
C	C7	0.174(9)	0.525(8)	0.445(8)
C	C8	0.580(8)	0.516(9)	0.205(8)

Table S34: Atom coordinates of $Pd(acac)_2$ at 220K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.331(2)	0.206(3)	0.503(2)
O	O3	0.572(9)	0.199(9)	0.361(7)
C	C4	0.510(8)	0.389(8)	0.308(8)
C	C5	0.305(4)	0.395(6)	0.428(3)
C	C6	0.385(5)	0.486(8)	0.336(2)
C	C7	0.175(9)	0.526(8)	0.443(8)
C	C8	0.580(8)	0.515(9)	0.205(8)

Table S35: Atom coordinates of $Pd(acac)_2$ at 235K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.333()	0.205()	0.503()
O	O3	0.574()	0.200()	0.360()
C	C4	0.511()	0.391()	0.307()
C	C5	0.307()	0.394()	0.428()
C	C6	0.387()	0.486()	0.336()
C	C7	0.176()	0.525()	0.445()
C	C8	0.581()	0.518()	0.204()

Table S36: Atom coordinates of $Pd(acac)_2$ at 250K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.330(1)	0.206(3)	0.502(1)
O	O3	0.573(9)	0.199(9)	0.362(7)
C	C4	0.511(8)	0.389(9)	0.308(8)
C	C5	0.305(4)	0.395(6)	0.427(3)
C	C6	0.387(6)	0.486(8)	0.336(4)
C	C7	0.174(9)	0.527(8)	0.442(8)
C	C8	0.583(8)	0.515(9)	0.206(8)

Table S37: Atom coordinates of $Pd(acac)_2$ at 265K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.332(1)	0.206(3)	0.503(1)
O	O3	0.573(9)	0.199(9)	0.362(7)
C	C4	0.511(8)	0.389(9)	0.309(8)
C	C5	0.307(4)	0.395(6)	0.428(3)
C	C6	0.387(6)	0.486(8)	0.337(4)
C	C7	0.176(9)	0.527(8)	0.443(8)
C	C8	0.582(8)	0.515(9)	0.207(8)

Table S38: Atom coordinates of $Pd(acac)_2$ at 280K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.331(1)	0.206(3)	0.503(1)
O	O3	0.573(9)	0.199(9)	0.362(7)
C	C4	0.511(8)	0.389(9)	0.309(8)
C	C5	0.306(4)	0.395(6)	0.428(3)
C	C6	0.386(6)	0.486(8)	0.337(4)
C	C7	0.175(9)	0.527(8)	0.444(8)
C	C8	0.582(8)	0.514(9)	0.206(8)

Table S39: Atom coordinates of $Pd(acac)_2$ at 295K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.332(1)	0.207(3)	0.502(1)
O	O3	0.573(9)	0.200(9)	0.361(7)
C	C4	0.511(8)	0.391(9)	0.309(7)
C	C5	0.307(5)	0.396(7)	0.428(3)
C	C6	0.387(5)	0.487(9)	0.337(4)
C	C7	0.177(9)	0.528(8)	0.443(9)
C	C8	0.582(9)	0.516(9)	0.207(8)

Table S40: Atom coordinates of $Pd(acac)_2$ at 310K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.333(1)	0.206(3)	0.502(1)
O	O3	0.574(9)	0.201(9)	0.361(8)
C	C4	0.512(8)	0.391(9)	0.308(8)
C	C5	0.307(5)	0.395(6)	0.427(4)
C	C6	0.388(6)	0.487(8)	0.337(4)
C	C7	0.177(9)	0.526(8)	0.443(8)
C	C8	0.583(8)	0.518(9)	0.207(9)

Table S41: Atom coordinates of $Pd(acac)_2$ at 325K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.331(1)	0.205(3)	0.502(1)
O	O3	0.573(9)	0.200(9)	0.362(8)
C	C4	0.510(8)	0.390(9)	0.309(8)
C	C5	0.305(5)	0.394(6)	0.428(4)
C	C6	0.386(6)	0.486(8)	0.337(4)
C	C7	0.174(9)	0.524(8)	0.444(8)
C	C8	0.582(8)	0.516(9)	0.207(9)

Table S42: Atom coordinates of $Pd(acac)_2$ at 340K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.331(1)	0.205(3)	0.503(1)
O	O3	0.572(9)	0.200(9)	0.363(8)
C	C4	0.510(8)	0.390(9)	0.310(8)
C	C5	0.305(5)	0.394(6)	0.429(4)
C	C6	0.386(6)	0.486(8)	0.338(4)
C	C7	0.175(9)	0.524(9)	0.445(8)
C	C8	0.580(8)	0.516(9)	0.209(9)

Table S43: Atom coordinates of $Pd(acac)_2$ at 355K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.332(1)	0.205(3)	0.504(1)
O	O3	0.571(9)	0.200(9)	0.361(8)
C	C4	0.508(9)	0.390(9)	0.309(9)
C	C5	0.306(5)	0.394(5)	0.431(3)
C	C6	0.385(6)	0.486(9)	0.339(4)
C	C7	0.175(9)	0.525(8)	0.448(8)
C	C8	0.577(9)	0.517(9)	0.207(9)

Table S44: Atom coordinates of $Pd(acac)_2$ at 370K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.332(1)	0.205(3)	0.503(2)
O	O3	0.572(9)	0.201(9)	0.362(7)
C	C4	0.510(8)	0.391(9)	0.310(8)
C	C5	0.306(4)	0.394(5)	0.429(4)
C	C6	0.386(5)	0.486(8)	0.339(4)
C	C7	0.176(9)	0.524(9)	0.445(8)
C	C8	0.580(8)	0.518(9)	0.209(9)

Table S45: Atom coordinates of $Pd(acac)_2$ at 385K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.333(1)	0.204(3)	0.504(2)
O	O3	0.571(9)	0.200(9)	0.362(7)
C	C4	0.508(8)	0.389(9)	0.310(8)
C	C5	0.306(4)	0.393(5)	0.430(4)
C	C6	0.385(5)	0.484(8)	0.339(4)
C	C7	0.176(9)	0.523(9)	0.447(8)
C	C8	0.578(8)	0.516(9)	0.208(9)

Table S46: Atom coordinates of $Pd(acac)_2$ at 400K.

Atom	Label	x	y	z
Pd	Pd	0.500(0)	0.000(0)	0.500(0)
O	O2	0.332(1)	0.203(3)	0.502(2)
O	O3	0.573(9)	0.201(9)	0.363(7)
C	C4	0.511(8)	0.390(9)	0.311(8)
C	C5	0.306(4)	0.391(6)	0.428(3)
C	C6	0.387(6)	0.484(8)	0.338(4)
C	C7	0.176(9)	0.520(8)	0.443(8)
C	C8	0.582(8)	0.517(9)	0.210(9)

Comparison between $Cu(acac)_2$ and $Pd(acac)_2$

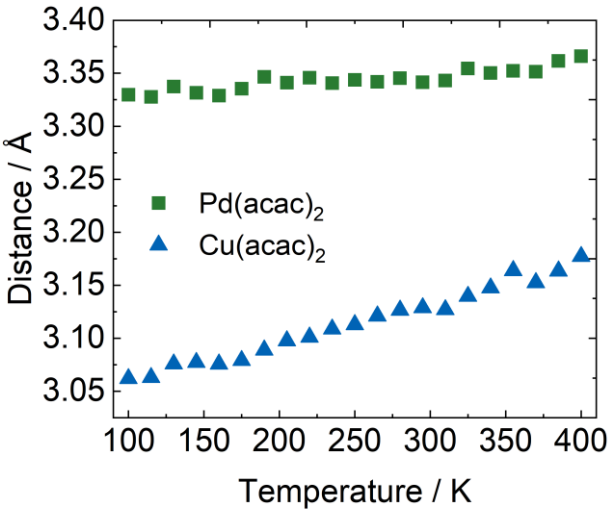

Figure S3: M-π distances of two adjacent $M(acac)_2$ molecules within the stacks along [010].

Density Functional Theory Calculations

To obtain an idea which compound, $Cu(acac)_2$ or $Pd(acac)_2$ is easier be deformed along the stacks (i.e. along X_1 / [010]) we performed DFT-based model calculations. In the model calculations we monitor the energy (*E*) of two neighboring complexes within one stack as a function of distance (*d*), see Figure S4a. The starting structures for the calculations were obtained from 100 K Rietveld refinements. Density functional theory calculations were performed using Gaussian 16.[6] The basis set 6-31G**[7,8] and the basis set exchange ECP_stutt97[9,10] were applied. The functional PBE[11,12] was used as: PBEPBE. Dispersion was added to some calculations by the functional GD3 with no effect on the qualitative outcomes.[13] For comparison reasons, calculated energies are normalised to the optimum as zero point and Figure S4b shows the change in energy compared to $d(E_{min})$. The steeper potential well of $Cu(acac)_2$ shows that more energy is needed to offset two adjacent $Cu(acac)_2$ molecules within the stacks compared to $Pd(acac)_2$. Qualitatively, the results indicate that M-π interactions between $M(acac)_2$ molecules within stacks are relatively stronger for M = Cu^{2+}; however, in the proposed mechanism (see main text), the presence of M-π interactions and not so much the strength is important. For $Pd(acac)_2$, the M-π interactions within the stack *and* H-π interactions between molecules of different stacks form a wine-rack motif which facilitates the occurrence of linear NTE.

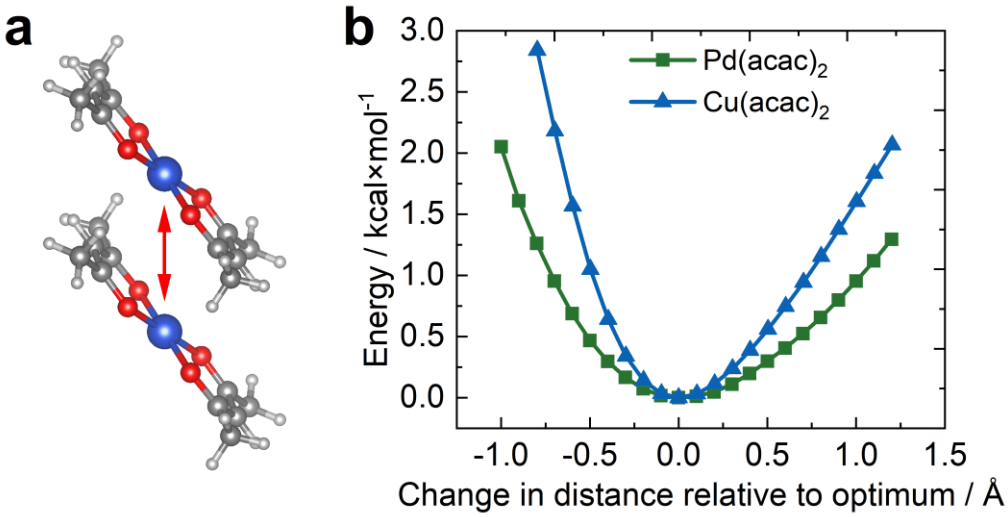

Figure S4: (a) shows the model used in the calculations and the red arrows indicates the distance that was varied, i.e. the [010] direction in $M(acac)_2$. The steeper curve of $Cu(acac)_2$ in **(b)** indicates that a variation of the distance of $Cu(acac)_2$ out of $d(E_{min})$ comes with a larger energy penalty.

Infrared Analysis

The Infrared (IR) spectroscopy was performed on an ALPHA-P IR spectrometer by BRUKER. Prior to the analysis, the samples were grinded using a pestle and mortar. The absorption of the coordination compounds was analysed in a wavelength range from 2000-400 cm^{-1}.

The obtained IR-spectra, see Figure S5, are consistent with the literature.[14,15] It is apparent that some bands, for example those at 780 cm^{-1} or 1017 cm^{-1} are insensitive, others, such as all below 700 cm^{-1} are sensitive to the metal center.

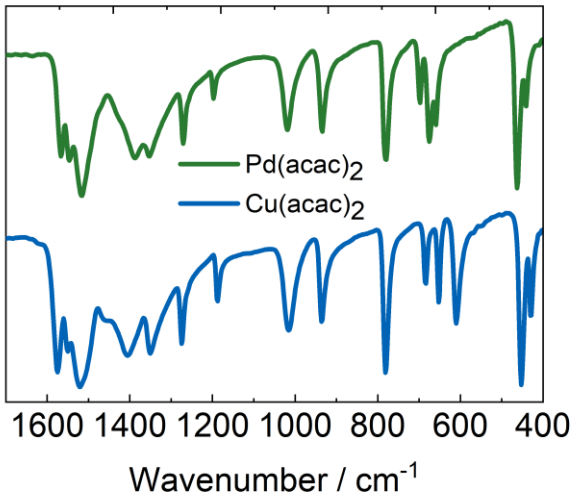

Figure S5: Visualisation of the IR-spectra of the coordination compounds.

Thermogravimetric analysis

The thermal stability of the coordination compounds was determined with a *Netzsch* STA 449F5 Jupiter machine using aluminum oxide pans with sample masses between 8-10 mg. The temperature of the oven cell was calibrated based on the melting points of the following metals: In, Sn, Bi and Zn. A baseline correction was performed by screening an empty sample pan with the respective temperature program prior to the experiment. The applied heating rate was 10Kmin^{-1}.

The observed thermal stability, see Figure S6, of the coordination compounds is consistent with the literature.[16,17]

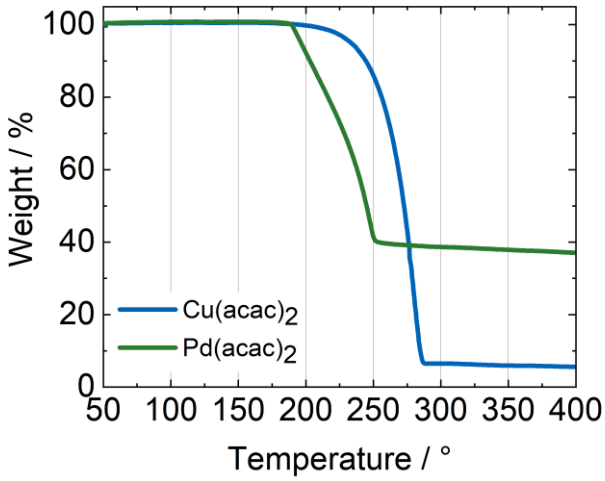

Figure S6: Visualisation of the thermogravimetric analysis of the coordination compounds. The applied heating rate was 10Kmin^{-1}.

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