Supporting information

Long-chain mercury carboxylates relevant to saponification in oil and tempera paintings: XRPD and ssNMR complementary study of the crystal structures

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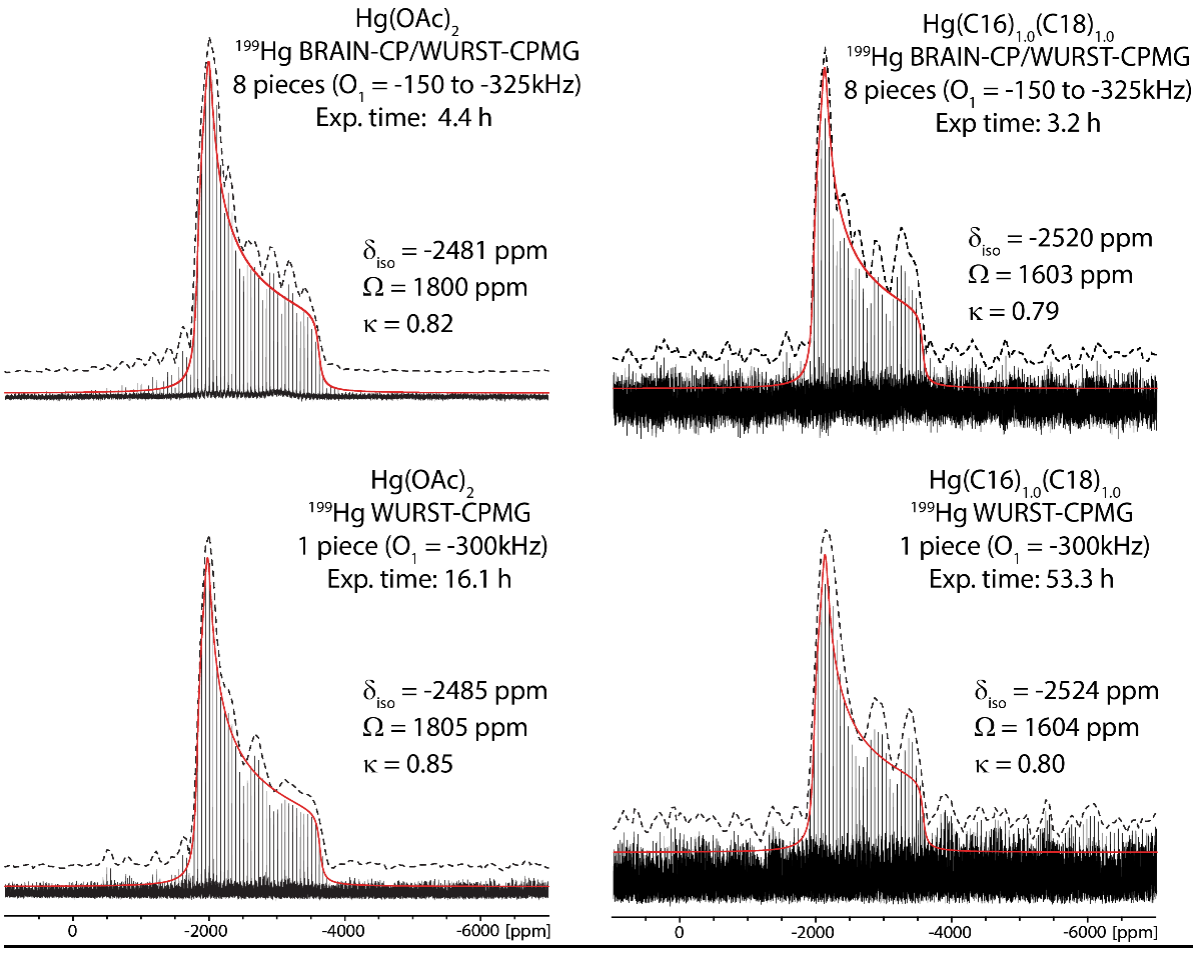

Fig. S1 The comparison of ^{199}Hg WURST-CPMG NMR and ^{199}Hg BRAIN-CP/WURST-CPMG NMR spectra; spectral envelope (black solid lines), spectral envelope obtained using USS software (black dashed lines) and fitted spectral shapes (red solid lines) of mercury acetate, $Hg(OAc)_2$, and mixed mercury carboxylate, $Hg(C16)_{1.0}$ $(C18)_{1.0}$.

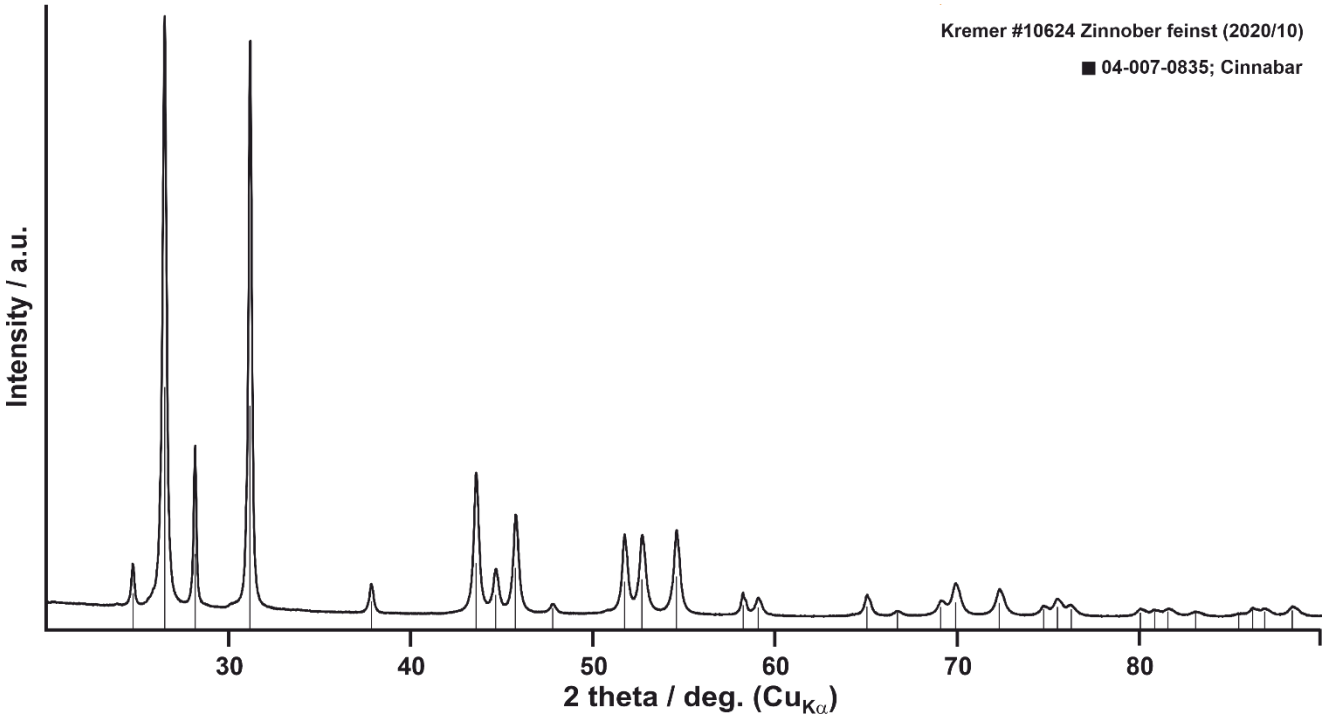

Fig. S2 XRPD pattern of cinnabar pigment (Kremer #10624 Zinnober).

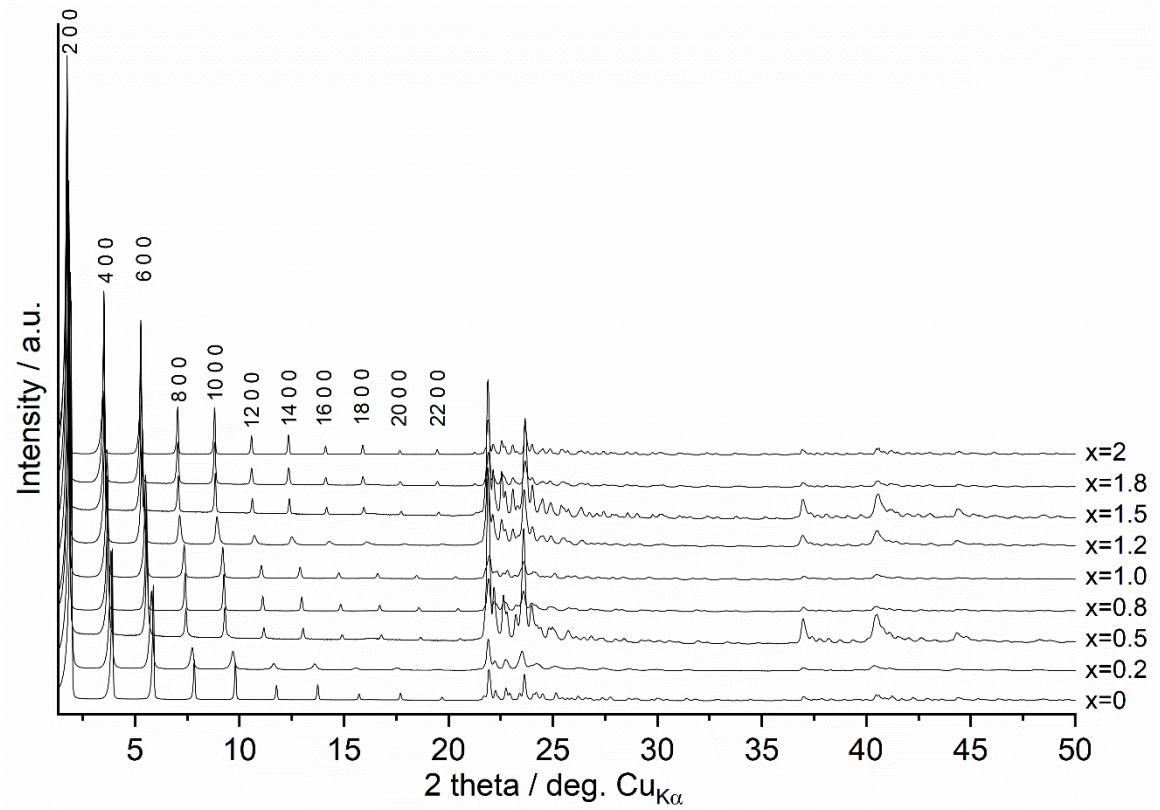

Fig. S3 Full range of XRPD pattern of synthesized mixed mercury carboxylates of the formula $Hg(C16)_x(C18)_{2-x}$ normalized according to the 200 diffraction line.

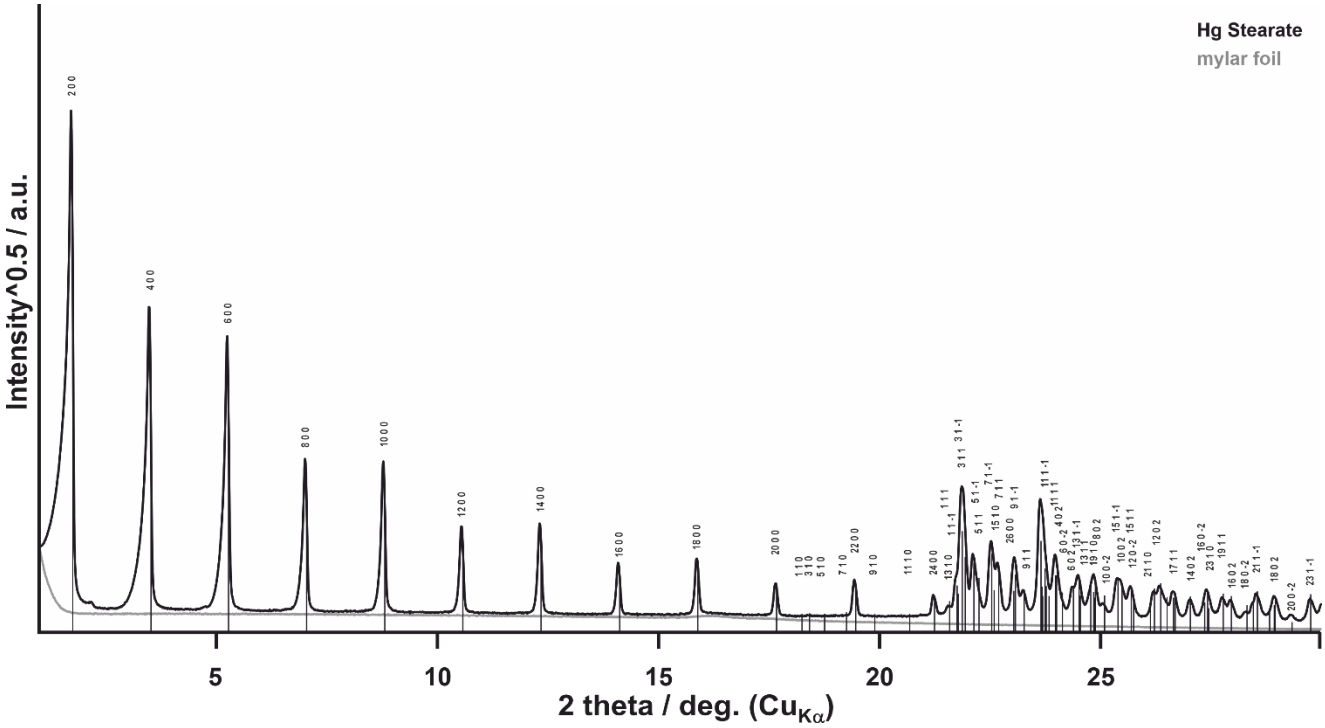

Fig. S4 XRPD pattern $Hg(C18)_2$ with indices according to C2/c space group.

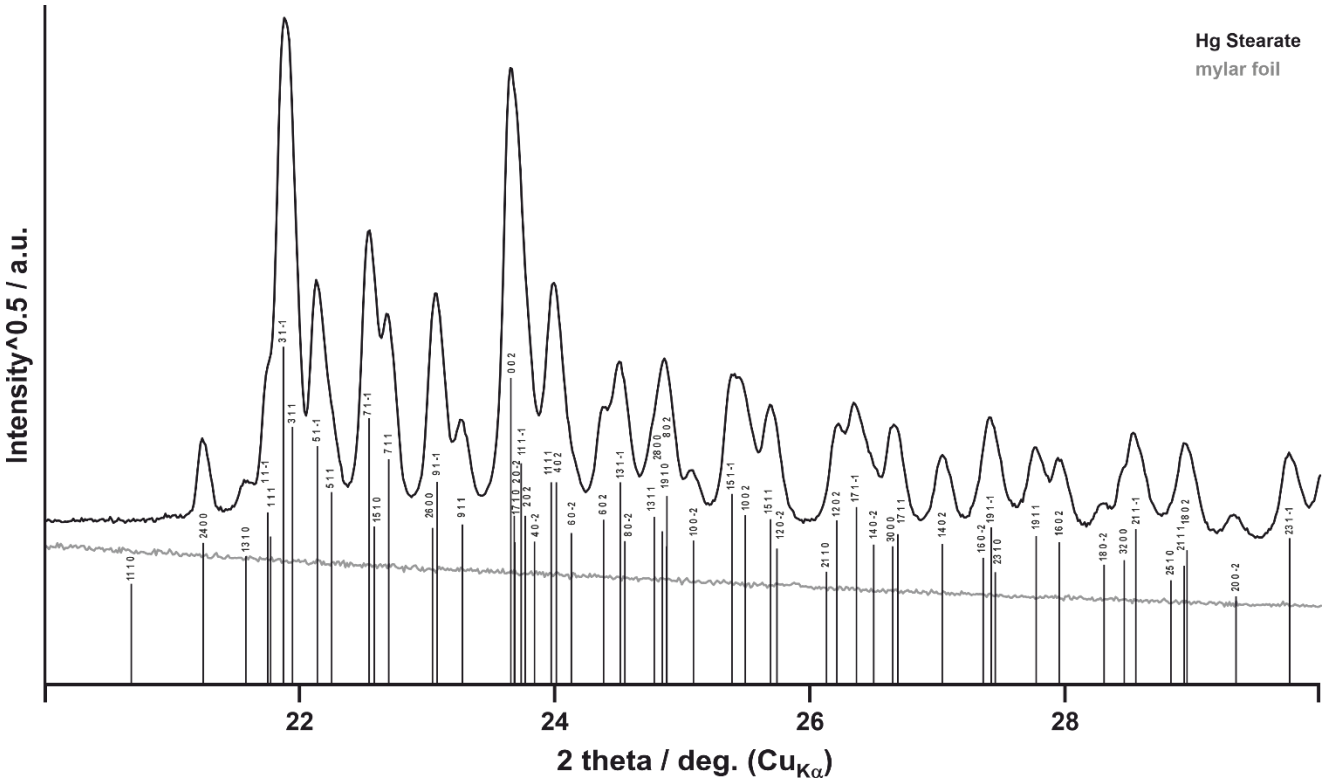

Fig. S5 XRPD pattern $Hg(C18)_2$ with indices according to C2/c space group, detail in the range of 20 to 30° 2theta.

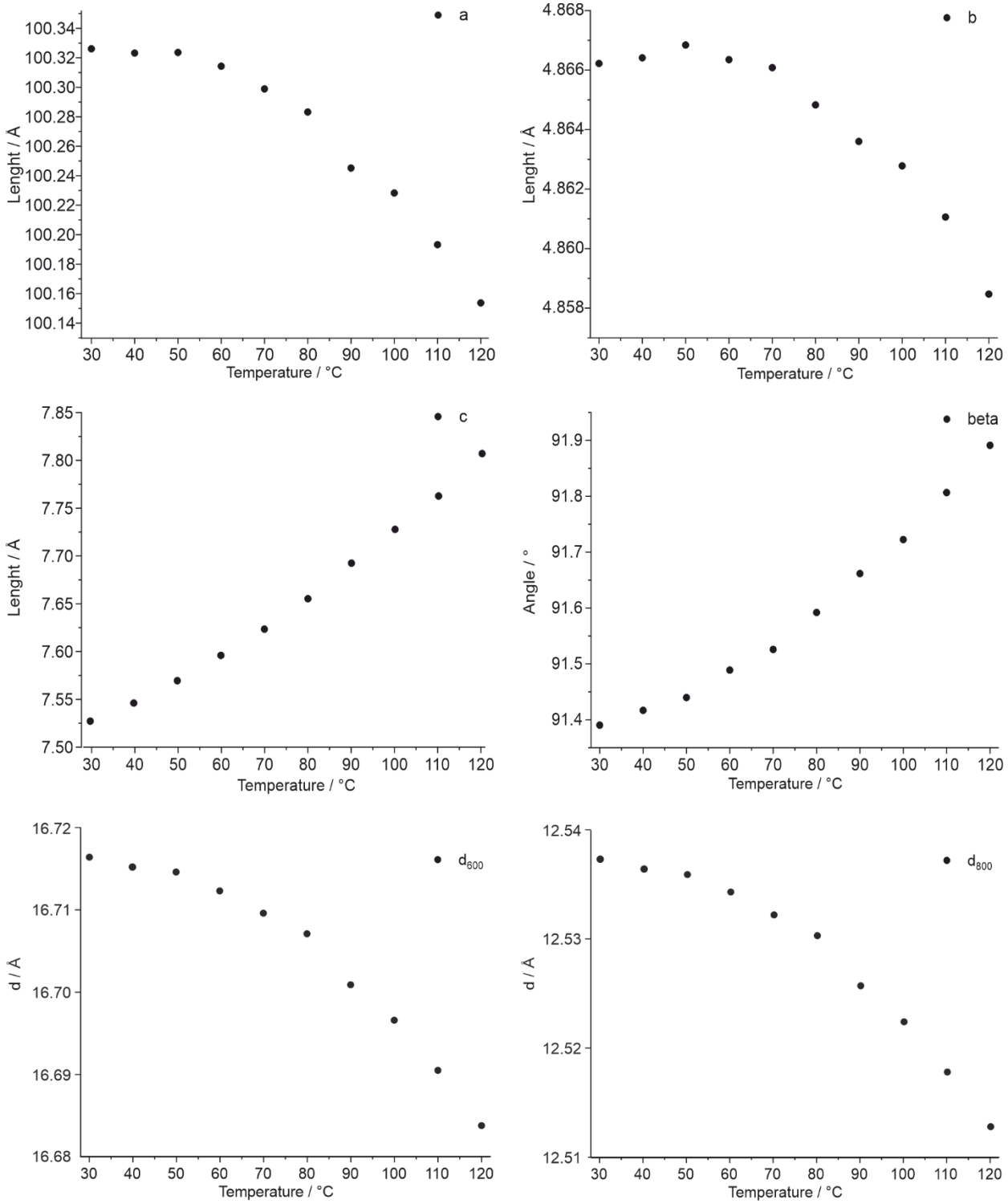

Fig. S6 Temperature-related changes of unit cell parameters of mercury stearate during heating from 30 to 120 °C. Error bars show standard uncertainties (k=3). For unit cell parameter *c*, the standard uncertainties are smaller than drawn points.

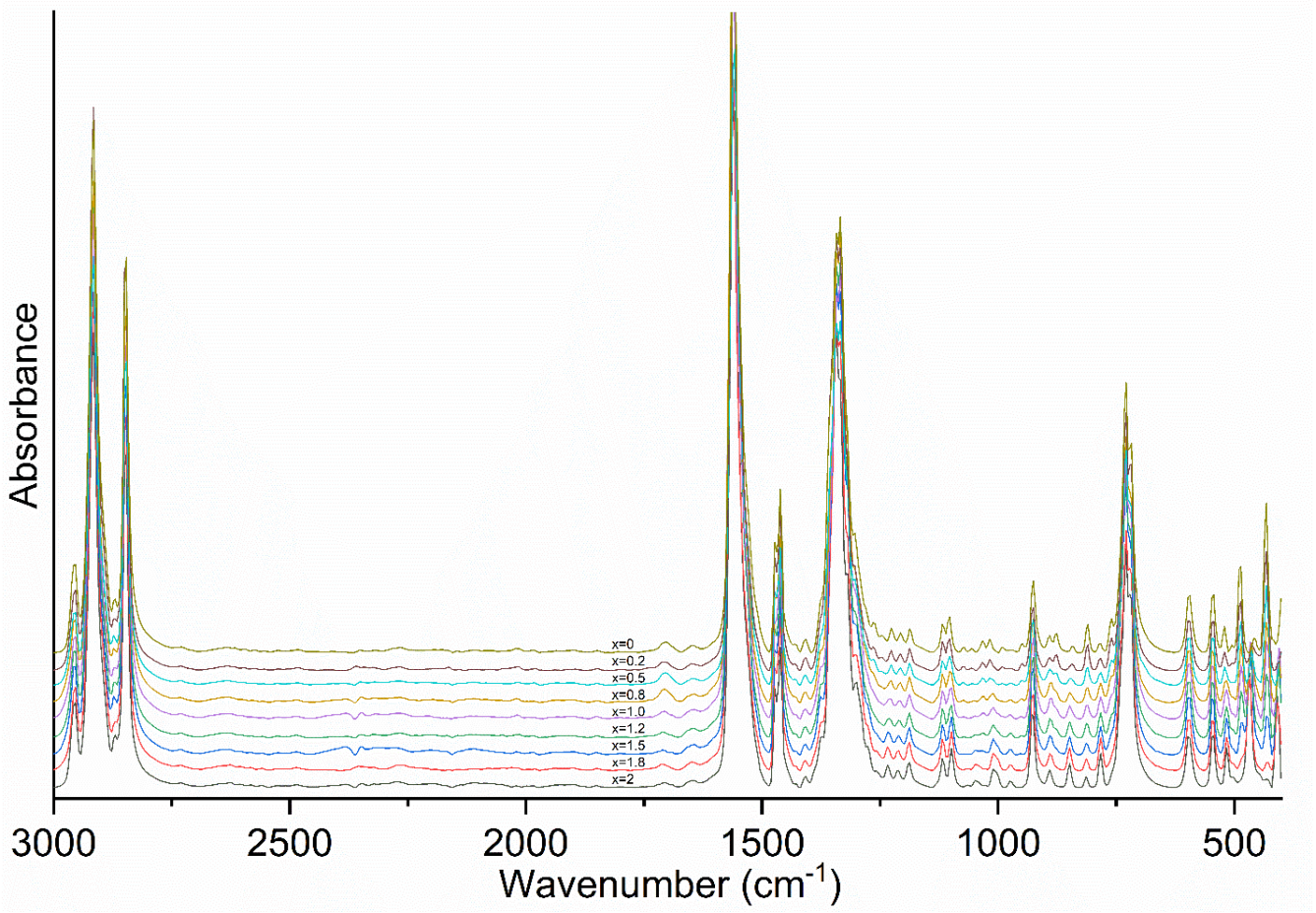

Fig. S7 Infrared spectra of mercury carboxylates $Hg(C16)_x(C18)_{2.0-x}$ in the 3000-400 cm^{-1} region.

Table S1 Infrared absorption bands positions 3000-400 (cm^{-1}) of mercury carboxylates $Hg(C16)_x(C18)_{2.0-x}$

x = 2	x=1.8	x = 1.5	x=1.2	x = 1.0	x=0.8	x = 0.5	x=0.2	x = 0	Assignment
2954 w	2954 w	2954 w	2954 w	2954 w	2954 w	2958 w	2954 w	2958 w	ν_{as} (CH_3)
2915 vs	2915 vs	2915 vs	2915 vs	2915 vs	2915 vs	2915 vs	2915 vs	2915 vs	ν_{as} (CH_2)
2869 vw	2869 vw	2873 vw	2869 vw	2869 vw	2873 vw	2873 vw	2873 vw	2869 vw	ν_s (CH_3)
2846 vs	2846 vs	2846 vs	2846 vs	2846 vs	2846 vs	2846 vs	2846 vs	2846 vs	ν_s (CH_2)
1705 vw	1712 vw	1711 vw	1711 vw	1708 vw	1708 vw	1704 vw	1708 vw	1704 vw	ν C=O
1643 vw	1650 vw	1643 vw	1643 vw	1643 vw	1643 vw	1643 vw	1643 vw	1650 vw	ν C=C
1562 vs	1562 vs	1562 vs	1562 vs	1562 vs	1562 vs	1558 vs	1558 vs	1562 vs	ν_{as} (COO^-)
1461 m	1461 m	1461 m	1461 m	1461 m	1461 m	1461 m	1461 m	1461 m	δ (CH_2)
1407 vw	1407 vw	1407 vw	1407 vw	1407 vw	1407 vw	1407 vw	1407 vw	1407 vw	
1376 sh	1376 sh	1376 sh	1376 sh	1376 sh	1376 sh	1376 sh	1376 sh	1376 sh	δ (CH_3)
1342 s	1342 s	1342 s	1342 s	1342 s	1342 s	1342 s	1342 s	1342 s	ν_s (COO^-)
1319 sh	1319 sh	1319 sh	1319 sh	1319 sh	1319 sh	1319 sh	1319 sh	1319 sh	
1299 sh	1303 sh	1307 sh	1307 sh	1307 sh	1307 sh	1303 sh	1303 sh	1303 sh	
-	-	-	-	-	-	1265 vw	1265 vw	1265 vw	
-	-	-	-	-	-	1246 vw	1246 vw	1246 vw	δ (CH_2)
1234 vw	1234 vw	1234 vw	1234 vw	1230 vw	1230 vw	1226 vw	1226 vw	1226 vw	
1214 vw	1214 vw	1211 vw	1211 vw	1211 vw	1211 vw	1207 vw	1207 vw	1207 vw	
1191 vw	1191 vw	1188 vw	1188 vw	1188 vw	1188 vw	1188 vw	1188 vw	1188 vw	
1118 vw	1118 vw	1118 vw	1118 vw	1118 vw	1118 vw	1118 vw	1118 vw	1118 vw	
1099 vw	1099 vw	1099 vw	1099 vw	1099 vw	1103 vw	1103 vw	1103 vw	1103 vw	ν C-C + δ C-C-C
-	-	-	1072 vw	1072 vw	1072 vw	1072 vw	1072 vw	1072 vw	
1048 w	1048 w	1048 vw	1048 vw	1048 vw	1048 vw	1056 vw	1056 vw	1056 vw	
-	-	-	1033 vw	1033 vw	1033 vw	1033 vw	1033 vw	1033 vw	
1010 w	1010 w	1010 w	1010 w	1010 vw	1010 vw	1018 vw	1018 vw	1018 vw	ν C-C
-	-	-	-	-	-	991 vw	991 vw	991 vw	
975 vw	971 vw	971 vw	971 vw	971 vw	971 vw	975 vw	-	-	
-	-	952 vw	952 vw	952 vw	952 vw	948 vw	948 vw	948 vw	δ (CH_2)
929 m	925 m	925 m	925 m	925 m	925 m	925 m	925 m	925 m	
890 vw	890 vw	890 vw	890 vw	887 vw	887 vw	890 vw	890 vw	890 vw	δ CH_3 + ν C-C
-	-	-	875 sh	875 sh	875 sh	875 vw	875 vw	875 vw	
848 vw	848 vw	848 vw	848 vw	848 vw	848 vw	848 vw	844 vw	840 vw	ν C-C
813 vw	813 vw	813 vw	813 vw	813 vw	809 vw	809 vw	809 vw	809 vw	δ (CH_2)
782 w	782 w	782 w	782 vw	782 vw	782 vw	782 vw	782 vw	782 vw	
-	-	-	759 sh	759 sh	759 sh	759 vw	759 vw	759 vw	
728 s	728 s	728 s	728 s	728 s	728 s	728 s	728 s	728 s	δ (CH_2)
597 w	597 w	597 w	597 w	593 w	597 w	597 w	597 w	593 w	ν C-C + δ C-C-C
543 w	547 w	547 w	547 w	547 w	547 w	547 w	543 w	543 w	δ (COO)
516 vw	516 vw	516 vw	516 vw	516 vw	516 vw	520 vw	520 vw	520 vw	
501 sh	501 sh	501 sh	501 sh	501 sh	501 sh	-	505 vw	505 vw	
-	-	485 vw	485 vw	485 vw	485 vw	485 vw	485 w	485 w	ν C-C(carboxyl)
466 vw	466 vw	466 vw	466 vw	466 vw	458 vw	458 vw	458 vw	458 vw	
-	-	431 vw	431 vw	431 vw	431 vw	431 vw	431 w	431 w	

vs – very strong, s – strong, m – medium, w – weak, vw – very weak, sh – shoulder, ν – stretching, δ – bending

Table S2 IR absorption bands positions (cm^{-1}) of synthesized mercury and lead palmitate and their mixture

$Hg(C16)_2$	$Pb(C16)_2$	$Hg(C16)_2$ + $Pb(C16)_2$ mixture
1562 vs	-	1562 vs
-	1538 vw	-
-	1510 m	1511 m
1465 m	1465 m	1465 m
1408 vw	1415 m	1415 m
1342 s	1334 vw; 1349 vw	1342 s
-	1315 w	1322 sh
-	1292 w	1295 w
-	1272 vw	1272 vw
-	1253 vw	1253 vw
1234 vw	1230 w	1230 vw
1211 vw	1211 w	1211 vw
1187 vw	1187 w	1187 vw
1118 vw	1118 vw	1118 vw
1099 vw	1099 vw	1099 vw
1045 vw	1049 vw	-
1006 vw	1010 vw	1010vw
971 vw	975 vw	971 vw
925 w	929 m	929 m
890 vw	890 vw	890 vw
848 vw	852 vw	848 vw
813 vw	813 vw	813 vw
783 vw	782 w	782 w
725 s	725 sh	725 s
-	717 vw	-
-	694 vw	701 sh
593 w	594 vw	594 vw
543 w	536 w	539 w
516 vw	512 vw	516 vw
-	493 w	493 w
466 w	458 w	466 w

vs – very strong, s – strong, m – medium, w – weak, vw – very weak, sh – shoulder

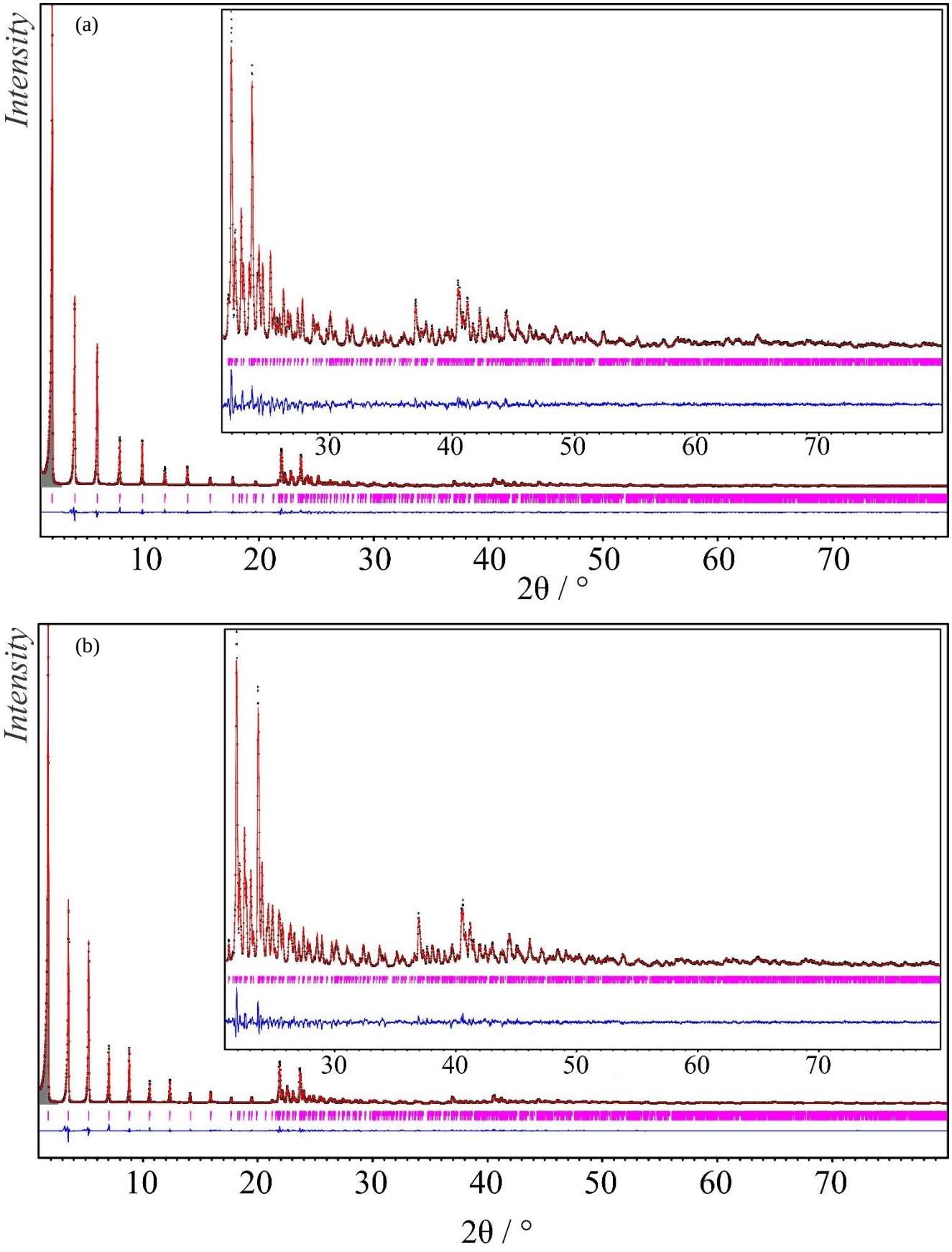

Fig. S8 The final Rietveld fit of the mercury palmitate (a) and mercury stearate (b). Black dots – measured pattern, red curve – calculated profile, magenta vertical bars – Braggs positions, blue line – difference curve.

Table S3 Crystallographic data of mercury stearate and mercury palmitate obtained from Rietveld refinement

	Mercury palmitate	**Mercury stearate**
formula	$Hg\ C_{32}\ H_{62}\ O_4$	$Hg\ C_{36}\ H_{70}\ O_4$
crystallographic system	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
a [Å]	90.135 (2)	100.294 (2)
b [Å]	4.85721 (10)	4.86437 (9)
c [Å]	7.52779 (16)	7.51745 (13)
β [°]	91.524 (3)	91.368 (2)
V [Å^3]	3294.55 (13)	3666.47 (12)
Z	4	4
Density [gcm^{-3}]	1.434	1.391
radiation	Cu Kα	Cu Kα
temperature [K]	293	293
$R_p/R_{wp}/R_{exp}$	0.061/0.079/0.038	0.062/0.084/0.037
$\chi 2$	4.33	5.198
restraints	47	53
constraints	141	159
parameters	95	101

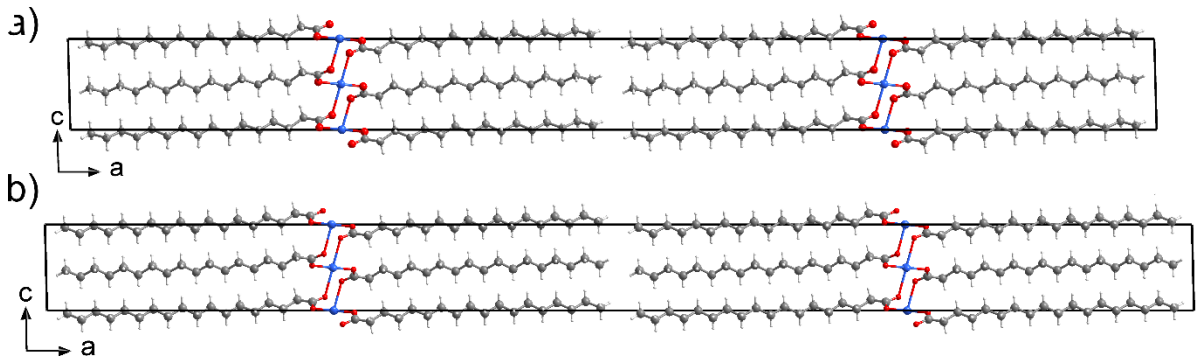

Fig. S9 Unit cells of the mercury palmitate (a) and mercury stearate (b).

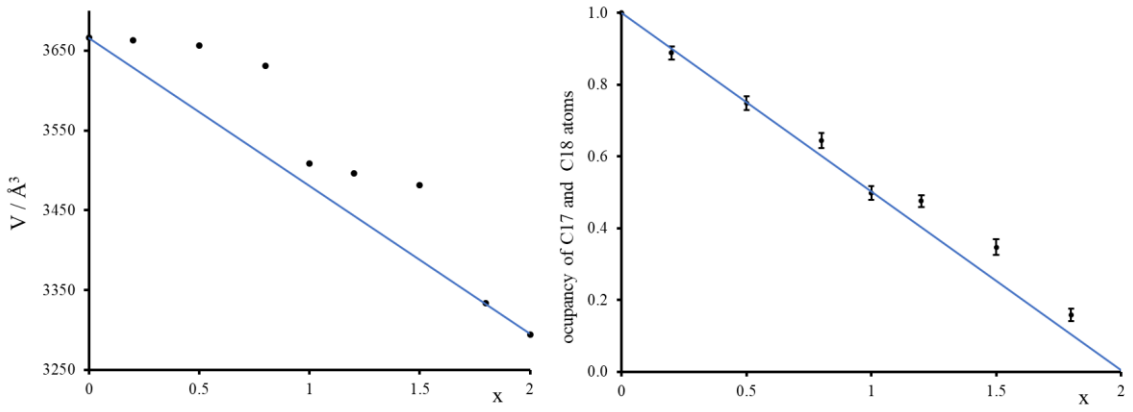

Fig. S10 Results of Rietveld refinement of XRPD patterns of mixed ($Hg(C16)_x(C18)_{2-x}$) mercury carboxylates with different molar ratios represented by *x*. In both graphs, the blue line shows the ideal linear dependency on *x*. **Left**: Dependency of the unit cell volume on the molar ratio *x*. Black dots are the results of the Rietveld refinement. Error bars are not shown because they are smaller than the size of the dots. **Right**: Dependency of the occupancy factor of atoms C17 and C18 on the molar ratio x with their error bars corresponding to 3σ.

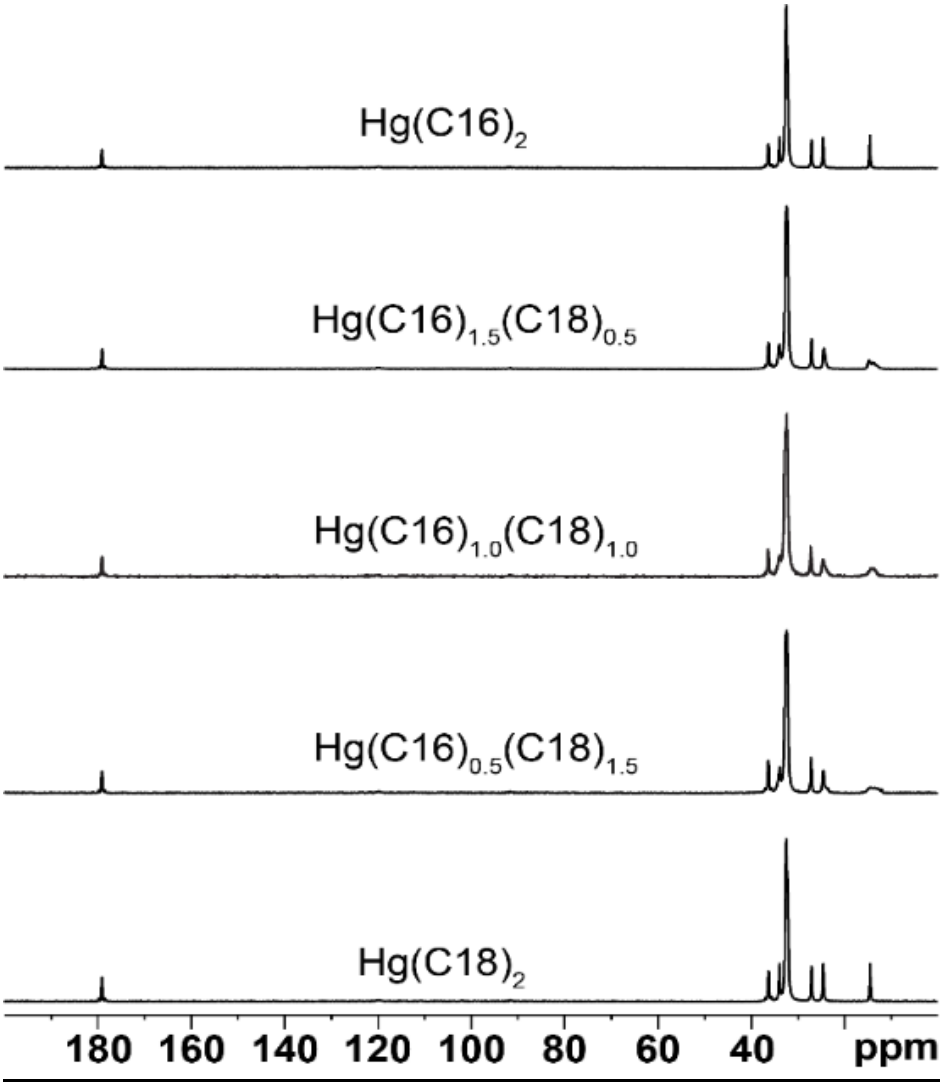

Fig. S11 Full range experimental ^{13}C CP/MAS NMR spectra of simple and mixed mercury-carboxylates.

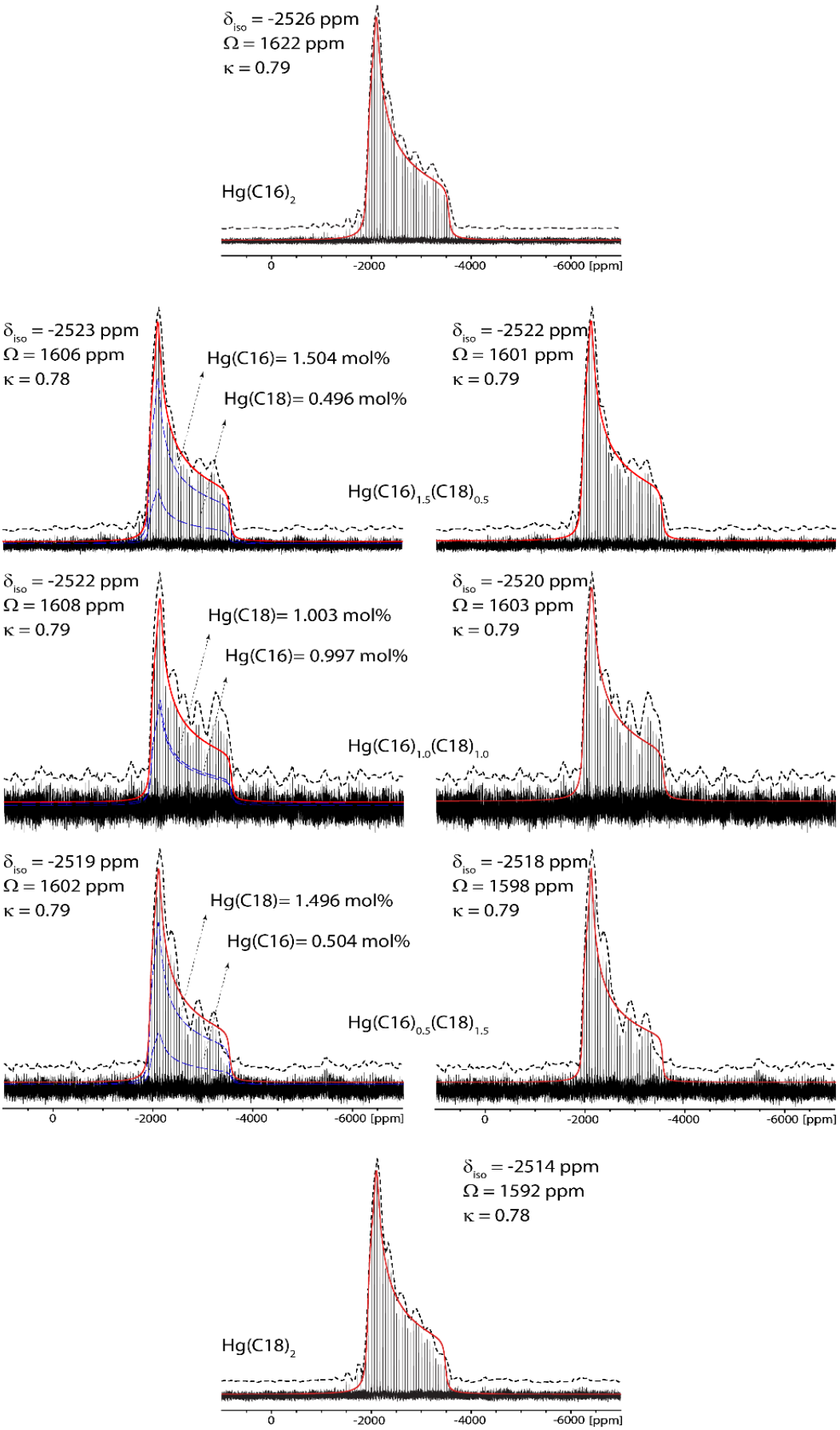

Fig. S12 Experimental ^{199}Hg BRAIN-CP/WURST-CPMG NMR spectra (black solid lines), spectral envelope obtained using USS software (black dashed lines) and fitted spectral shapes (red solid lines) of simple ($Hg(C16)_2$ and $Hg(C18)_2$) and mixed ($Hg(C16)_x(C18)_{2-x}$) mercury-carboxylates with NMR parameters fitted using two (blue dashed lines) and/or one spectral line(s).

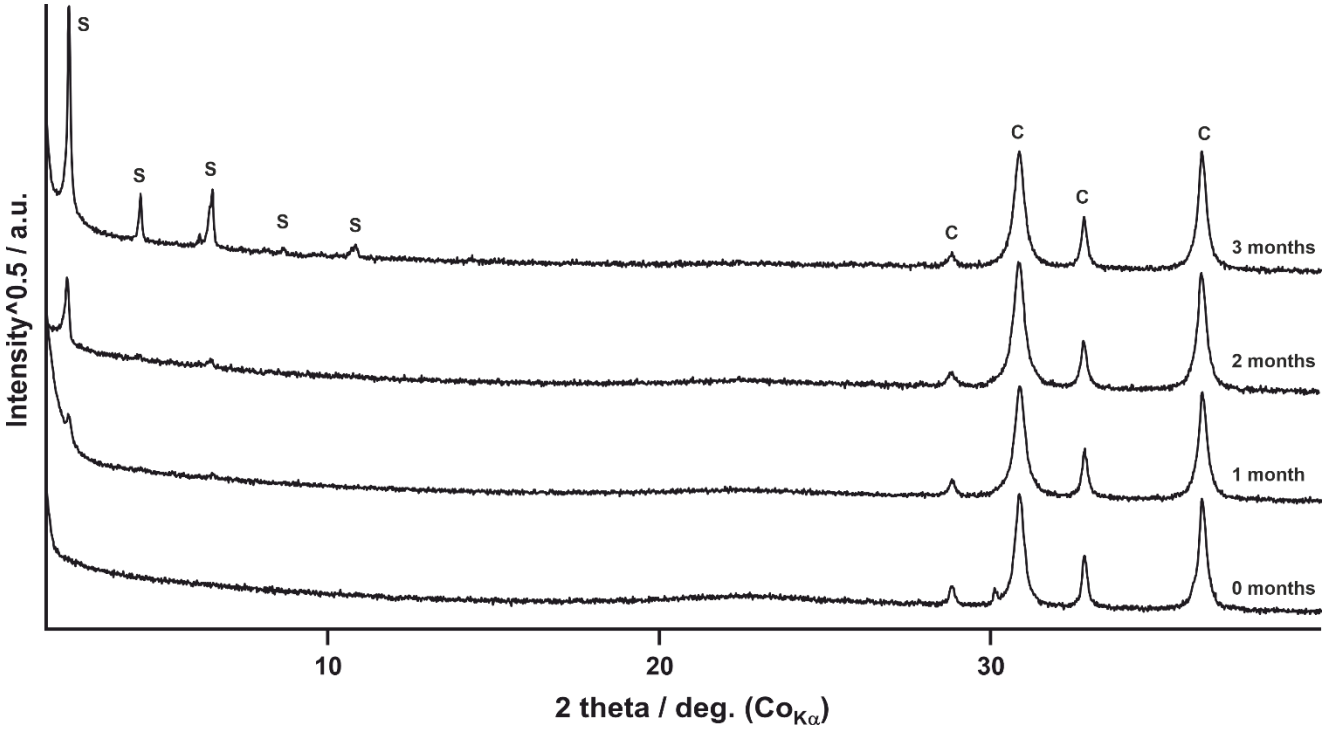

Fig. S13 Full range XRPD patterns of the naturally aged model mixture: cinnabar and egg yolk after 0 ,1, 2 and 3 months.

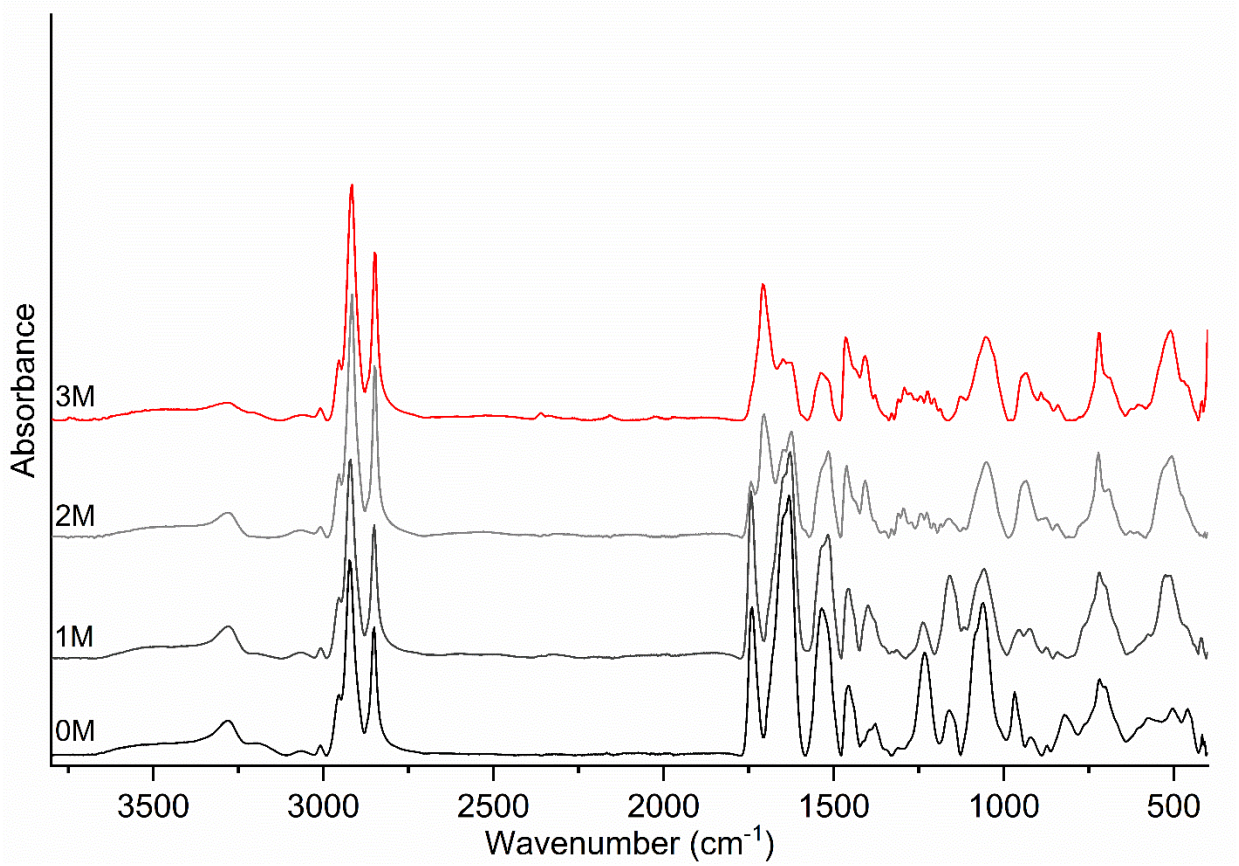

Fig. S14 FTIR spectra (region 4000-500 cm^{-1}) of the naturally aged model mixture: cinnabar and egg yolk after 0 month (0M) 1 month (1M), 2 month (2M) and 3 month (3M).