

# Structural insights into layered tetrahalocuprates(II) based on small unsaturated and cyclic primary ammonium cations

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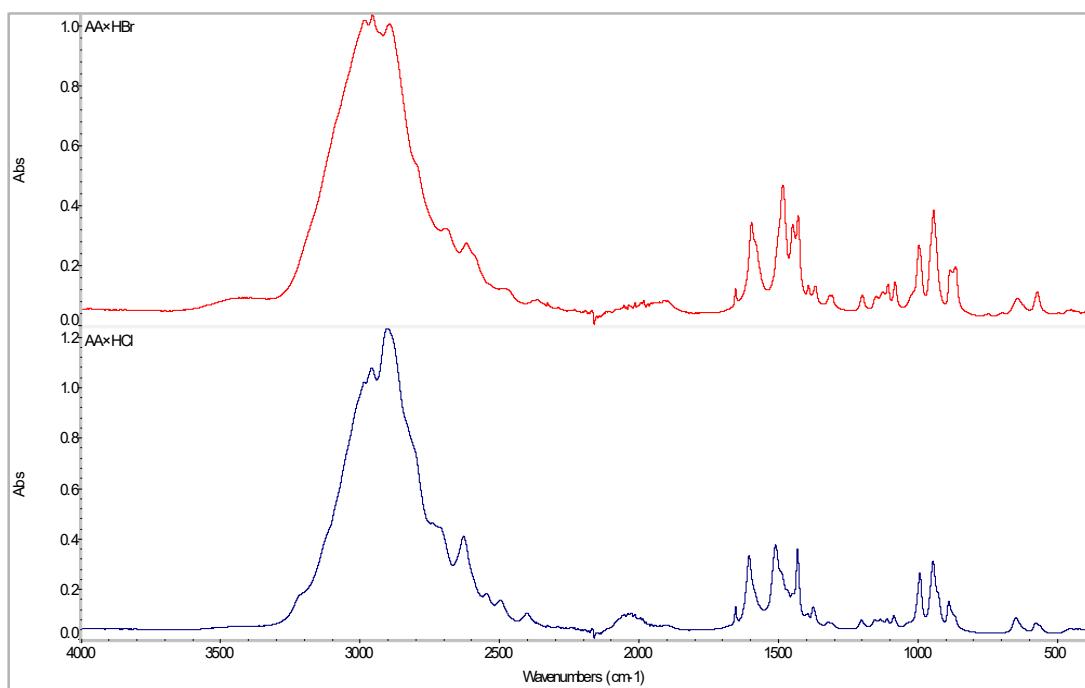
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## Electronic Supplementary Information

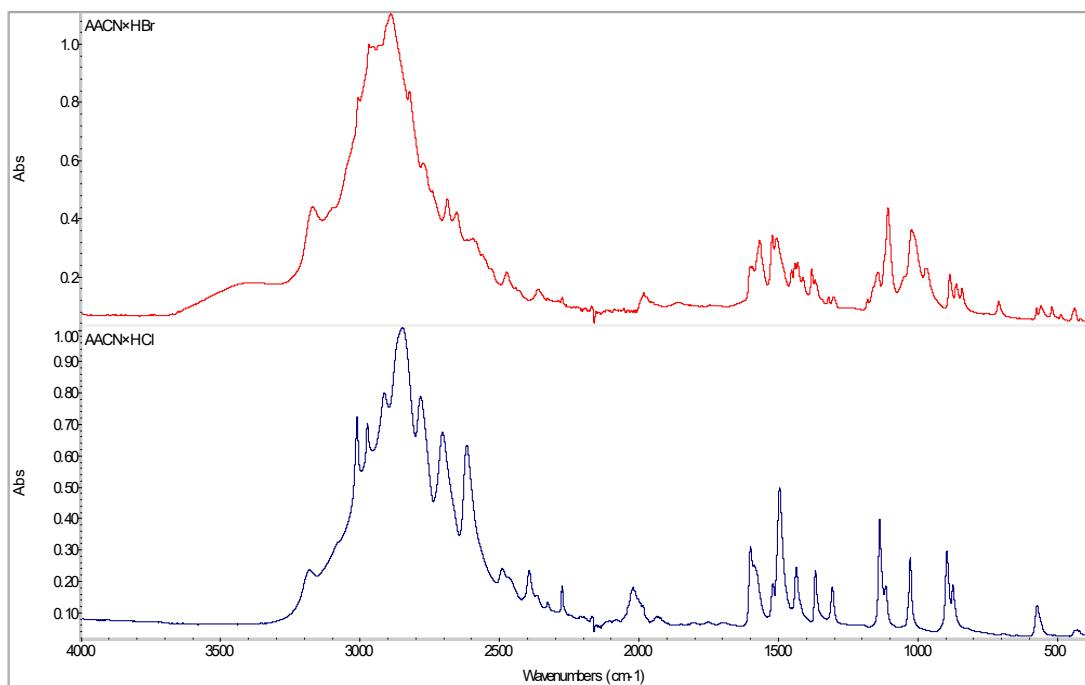
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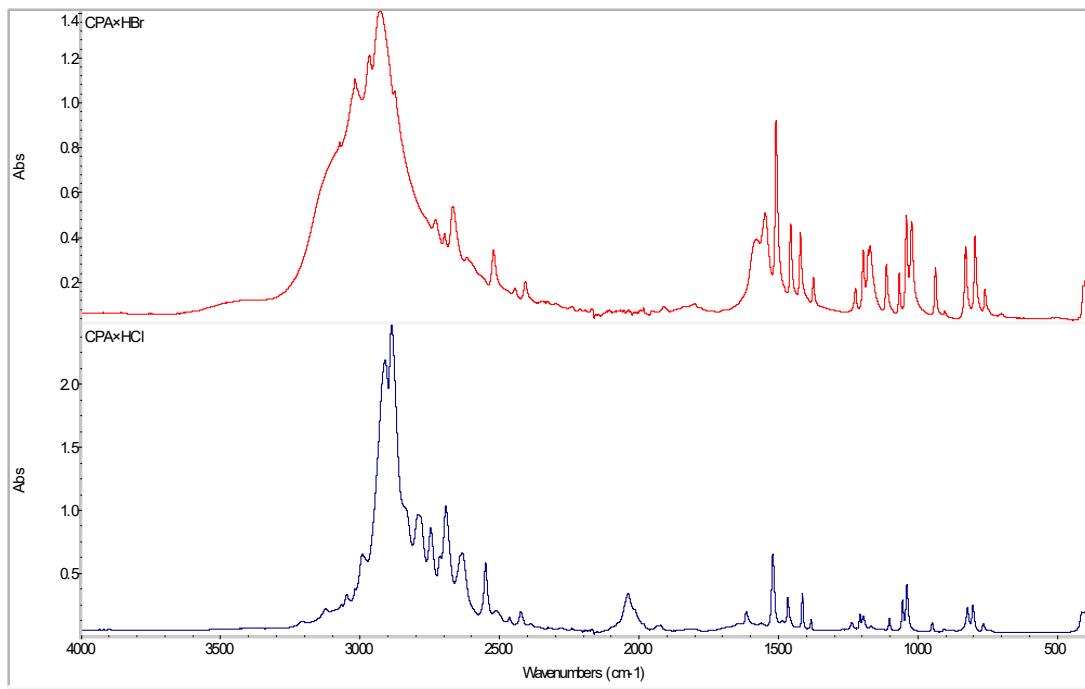
## FTIR spectra of prepared compounds



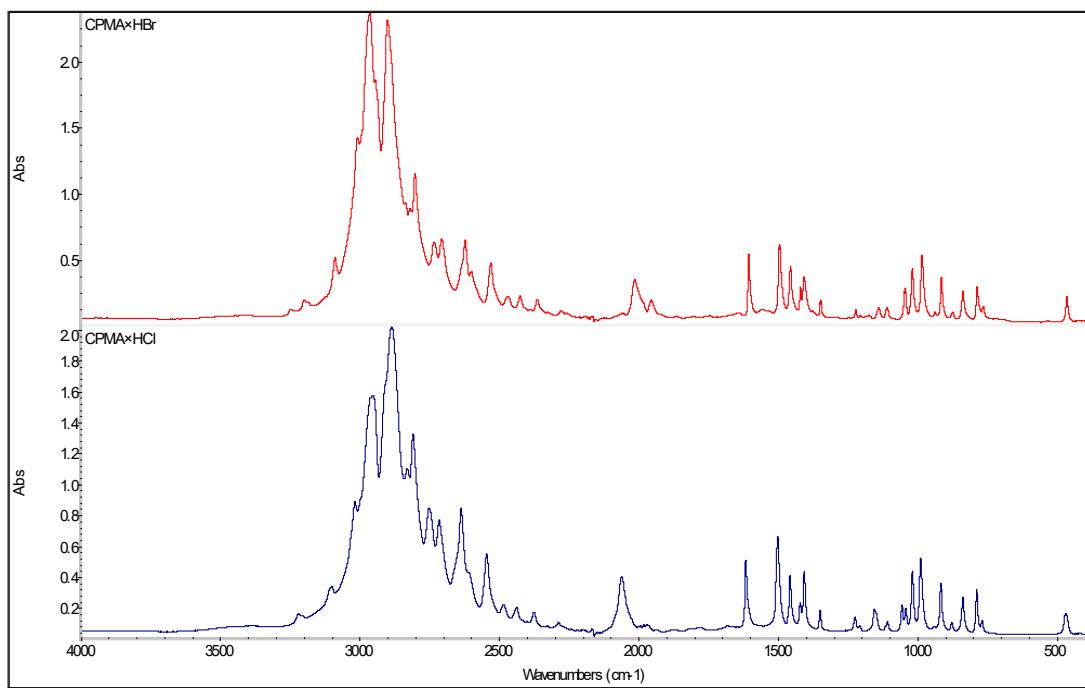
**Figure S1.** FTIR spectra of **aa**×HCl (bottom) and **aa**×HBr (top). As expected, the spectra are qualitatively similar.



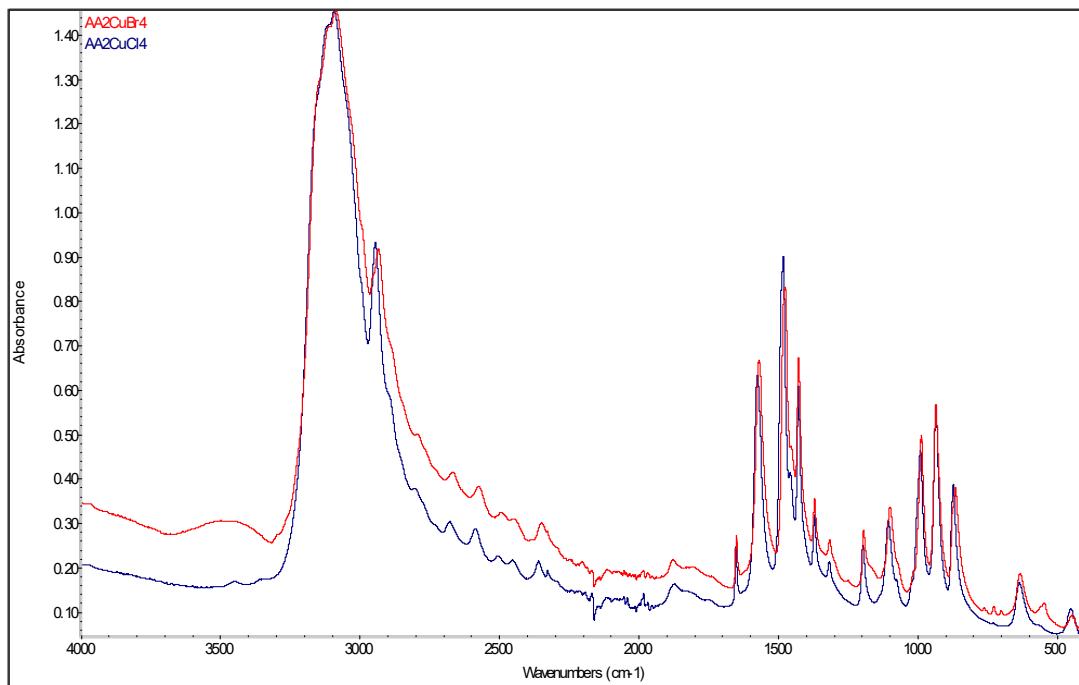
**Figure S2.** FTIR spectra of **aacn**×HCl (bottom) and **aacn**×HBr (top). As expected, the spectra are qualitatively similar.



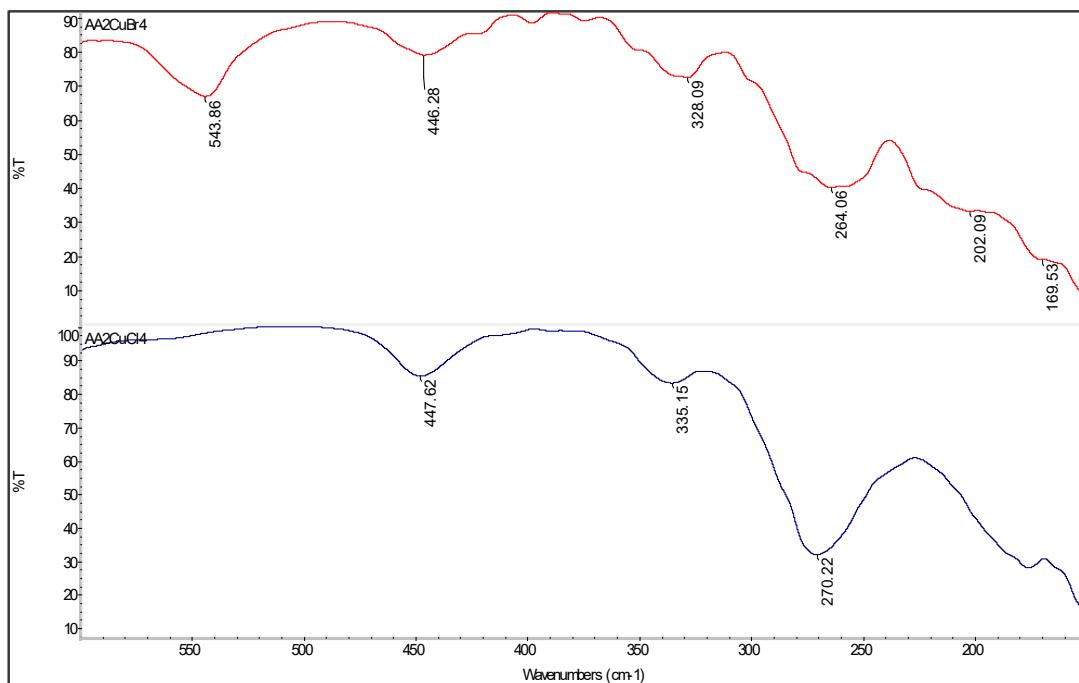
**Figure S3.** FTIR spectra of **cpa×HCl** (bottom) and **cpa×HBr** (top). There are some differences in C-H and N-H region ( $2500\text{-}3200\text{ cm}^{-1}$ ) indicating differences in hydrogen bonding patterns, but the rest of the spectra is qualitatively similar.



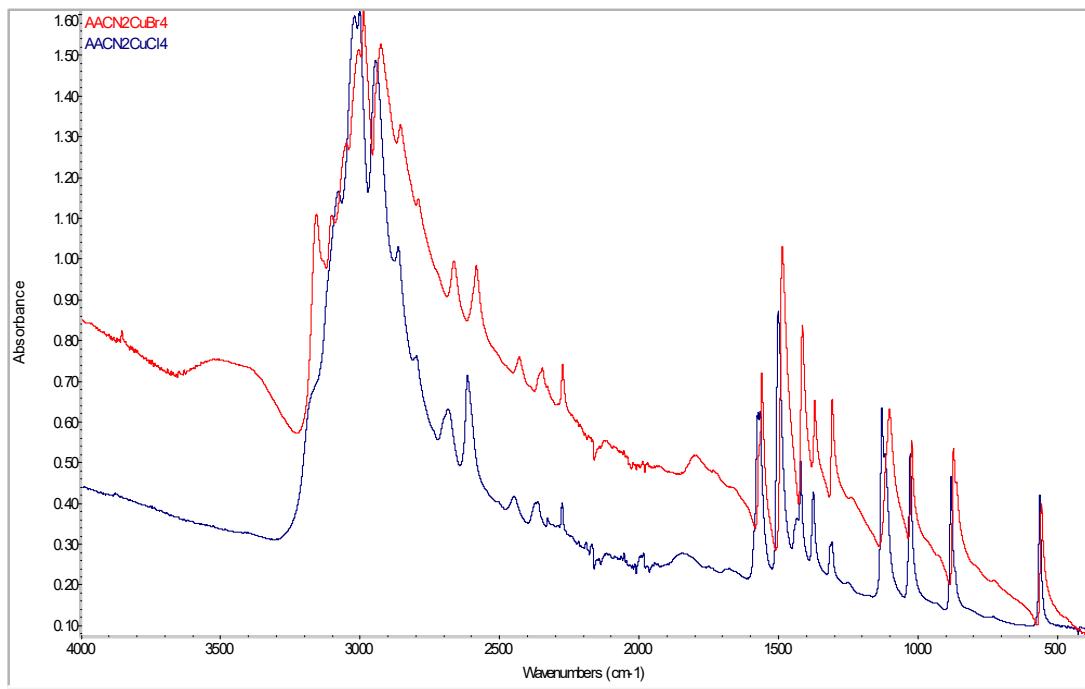
**Figure S4.** FTIR spectra of **cpma×HCl** (bottom) and **cpma×HBr** (top). As expected, the spectra are qualitatively similar.



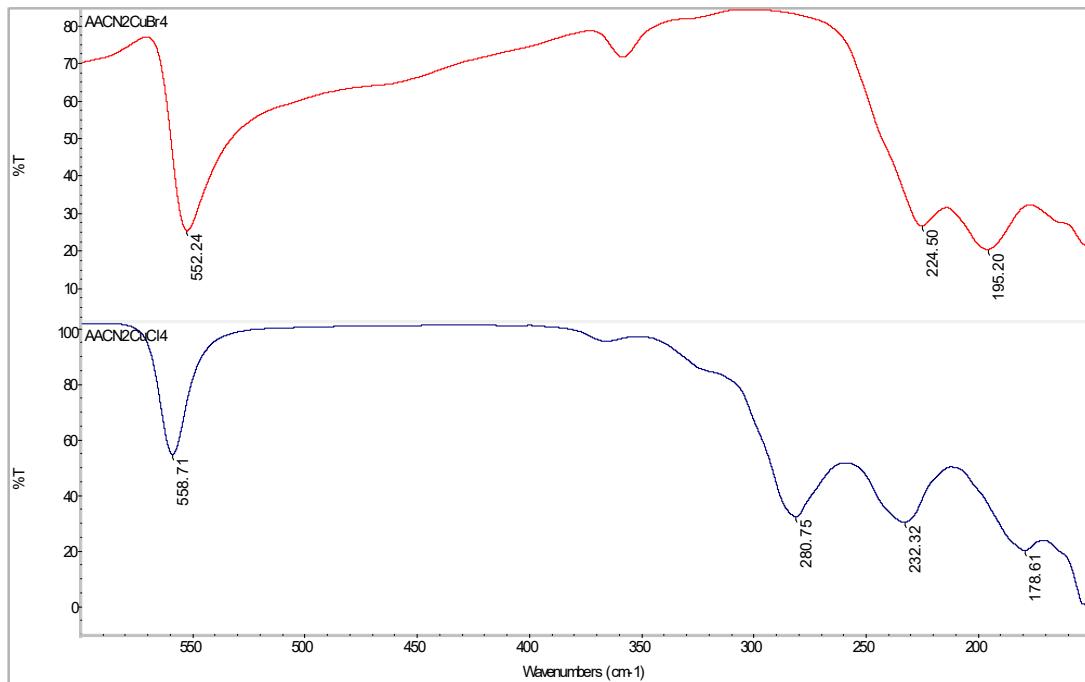
**Figure S5.** FTIR spectra of  $\text{aa}_2\text{CuCl}_4$  (blue) and  $\text{aa}_2\text{CuBr}_4$  (red). As most of the absorption bands originates from the organic cation, the spectra are practically identical.



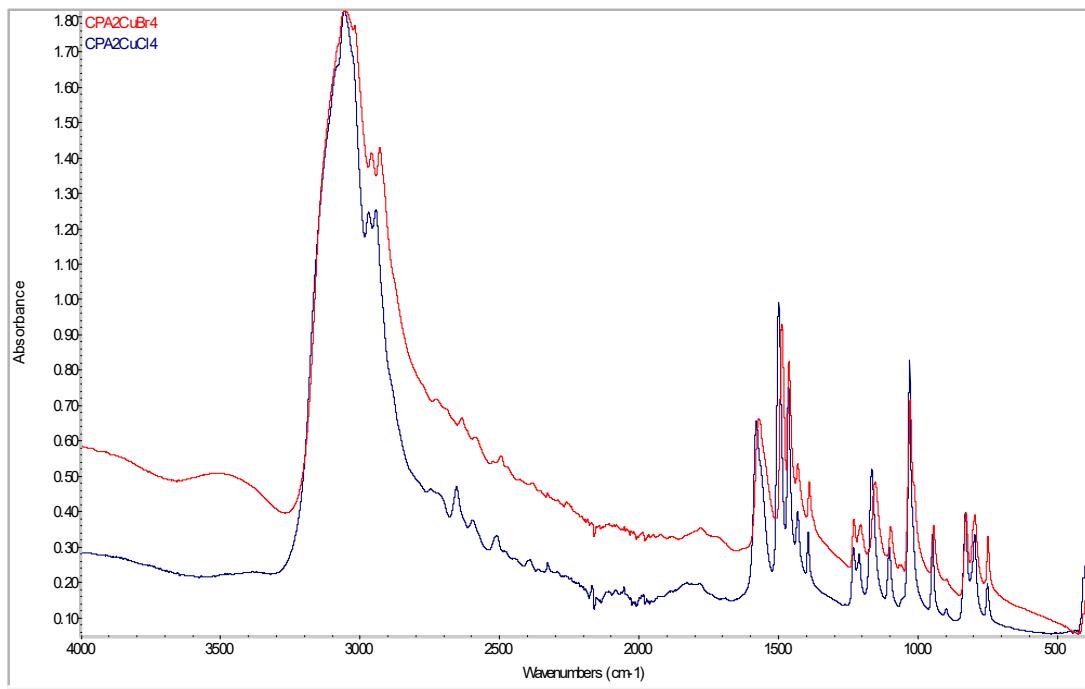
**Figure S6.** Far-FTIR spectra of  $\text{aa}_2\text{CuCl}_4$  (bottom) and  $\text{aa}_2\text{CuBr}_4$  (top). Tetrahhalocuprate bands are present as a broad maxima at  $270 \text{ cm}^{-1}$  for  $\text{aa}_2\text{CuCl}_4$  and as a weak broad maxima at  $202 \text{ cm}^{-1}$  for  $\text{aa}_2\text{CuBr}_4$ .



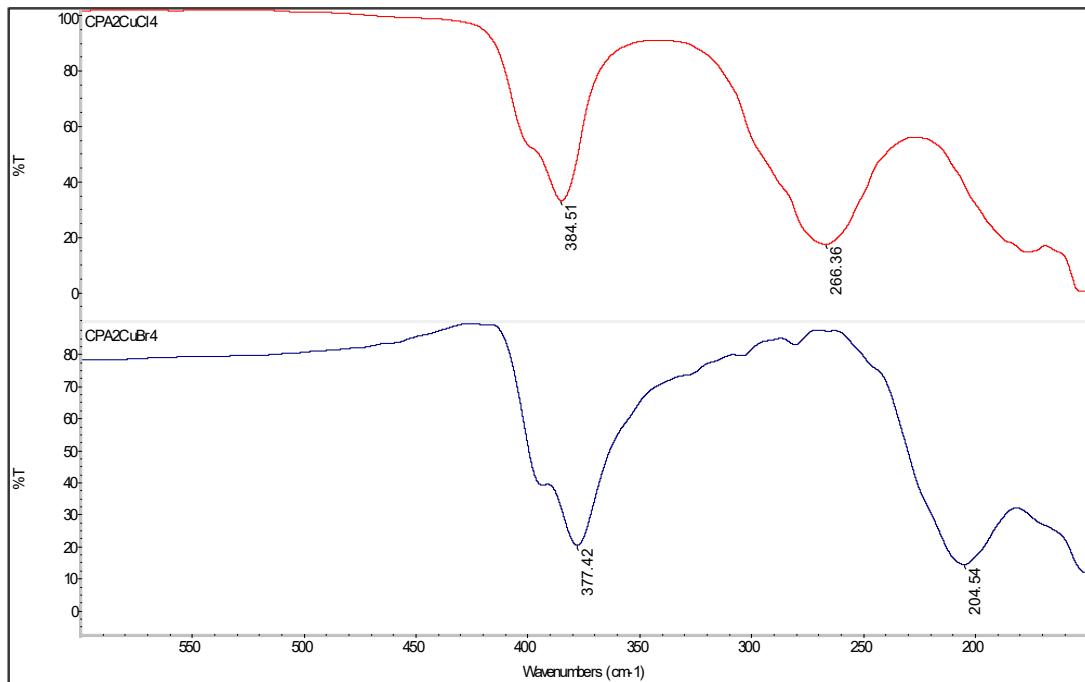
**Figure S7.** FTIR spectra of AACN<sub>2</sub>CuCl<sub>4</sub> (blue) and AACN<sub>2</sub>CuBr<sub>4</sub> (red). As most of the absorption bands originates from the organic cation, the spectra are practically identical, if not slightly shifted.



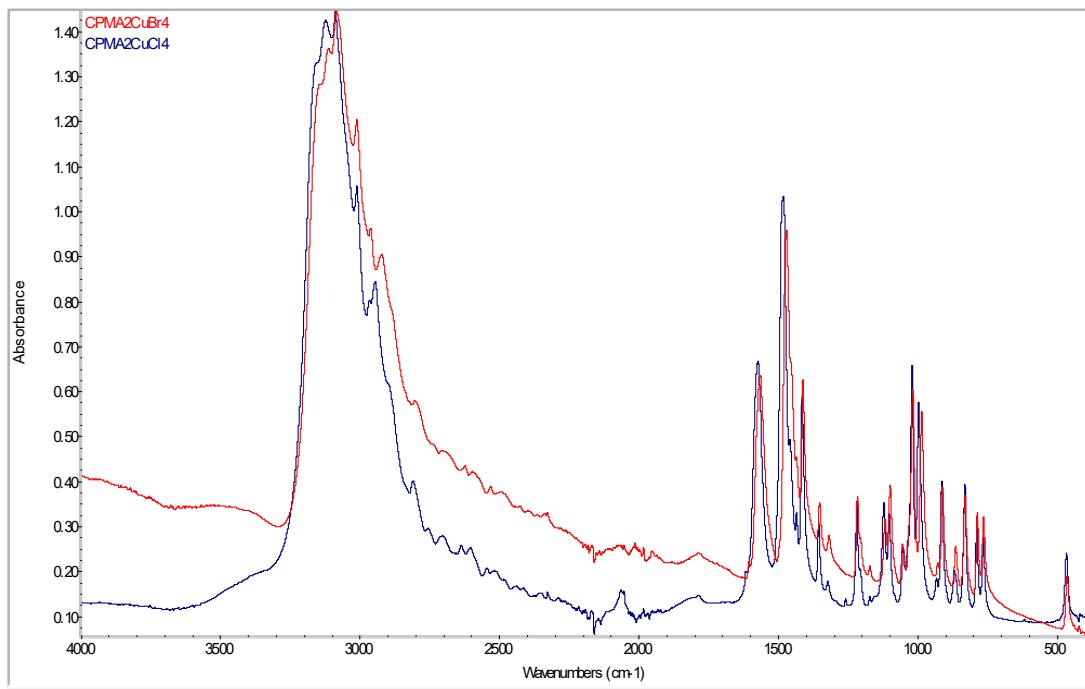
**Figure S8.** Far-FTIR spectra of AACN<sub>2</sub>CuCl<sub>4</sub> (bottom) and AACN<sub>2</sub>CuBr<sub>4</sub> (top). Tetrahalocuprate bands are present as two bands at 280 and 232 cm<sup>-1</sup> for AACN<sub>2</sub>CuCl<sub>4</sub> and as two bands at 224 and 195 cm<sup>-1</sup> for AACN<sub>2</sub>CuBr<sub>4</sub>.



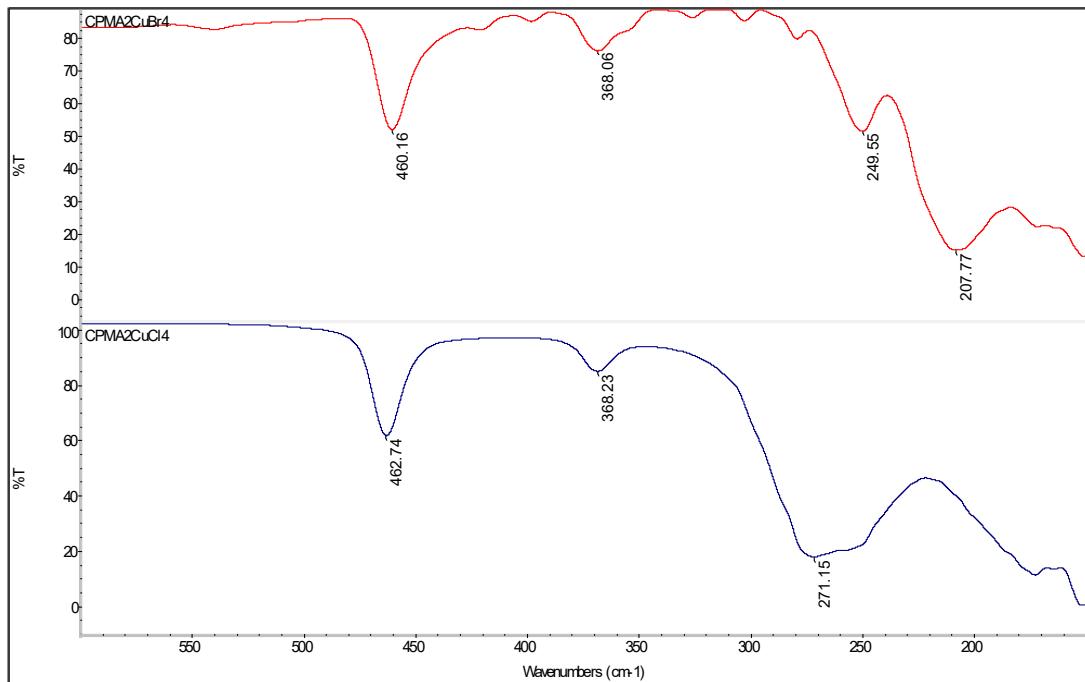
**Figure S9.** FTIR spectra of  $\text{cpa}_2\text{CuCl}_4$  (blue) and  $\text{cpa}_2\text{CuBr}_4$  (red). As most of the absorption bands originates from the organic cation, the spectra are practically identical.



**Figure S10.** Far-FTIR spectra of  $\text{cpa}_2\text{CuCl}_4$  (bottom) and  $\text{cpa}_2\text{CuBr}_4$  (top). Tetrahalocuprate bands are present as a broad maxima at  $266 \text{ cm}^{-1}$  for  $\text{cpa}_2\text{CuCl}_4$  and as a broad maxima at  $204 \text{ cm}^{-1}$  for  $\text{cpa}_2\text{CuBr}_4$ .



**Figure S11.** FTIR spectra of  $\text{cpma}_2\text{CuCl}_4$  (blue) and  $\text{cpma}_2\text{CuBr}_4$  (red). As most of the absorption bands originates from the organic cation, the spectra are practically identical, if not slightly shifted.



**Figure S12.** Far-FTIR spectra of  $\text{cpma}_2\text{CuCl}_4$  (bottom) and  $\text{cpma}_2\text{CuBr}_4$  (top). Tetrahalocuprate bands are present as a broad maxima at 271 cm<sup>-1</sup> for  $\text{cpma}_2\text{CuCl}_4$  and as two bands at 249 and 207 cm<sup>-1</sup> for  $\text{cpma}_2\text{CuBr}_4$ .

## Crystallographic and structural data

**Table S1.** Experimental and crystallographic data for **cpa<sub>2</sub>CuCl<sub>4</sub>** and **cpma<sub>2</sub>CuCl<sub>4</sub>** (refined from SCXRD data).

Compound	<b>cpa<sub>2</sub>CuCl<sub>4</sub></b>	<b>cpma<sub>2</sub>CuCl<sub>4</sub></b>
Empirical formula	C <sub>6</sub> H <sub>16</sub> Cl <sub>4</sub> CuN <sub>2</sub>	C <sub>8</sub> H <sub>20</sub> Cl <sub>4</sub> CuN <sub>2</sub>
<i>M</i> <sub>r</sub>	321.55	349.6
<i>T/K</i>		169.99(10)
Crystal system	monoclinic	orthorhombic
Space group	<i>C2/c</i>	<i>Pccn</i>
<i>a</i> /Å	22.4129(18)	26.7751(6)
<i>b</i> /Å	7.5883(4)	7.6209(2)
<i>c</i> /Å	7.2539(4)	7.1258(2)
$\alpha/^\circ$	90	90
$\beta/^\circ$	93.020(6)	90
$\gamma/^\circ$	90	90
<i>V</i> /Å <sup>3</sup>	1232.00(14)	1454.02(6)
<i>Z</i>	4	4
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	1.734	1.597
$\mu$ /mm <sup>-1</sup>	10.171	8.668
<i>F</i> (000)	652	716
Crystal size/mm <sup>3</sup>	0.152 × 0.081 × 0.026	0.353 × 0.272 × 0.062
Radiation	Cu K $\alpha$ ( $\lambda = 1.54184$ )	
2 $\Theta$ range/°	7.9 to 161.47	6.602 to 160.856
Index ranges	$-27 \leq h \leq 27$ , $-9 \leq k \leq 9$ , $-8 \leq l \leq 9$	$-34 \leq h \leq 34$ , $-9 \leq k \leq 9$ , $-7 \leq l \leq 9$
Reflections collected	2286	16493
Independent reflections	2286 [merged <i>R</i> <sub>int</sub> , <i>R</i> <sub>sigma</sub> = 0.0385]	1588 [ <i>R</i> <sub>int</sub> = 0.0857, <i>R</i> <sub>sigma</sub> = 0.0350]
Data/restraints/parameters	2286/2/73	1588/0/71
Goodness-of-fit on <i>F</i> <sup>2</sup> , <i>S</i> <sup>b</sup>	1.127	1.144
Final <i>R</i> and <i>wR</i> <sup>c</sup> values [ <i>I</i> ≥ 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0685, <i>wR</i> <sub>2</sub> = 0.1924	<i>R</i> <sub>1</sub> = 0.0772, <i>wR</i> <sub>2</sub> = 0.2162
Final <i>R</i> and <i>wR</i> <sup>c</sup> values [all data]	<i>R</i> <sub>1</sub> = 0.0823, <i>wR</i> <sub>2</sub> = 0.2129	<i>R</i> <sub>1</sub> = 0.0783, <i>wR</i> <sub>2</sub> = 0.2169

Largest diff. peak/hole / e Å <sup>-3</sup>	1.02/-1.04	2.05/-0.60
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<sup>a</sup>w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (g<sub>1</sub>P)<sup>2</sup> + g<sub>2</sub>P] where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3

<sup>b</sup>S = {Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup>]/(N<sub>r</sub> - N<sub>p</sub>)}<sup>1/2</sup> where N<sub>r</sub> = number of independent reflections, N<sub>p</sub> = number of refined parameters.

<sup>c</sup>R = Σ||F<sub>o</sub>| - |F<sub>c</sub>||/ Σ|F<sub>o</sub>|; wR = {Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[w(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]}<sup>1/2</sup>

**Table S2.** Crystallographic data for **aacn<sub>2</sub>CuCl<sub>4</sub>** (refined from temperature-dependent SCXRD data). All experiments have the common empirical formula (C<sub>4</sub>H<sub>10</sub>Cl<sub>4</sub>CuN<sub>4</sub>), M<sub>r</sub> (319.50), crystal system and space group (orthorhombic *Pbca*), crystal size (0.12×0.12×0.03 mm<sup>3</sup>) and used the same radiation (Cu Kα).

T/K	a/Å	b/Å	c/Å	V/Å <sup>3</sup>	ρ <sub>calc</sub> g/cm <sup>3</sup>	μ/mm <sup>-1</sup>
169.99(10)	7.30280(10)	7.06850(10)	21.8484(3)	1127.81(3)	1.882	11.168
179.99(10)	7.30850(10)	7.07560(10)	21.8414(2)	1129.46(2)	1.879	11.152
189.99(10)	7.31460(10)	7.08220(10)	21.8363(2)	1131.20(2)	1.876	11.134
200.00(10)	7.32060(10)	7.08740(10)	21.8341(2)	1132.84(2)	1.873	11.118
209.99(10)	7.32720(10)	7.09280(10)	21.8337(2)	1134.71(2)	1.87	11.1
219.99(10)	7.33290(10)	7.09930(10)	21.8313(2)	1136.50(2)	1.867	11.082
229.98(10)	7.33630(10)	7.10490(10)	21.8293(2)	1137.82(2)	1.865	11.07
239.98(10)	7.34060(10)	7.11080(10)	21.8283(2)	1139.38(2)	1.863	11.054
249.97(10)	7.34540(10)	7.11720(10)	21.8303(3)	1141.26(3)	1.859	11.036
260.00(10)	7.34830(10)	7.12320(10)	21.8300(4)	1142.66(3)	1.857	11.023
270.00(10)	7.35070(10)	7.12810(10)	21.8347(4)	1144.06(3)	1.855	11.009
279.99(10)	7.35470(10)	7.13310(10)	21.8437(3)	1145.96(3)	1.852	10.991
289.99(10)	7.35630(10)	7.1398(2)	21.8517(5)	1147.71(4)	1.849	10.974
299.98(10)	7.3598(2)	7.1455(2)	21.8545(5)	1149.32(5)	1.846	10.959
319.98(11)	7.3640(2)	7.1573(2)	21.8482(7)	1151.54(6)	1.843	10.938
340.00(13)	7.3677(2)	7.1645(2)	21.8005(8)	1150.76(6)	1.844	10.945
359.99(16)	7.3611(2)	7.1744(4)	21.6970(9)	1145.85(9)	1.852	10.992
380.00(17)	7.3612(4)	7.1892(5)	21.6531(16)	1145.91(13)	1.852	10.992

**Table S3.** Crystallographic data for **aacn<sub>2</sub>CuCl<sub>4</sub>** (contd.).

T/K	Reflns.	Ind. reflns.	D/R/P	GooF	Final R [I>=2σ (I)]	Final R [all data]	Largest diff peak/hole / e Å <sup>-3</sup>
169.99(10)	28583	1174 [ $R_{\text{int}} = 0.0962$ , $R_{\text{sigma}} = 0.0245$ ]	1174/0/74	1.09	$R_1 = 0.0282$ , $wR_2 = 0.0728$	$R_1 = 0.0300$ , $wR_2 = 0.0734$	0.41/-0.37
179.99(10)	28913	1180 [ $R_{\text{int}} = 0.0970$ , $R_{\text{sigma}} = 0.0248$ ]	1180/0/82	1.11	$R_1 = 0.0272$ , $wR_2 = 0.0700$	$R_1 = 0.0285$ , $wR_2 = 0.0707$	0.41/-0.36
189.99(10)	29023	1188 [ $R_{\text{int}} = 0.0931$ , $R_{\text{sigma}} = 0.0251$ ]	1188/0/71	1.12	$R_1 = 0.0264$ , $wR_2 = 0.0647$	$R_1 = 0.0281$ , $wR_2 = 0.0654$	0.39/-0.37
200.00(10)	29106	1188 [ $R_{\text{int}} = 0.0842$ , $R_{\text{sigma}} = 0.0213$ ]	1188/0/71	1.1	$R_1 = 0.0260$ , $wR_2 = 0.0654$	$R_1 = 0.0276$ , $wR_2 = 0.0661$	0.36/-0.28
209.99(10)	29027	1191 [ $R_{\text{int}} = 0.0922$ , $R_{\text{sigma}} = 0.0217$ ]	1191/0/71	1.09	$R_1 = 0.0273$ , $wR_2 = 0.0673$	$R_1 = 0.0290$ , $wR_2 = 0.0679$	0.42/-0.32
219.99(10)	29155	1190 [ $R_{\text{int}} = 0.0812$ , $R_{\text{sigma}} = 0.0203$ ]	1190/0/74	1.09	$R_1 = 0.0268$ , $wR_2 = 0.0630$	$R_1 = 0.0287$ , $wR_2 = 0.0636$	0.32/-0.28
229.98(10)	29194	1187 [ $R_{\text{int}} = 0.0828$ , $R_{\text{sigma}} = 0.0199$ ]	1187/0/74	1.08	$R_1 = 0.0271$ , $wR_2 = 0.0630$	$R_1 = 0.0292$ , $wR_2 = 0.0638$	0.28/-0.29
239.98(10)	29169	1191 [ $R_{\text{int}} = 0.0820$ , $R_{\text{sigma}} = 0.0208$ ]	1191/0/71	1.07	$R_1 = 0.0297$ , $wR_2 = 0.0697$	$R_1 = 0.0324$ , $wR_2 = 0.0709$	0.31/-0.29
249.97(10)	29239	1193 [ $R_{\text{int}} = 0.0839$ , $R_{\text{sigma}} = 0.0209$ ]	1193/0/71	1.11	$R_1 = 0.0306$ , $wR_2 = 0.0726$	$R_1 = 0.0332$ , $wR_2 = 0.0741$	0.34/-0.30
260.00(10)	29202	1195 [ $R_{\text{int}} = 0.0879$ , $R_{\text{sigma}} = 0.0220$ ]	1195/0/71	1.11	$R_1 = 0.0308$ , $wR_2 = 0.0741$	$R_1 = 0.0338$ , $wR_2 = 0.0753$	0.31/-0.29
270.00(10)	29230	1199 [ $R_{\text{int}} = 0.0875$ , $R_{\text{sigma}} = 0.0222$ ]	1199/0/74	1.08	$R_1 = 0.0338$ , $wR_2 = 0.0780$	$R_1 = 0.0364$ , $wR_2 = 0.0794$	0.36/-0.35
279.99(10)	22936	1155 [ $R_{\text{int}} = 0.1256$ , $R_{\text{sigma}} = 0.0662$ ]	1155/0/62	1.2	$R_1 = 0.0463$ , $wR_2 = 0.1145$	$R_1 = 0.0514$ , $wR_2 = 0.1430$	0.73/-0.47
289.99(10)	29315	1192 [ $R_{\text{int}} = 0.0970$ , $R_{\text{sigma}} = 0.0252$ ]	1192/0/63	1.08	$R_1 = 0.0317$ , $wR_2 = 0.0846$	$R_1 = 0.0353$ , $wR_2 = 0.0864$	0.39/-0.34
299.98(10)	29212	1190 [ $R_{\text{int}} = 0.0922$ , $R_{\text{sigma}} = 0.0234$ ]	1190/0/62	1.09	$R_1 = 0.0351$ , $wR_2 = 0.0912$	$R_1 = 0.0398$ , $wR_2 = 0.0937$	0.47/-0.41
319.98(11)	28819	1192 [ $R_{\text{int}} = 0.1107$ , $R_{\text{sigma}} = 0.0244$ ]	1192/0/62	1.09	$R_1 = 0.0487$ , $wR_2 = 0.1263$	$R_1 = 0.0549$ , $wR_2 = 0.1313$	1.15/-0.37
340.00(13)	24076	1189 [ $R_{\text{int}} = 0.1025$ , $R_{\text{sigma}} = 0.0309$ ]	1189/0/62	1.05	$R_1 = 0.0506$ , $wR_2 = 0.1391$	$R_1 = 0.0562$ , $wR_2 = 0.1437$	1.47/-0.52
359.99(16)	23890	1119 [ $R_{\text{int}} = 0.0989$ , $R_{\text{sigma}} = 0.0312$ ]	1119/0/62	1.11	$R_1 = 0.0576$ , $wR_2 = 0.1539$	$R_1 = 0.0638$ , $wR_2 = 0.1641$	1.38/-0.75
380.00(17)	21546	1191 [ $R_{\text{int}} = 0.1201$ , $R_{\text{sigma}} = 0.0374$ ]	1191/0/62	1.07	$R_1 = 0.0596$ , $wR_2 = 0.1659$	$R_1 = 0.0658$ , $wR_2 = 0.1775$	1.27/-0.74

**Table S4.** Experimental and crystallographic data for **aa<sub>2</sub>CuCl<sub>4</sub>** and **aa<sub>2</sub>CuBr<sub>4</sub>** (refined from PXRD data).

Compound	<b>aa<sub>2</sub>CuCl<sub>4</sub></b>	<b>aa<sub>2</sub>CuBr<sub>4</sub></b>
Empirical formula	C <sub>6</sub> H <sub>16</sub> Cl <sub>4</sub> CuN <sub>2</sub>	C <sub>6</sub> H <sub>16</sub> Br <sub>4</sub> CuN <sub>2</sub>
M <sub>r</sub>	321.56	499.36
Crystal system	monoclinic	monoclinic
Space group	<i>C</i> 2/c	<i>P</i> 2 <sub>1</sub>
<i>a</i> /Å	24.1014(7)	12.497(3)
<i>b</i> /Å	7.52712(15)	7.7672(13)
<i>c</i> /Å	7.36310(14)	7.5908(7)
$\alpha/^\circ$	90	90
$\beta/^\circ$	92.270(2)	105.998(13)
$\gamma/^\circ$	90	90
<i>V</i> /Å <sup>3</sup>	1334.72(5)	708.28(19)
<i>Z</i>	4	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.60024(7)	2.3415(6)
$\mu/\text{mm}^{-1}$	9.3647(4)	12.556(3)
Radiation	Cu K $\alpha$	Mo K $\alpha$
2 $\Theta$ range/°	2.000 to 70.000	2.000 to 35.000
Data/parameters	10358/42	4608/51
Goodness-of-fit, $\chi^a$	4.59	3.47
Final <i>R<sub>p</sub></i> and <i>R<sub>wp</sub></i> <sup>b</sup> values/%	4.34, 6.49	4.24, 5.84

<sup>a</sup>  $\chi = \sqrt{\frac{\sum_{i=1}^N w_i (y_{obs,i} - y_{calc,i}(\mathbf{p}))^2}{N-P}}$ , where  $w_i$  is weight (herein equal to  $\sqrt{y_{obs,i}}$ ),  $y_{obs,i}$  is the *i*-th observed intensity,  $y_{calc,i}$  *i*-th calculated intensity,  $\mathbf{p}$  parameter vector, *N* number of observations and *P* number of parameters

$${}^b R_p = \frac{\sum_{i=1}^N |y_{obs,i} - y_{calc,i}(\mathbf{p})|}{\sum_{i=1}^N y_{obs,i}}, R_{wp} = \sqrt{\frac{\sum_{i=1}^N w_i (y_{obs,i} - y_{calc,i}(\mathbf{p}))^2}{\sum_{i=1}^N w_i y_{obs,i}^2}}$$

**Table S5.** Experimental and crystallographic data for **aacn<sub>2</sub>CuBr<sub>4</sub>**, **cpa<sub>2</sub>CuBr<sub>4</sub>** and **cpma<sub>2</sub>CuBr<sub>4</sub>** (refined from PXRD data).

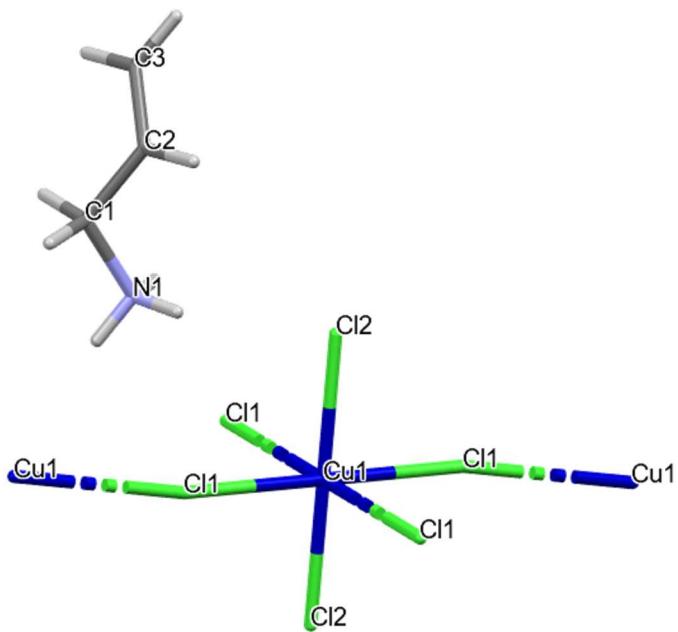
Compound	<b>aacn<sub>2</sub>CuBr<sub>4</sub></b>	<b>cpa<sub>2</sub>CuBr<sub>4</sub></b>	<b>cpma<sub>2</sub>CuBr<sub>4</sub></b>
Empirical formula	C <sub>4</sub> H <sub>10</sub> Br <sub>4</sub> CuN <sub>4</sub>	C <sub>6</sub> Br <sub>4</sub> CuN <sub>2</sub> (hydrogen atoms not modelled)	C <sub>8</sub> H <sub>20</sub> Br <sub>4</sub> CuN <sub>2</sub>
<i>M</i> <sub>r</sub>	497.31	483.23	527.41
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Bmab</i>	<i>B2cb</i>
<i>a</i> /Å	10.0769(5)	7.8065(5)	7.7753(4)
<i>b</i> /Å	8.2902(4)	8.0860(5)	7.9773(4)
<i>c</i> /Å	7.5448(3)	21.8629(9)	26.002(2)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	106.676(4)	90	90
$\gamma/^\circ$	90	90	90
<i>V</i> /Å <sup>3</sup>	603.77(5)	1380.05(13)	1612.80(18)
<i>Z</i>	4	4	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	2.7355(2)	2.3258(2)	2.1306(2)
$\mu/\text{mm}^{-1}$	14.7330(12)	12.8850(12)	11.0329(12)
Radiation	Mo Kα		
2θ range/°	2.000 to 35.000		
Data/parameters	4608/43	4608/31	4608/52
Goodness-of-fit, $\chi^a$	3.24	3.67	3.88
Final <i>R</i> <sub>p</sub> and <i>R</i> <sub>wp</sub> <sup>b</sup> values/%	3.94, 6.17	4.49, 6.19	5.00, 6.52

<sup>a</sup>  $\chi = \sqrt{\frac{\sum_{i=1}^N w_i (y_{\text{obs},i} - y_{\text{calc},i}(\mathbf{p}))^2}{N-P}}$ , where  $w_i$  is weight (herein equal to  $\sqrt{y_{\text{obs},i}}$ ),  $y_{\text{obs},i}$  is the *i*-th observed intensity,  $y_{\text{cal},i}$  *i*-th calculated intensity,  $\mathbf{p}$  parameter vector, *N* number of observations and *P* number of parameters

$$^b R_p = \frac{\sum_{i=1}^N |y_{\text{obs},i} - y_{\text{calc},i}(\mathbf{p})|}{\sum_{i=1}^N y_{\text{obs},i}}, R_{\text{wp}} = \sqrt{\frac{\sum_{i=1}^N w_i (y_{\text{obs},i} - y_{\text{calc},i}(\mathbf{p}))^2}{\sum_{i=1}^N w_i y_{\text{obs},i}^2}}$$

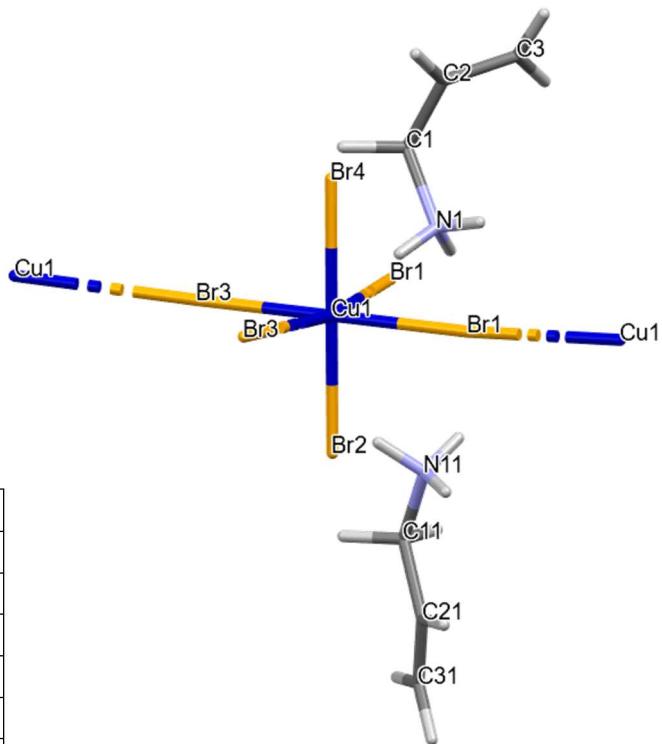
**Table S6.** Selected bond lengths, angles and torsions in the crystal structure of  $\text{aa}_2\text{CuCl}_4$ . Atom numeration is given on the picture below.

bond lengths/ $\text{\AA}$				
Cu1	Cl1	2.351(4)		
Cu1	Cl2	2.294(3)		
Cu1	Cl1_a	2.933(4)		
N1	C1	1.454(12)		
C1	C2	1.458(12)		
C2	C3	1.31(3)		
bond angles/ $^\circ$				
Cl1	Cu1	Cl2	90.00(13)	
Cl2	Cu1	Cl1_a	90.00(13)	
Cl1	Cu1	Cl1_a	180	
Cl2	Cu1	Cl2_a	180	
Cl1	Cu1	Cl2_a	90.00(13)	
Cl1_a	Cu1	Cl2_a	90.00(13)	
N1	C1	C2	113.7(11)	
C1	C2	C3	120.1(17)	
torsion angles/ $^\circ$				
N1	C1	C2	C3	123(3)
distance between ammonium nitrogen atom and axial chloride ions/ $\text{\AA}$				
<i>min</i>	2	3	<i>max</i>	<i>avg</i>
3.23	3.46	3.94	4.35	3.74



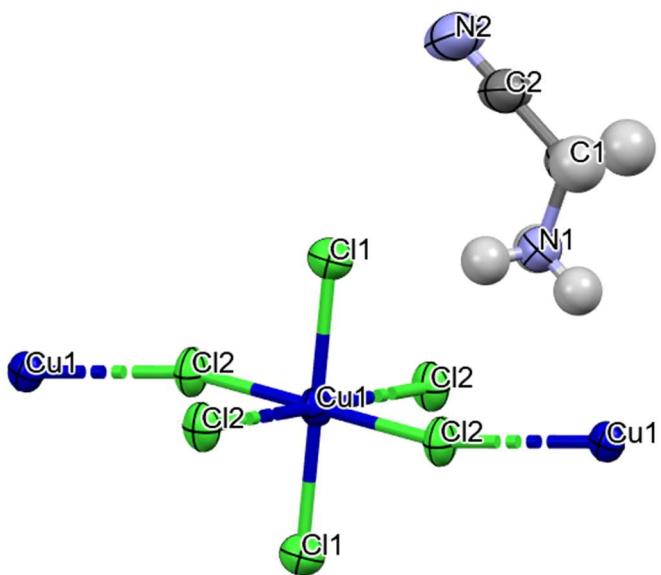
**Table S7.** Selected bond lengths, angles and torsions in the crystal structure of **aa<sub>2</sub>CuBr<sub>4</sub>**. Atom numeration is given on the picture on the side.

bond lengths/Å				
Br1	Cu1	2.46(2)		
Br4	Cu1	2.33(3)		
Br1	Cu1_b	2.80(2)		
Br2	Cu1	2.33(3)		
Br3	Cu1	2.45(2)		
Br3_b	Cu1	3.17(3)		
N1	C1	1.43(16)		
C1	C2	1.5(2)		
C2	C3	1.3(4)		
N11	C11	1.46(15)		
C11	C21	1.44(19)		
C21	C31	1.3(2)		
bond angles/°				
Cu1	Br1	Cu1_b	176.4(13)	
Br1	Cu1	Br4	89.9(9)	
Br2	Cu1	Br4	179.9(11)	
Br3	Cu1	Br1_a	84.7(6)	
Br1	Cu1	Br2	90.0(10)	
Br1	Cu1	Br1_a	95.3(7)	
Br2	Cu1	Br1_a	88.2(9)	
Br4	Cu1	Br1_a	91.8(8)	
Br1	Cu1	Br3	179.9(14)	
Br2	Cu1	Br3	90.0(9)	
Br3	Cu1	Br4	90.2(10)	
N1	C1	C2	116(14)	
C1	C2	C3	119	
N11	C11	C21	114(11)	
C11	C21	C31	121(17)	
torsion angles/°				
N1	C1	C2	C3	77(-1)
N11	C11	C21	C31	-170(-1)
distance between ammonium nitrogen atom and axial chloride ions/Å				
<i>min</i>	2	3	<i>max</i>	<i>avg</i>
2.95	3.80	3.97	4.94	3.91



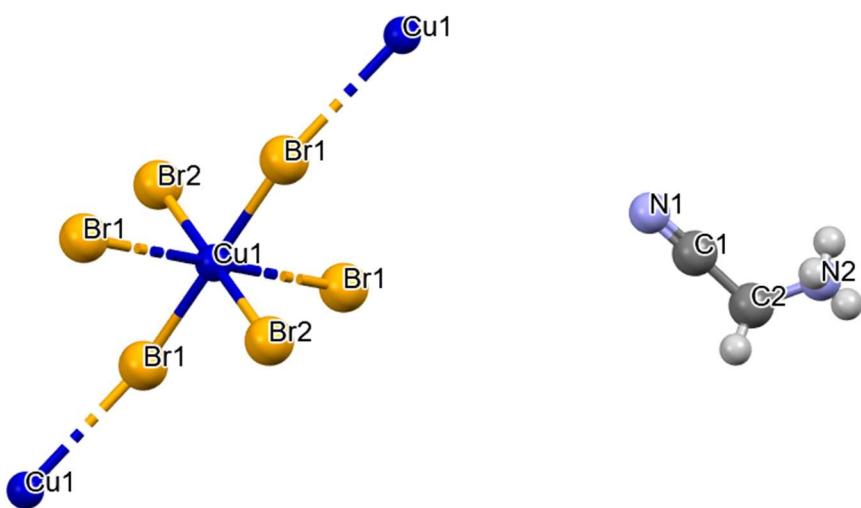
**Table S8.** Selected bond lengths, angles and torsions in the crystal structure of **aacn<sub>2</sub>CuCl<sub>4</sub>**. Atom numeration is given on the picture below.

bond lengths/Å				
Cu1	Cl1	2.3000(7)		
Cu1	Cl2_c	2.2898(5)		
Cu1	Cl2_a	2.8738(6)		
N1	C1	1.457(4)		
N2	C2	1.133(4)		
C1	C2	1.461(5)		
bond angles/°				
Cl1	Cu1	Cl2	89.86(2)	
Cl1	Cu1	Cl2_c	90.15(2)	
Cl1	Cu1	Cl2_a	93.04(2)	
Cl1	Cu1	Cl2_e	86.96(2)	
Cl1	Cu1	Cl1_c	180	
Cl2	Cu1	Cl2_a	91.66(2)	
N1	C1	C2	111.8(3)	
N2	C2	C1	179.5(4)	
torsion angles undefined				
distance between ammonium nitrogen atom and axial chloride ions/Å				
min	2	3	max	avg
3.23	3.36	3.77	4.14	3.63



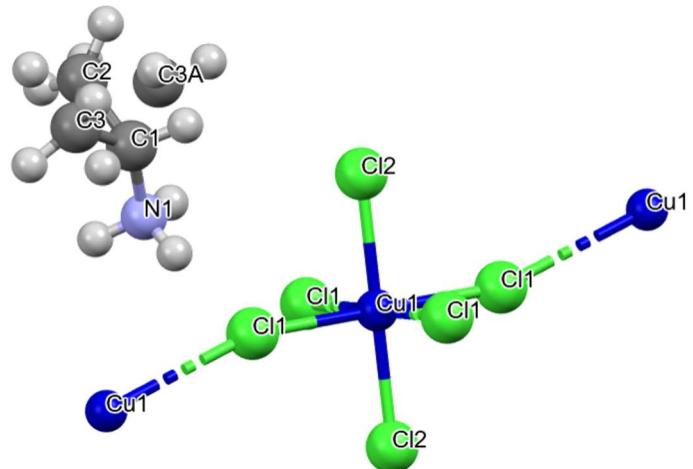
**Table S9.** Selected bond lengths, angles and torsions in the crystal structure of **aacn<sub>2</sub>CuBr<sub>4</sub>**. Atom numeration is given on the picture below.

bond lengths/Å				
Br1	Cu1	2.490(5)		
Br2	Cu1	2.428(6)		
Br1_a	Cu1	3.198(6)		
N1	C1	1.2(2)		
N2	C2	1.48(17)		
C1	C2	1.46(19)		
bond angles/°				
Br1	Cu1	Br2	89.2(3)	
Br2	Cu1	Br1_a	90.8(3)	
Br1	Cu1	Br1_a	180	
Br2	Cu1	Br2_a	180	
Br1	Cu1	Br2_a	90.8(3)	
Br1_a	Cu1	Br2_a	89.2(3)	
N1	C1	C2	179(19)	
N2	C2	C1	110(7)	
torsion angles undefined				
distance between ammonium nitrogen atom and axial chloride ions/Å				
min	2	3	max	avg
3.40	3.55	4.04	4.91	3.98



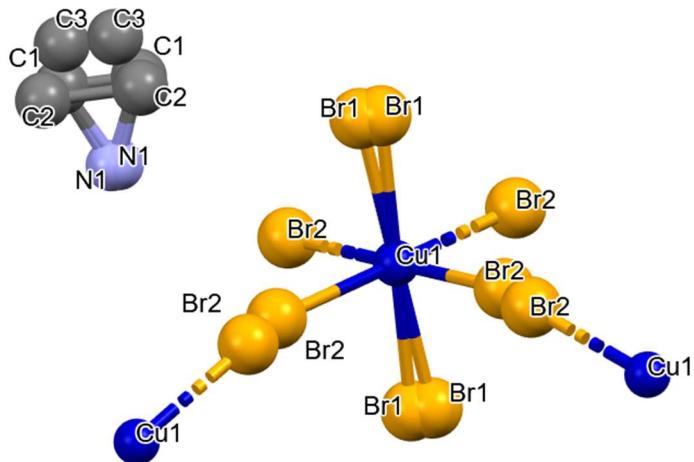
**Table S10.** Selected bond lengths, angles and torsions in the crystal structure of **cpa<sub>2</sub>CuCl<sub>4</sub>**. Atom numeration is given on the picture below.

bond lengths/Å				
Cu1	Cl1	2.2936(15)		
Cu1	Cl2	2.2884(16)		
Cu1	Cl1_a	3.0046(15)		
N1	C1	1.436(12)		
C1	C2	1.422(14)		
C1	C3	1.285(18)		
C1	C3A	1.21(2)		
C2	C3	1.486(16)		
C2	C3A	1.48(2)		
bond angles/°				
Cl1	Cu1	Cl2	89.64(5)	
Cl2	Cu1	Cl1_a	90.37(5)	
Cl1	Cu1	Cl1_a	180	
Cl2	Cu1	Cl2_a	180	
Cl1	Cu1	Cl2_a	90.37(5)	
Cl1_a	Cu1	Cl2_a	89.64(5)	
N1	C1	C3	131.8(12)	
C2	C1	C3A	68.0(12)	
C1	C3	C2	61.2(8)	
N1	C1	C2	123.6(10)	
C2	C1	C3	66.4(9)	
C1	C2	C3A	49.1(11)	
N1	C1	C3A	147.0(17)	
C1	C2	C3	52.4(8)	
C1	C3A	C2	62.9(12)	
torsion angles/°				
N1	C1	C2	C3	125.7(15)
N1	C1	C3	C2	-114.8(16)
distance between ammonium nitrogen atom and axial chloride ions/Å				
min	2	3	max	avg
3.21	3.41	3.85	4.40	3.71



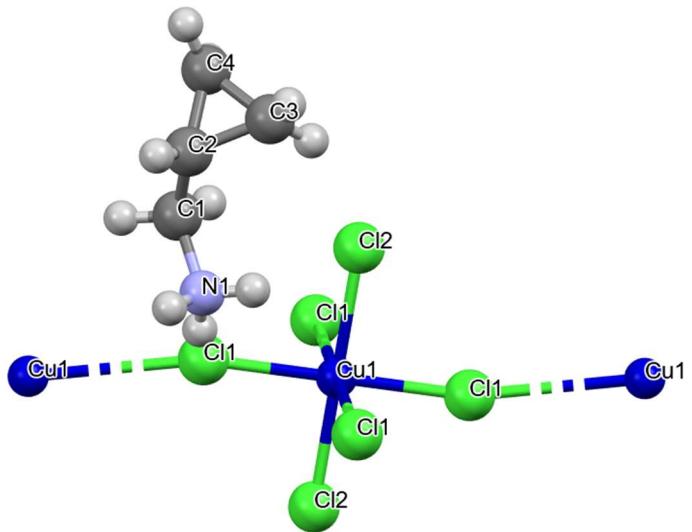
**Table S11.** Selected bond lengths, angles and torsions in the crystal structure of **cpa<sub>2</sub>CuBr<sub>4</sub>**. Atom numeration is given on the picture below. Atoms marked by asterisk (\*) are in disorder.

bond lengths/Å				
*Br1	Cu1	2.437(4)		
*Br2	Cu1	2.47(5)		
*N1	*C1	1.50(4)		
*C1	*C2	1.50(7)		
*C1	*C3	1.50(8)		
*C2	*C3	1.51(10)		
bond angles/°				
*Br1	Cu1	*Br2	90.0(3)	
*Br1	Cu1	*Br1_b	180	
*Br1	Cu1	*Br2_c	84.6(3)	
*Br1	Cu1	*Br1_a	172.4(3)	
*Br1	Cu1	*Br2_b	90.0(3)	
*Br2	Cu1	*Br2_a	90.5(15)	
*Br1	Cu1	*Br2_a	95.4(3)	
*Br1	Cu1	*Br1_c	7.6(3)	
*N1	*C1	*C2	109(3)	
*C1	*C2	*C3	60(4)	
*N1	*C1	*C3	111(5)	
*C1	*C3	*C2	60(4)	
*C2	*C1	*C3	61(4)	
torsion angles/°				
*N1	*C1	*C2	*C3	-104(5)
*N1	*C1	*C3	*C2	101(4)
distance between ammonium nitrogen atom and axial chloride ions/Å				
min	2	3	max	avg
3.69	3.82	4.03	4.41	3.99



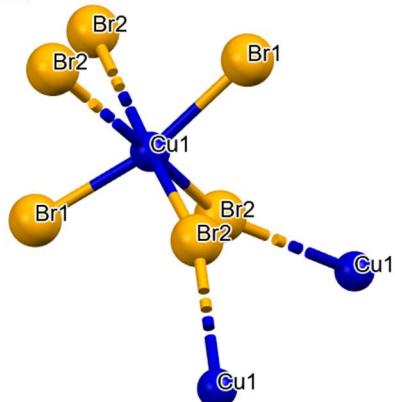
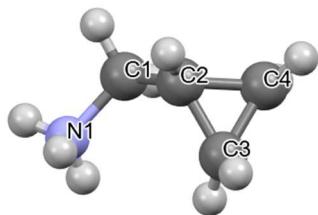
**Table S12.** Selected bond lengths, angles and torsions in the crystal structure of **cpma<sub>2</sub>CuCl<sub>4</sub>**. Atom numeration is given on the picture below.

bond lengths/Å				
Cu1	Cl1	2.2810(13)		
Cu1	Cl2	2.3133(16)		
Cu1	Cl1_a	2.9790(13)		
N1	C1	1.466(9)		
C1	C2	1.483(11)		
C2	C3	1.493(14)		
C2	C4	1.495(12)		
C3	C4	1.493(14)		
bond angles/°				
Cl1	Cu1	Cl2	90.67(5)	
Cl2	Cu1	Cl1_a	89.33(5)	
N1	C1	C2	112.6(6)	
C3	C2	C4	60.0(7)	
Cl1	Cu1	Cl1_a	180	
Cl2	Cu1	Cl2_a	180	
C1	C2	C3	116.2(8)	
C2	C3	C4	60.1(6)	
Cl1	Cu1	Cl2_a	89.33(5)	
Cl1_a	Cu1	Cl2_a	90.67(5)	
C1	C2	C4	118.9(8)	
C2	C4	C3	59.9(7)	
torsion angles/°				
N1	C1	C2	C3	80.6(9)
N1	C1	C2	C4	149.1(7)
C1	C2	C3	C4	109.8(9)
C1	C2	C4	C3	-
distance between ammonium nitrogen atom and axial chloride ions/Å				
min	2	3	max	avg
3.26	3.35	3.80	4.38	3.70



**Table S13.** Selected bond lengths, angles and torsions in the crystal structure of **cpma<sub>2</sub>CuBr<sub>4</sub>**. Atom numeration is given on the picture below.

bond lengths/Å				
Br1	Cu1	2.400(8)		
Br2	Cu1	2.46(9)		
Br2_a	Cu1	3.18(9)		
N1	C1	1.46(6)		
C3	C4	1.50(18)		
C1	C2	1.48(9)		
C2	C3	1.49(15)		
C2	C4	1.50(16)		
bond angles/°				
Br1	Cu1	Br2	90.0(5)	
Br2	Cu1	Br1_a	98.2(6)	
Br1	Cu1	Br1_a	168.1(4)	
Br2	Cu1	Br2_a	94(3)	
Br1	Cu1	Br2_a	98.2(6)	
Br1_a	Cu1	Br2_a	90.0(5)	
N1	C1	C2	111(6)	
C1	C2	C3	117(7)	
C1	C2	C4	117(8)	
C2	C4	C3	60(7)	
C2	C3	C4	60(8)	
C3	C2	C4	60(8)	
torsion angles/°				
N1	C1	C2	C3	56(11)
N1	C1	C2	C4	125(9)
C1	C2	C3	C4	107(9)
C1	C2	C4	C3	-108(9)
distance between ammonium nitrogen atom and axial chloride ions/Å				
min	2	3	max	avg
3.66	3.75	4.17	4.25	3.96

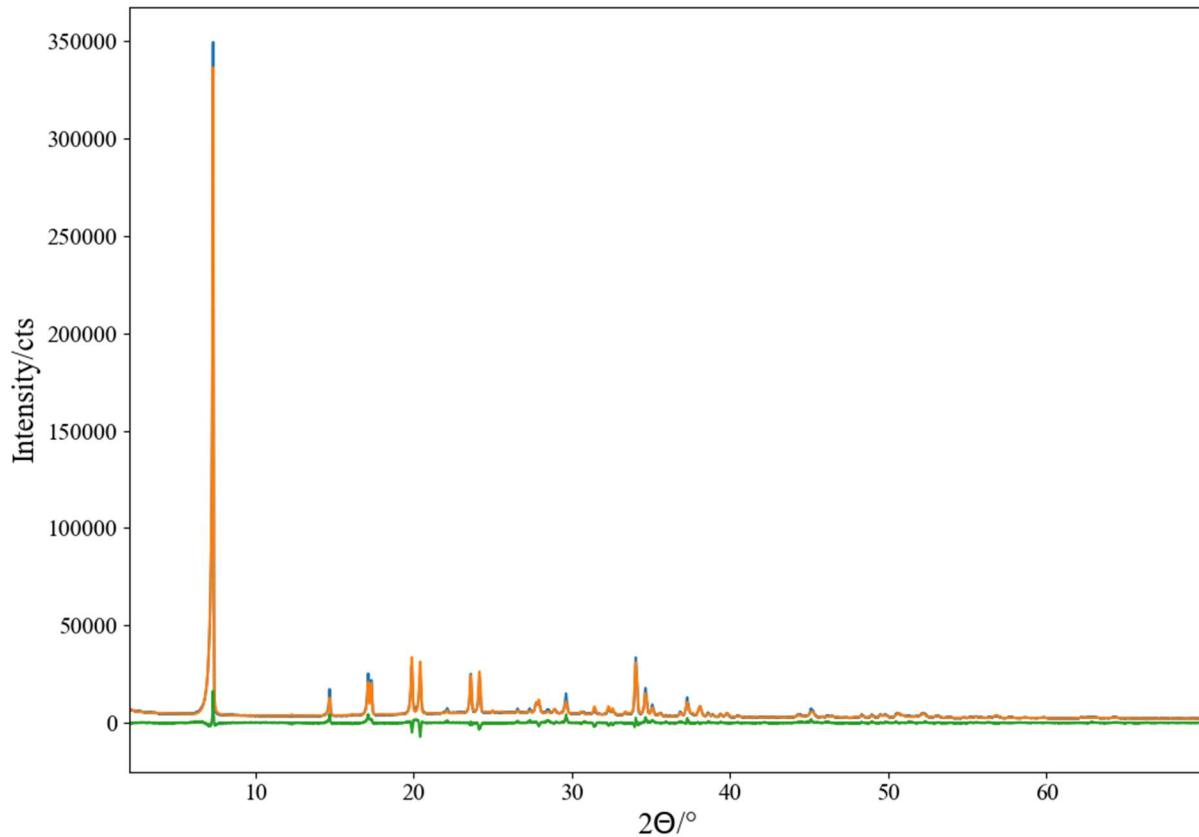


**Table S14.** Selected bond lengths, angles and torsions in the crystal structure of **cpma<sub>2</sub>CuBr<sub>4</sub>**. Atom numeration is given on the picture below.

$d(\text{Cu}-\text{Cl}_{\text{eq}2})/\text{\AA}$	$d(\text{Cu}-\text{Cl}_{\text{ax}})/\text{\AA}$	$d(\text{Cu}-\text{Cl}_{\text{eq}2})/\text{\AA}$	$\Delta/\%$
2.2850(4)	2.3062(4)	2.8339(4)	1.0524(13)
2.2851(4)	2.3054(4)	2.8384(4)	1.0702(13)
2.2852(4)	2.3049(4)	2.8430(4)	1.0879(13)
2.2854(4)	2.3045(4)	2.8468(4)	1.1023(14)
2.2858(4)	2.3039(4)	2.8507(4)	1.1171(14)
2.2861(4)	2.3034(4)	2.8545(4)	1.1316(14)
2.2859(4)	2.3030(4)	2.8576(4)	1.1446(14)
2.2864(5)	2.3015(4)	2.8605(5)	1.1577(17)
2.2873(5)	2.3017(4)	2.8632(5)	1.1653(17)
2.2875(5)	2.3008(4)	2.8659(5)	1.1771(17)
2.2879(5)	2.3003(4)	2.8675(5)	1.1834(17)
2.2894(5)	2.3001(4)	2.8714(5)	1.1950(17)
2.2898(5)	2.3000(7)	2.8738(6)	1.203(2)
2.2909(8)	2.2991(9)	2.8776(8)	1.217(3)
2.2907(8)	2.2968(9)	2.8803(8)	1.234(3)
2.2888(11)	2.2920(13)	2.8805(11)	1.251(4)
2.2898(11)	2.290(13)	2.8833(12)	1.264(4)

## Rietveld refinement results and TOPAS input files

aa<sub>2</sub>CuCl<sub>4</sub>



**Figure S13.** PXRD data for aa<sub>2</sub>CuCl<sub>4</sub> (blue), calculated pattern (orange) and difference between observed and calculated pattern (green).

```
xdd aa2cucl4.xy
'Auto_T(10)
macro rotrans {@}
do_errors
iters 5
      r_wp  6.48712735 r_exp  1.41239667 r_p  4.34550665 r_wp_dash  13.8361246 r_p_dash
13.6258063 r_exp_dash  3.01244222 weighted_Durbin_Watson  0.105724047 gof  4.59299253
lam
ymin_on_ymax 0.0001
la 0.66050 lo 1.540598 lh 0.5
la 0.33950 lo 1.544426 lh 0.5
      bkg @ 3486.18135`_4.59098099 -1668.1724`_7.38340701 84.5439598`_7.02893062 -
40.8421453`_6.67106647 462.008439`_6.34879313 -625.489019`_6.27499905 234.712707`_6.11572235
149.696503`_5.98637834 -121.896043`_5.76068825 -104.989029`_5.7634446 151.151396`_5.58692193
-45.9410744`_5.5345654 46.4415792`_5.29791197 -43.0781029`_5.10351641 41.1663361`_4.69575019
-50.2477929`_4.50670915
x_calculation_step 0.005
```

```

Radius(240)
LP_Factor(0)
Zero_Error(@,-0.01634`_0.00025)
      xdd_out "aa2cucl4.txt" load out_record out_fmt out_eqn
{
  " %11.6f  " = X;
  " %11.6f  " = Yobs;
  " %11.6f  " = Ycalc;
  " %11.6f\n" = Yobs-Ycalc;
}
Full_Axial_Model(12, 15, 12,    2.98935_0.17532,   7.67760_0.64523)

str
phase_name "aa2CuCl4"
space_group "C2/c"
a @ 24.101374`_0.000713
b @ 7.527117`_0.000152
c @ 7.363098`_0.000141
be @ 92.26955`_0.00217
CS_G(@, 262.39647`_2.62288)
Strain_L(@, 0.16013`_0.00310)
Strain_G(@, 0.23372`_0.00501)
prm beq3 5.79370`_0.07096 min 1 max 10
scale @ 0.000841325554`_3.425e-006
site          Cu1      x  0.25000`_0.00000  y  0.25000`_0.00000  z
0.00000`_0.00000          occ Cu  1           beq =beq3;
site          Cl1      x  0.25935`_0.00013  y  0.47029`_0.00063  z
0.22310`_0.00065          occ Cl  1           beq =beq3;
site          Cl2      x  0.34469`_0.00012  y  0.21903`_0.00066  z
0.02270`_0.00037          occ Cl  1           beq =beq3;
site          C3       x  0.03092`_0.00035  y  0.80578`_0.00258  z
0.04008`_0.00572          occ C   1           beq =beq3;
site          C1       x  0.12492`_0.00029  y  0.81737`_0.00165  z
-0.05566`_0.00213          occ C   1           beq =beq3;
site          C2       x  0.07066`_0.00025  y  0.73152`_0.00215  z
0.04958`_0.00399          occ C   1           beq =beq3;
site          N1       x  0.17051`_0.00017  y  0.70620`_0.00116  z
0.01188`_0.00084          occ N   1           beq =beq3;
site          H1       x  0.16753`_0.00268  y  0.60227`_0.00481
z   -0.03604`_0.01212          occ H   1           beq =beq3*1.5;
site          H2       x  0.20154`_0.00026  y  0.75307`_0.00800
z   -0.01643`_0.01376          occ H   1           beq =beq3*1.5;
site          H3       x  0.16947`_0.00286  y  0.69737`_0.01267
z   0.12815`_0.00184          occ H   1           beq =beq3*1.5;

```

```

z      site      H4      occ      H      x  0.13196`_0.00071      y      0.84889`_0.00287
z      -0.18608`_0.00217      occ      H      1      beq =beq3*1.5;

z      site      H5      occ      H      x  0.12444`_0.00039      y      0.92808`_0.00135
z      0.02176`_0.00309      occ      H      1      beq =beq3*1.5;

z      site      H6      occ      H      x  0.06380`_0.00054      y      0.61491`_0.00280
z      -0.11451`_0.00494      occ      H      1      beq =beq3*1.5;

z      site      H7      occ      H      x  0.03778`_0.00069      y      0.92239`_0.00298
z      0.10502`_0.00613      occ      H      1      beq =beq3*1.5;

z      site      H8      occ      H      x  -0.00659`_0.00033      y      0.74643`_0.00306
z      0.04429`_0.00726      occ      H      1      beq =beq3*1.5;

normalize_FCs

rigid

prm CuCl1  2.35118`_0.00474 _LIMIT_MAX_ 2.4 min 2.20 max 2.4
prm CuCl2  2.29353`_0.00294 min 2.2 max 2.4

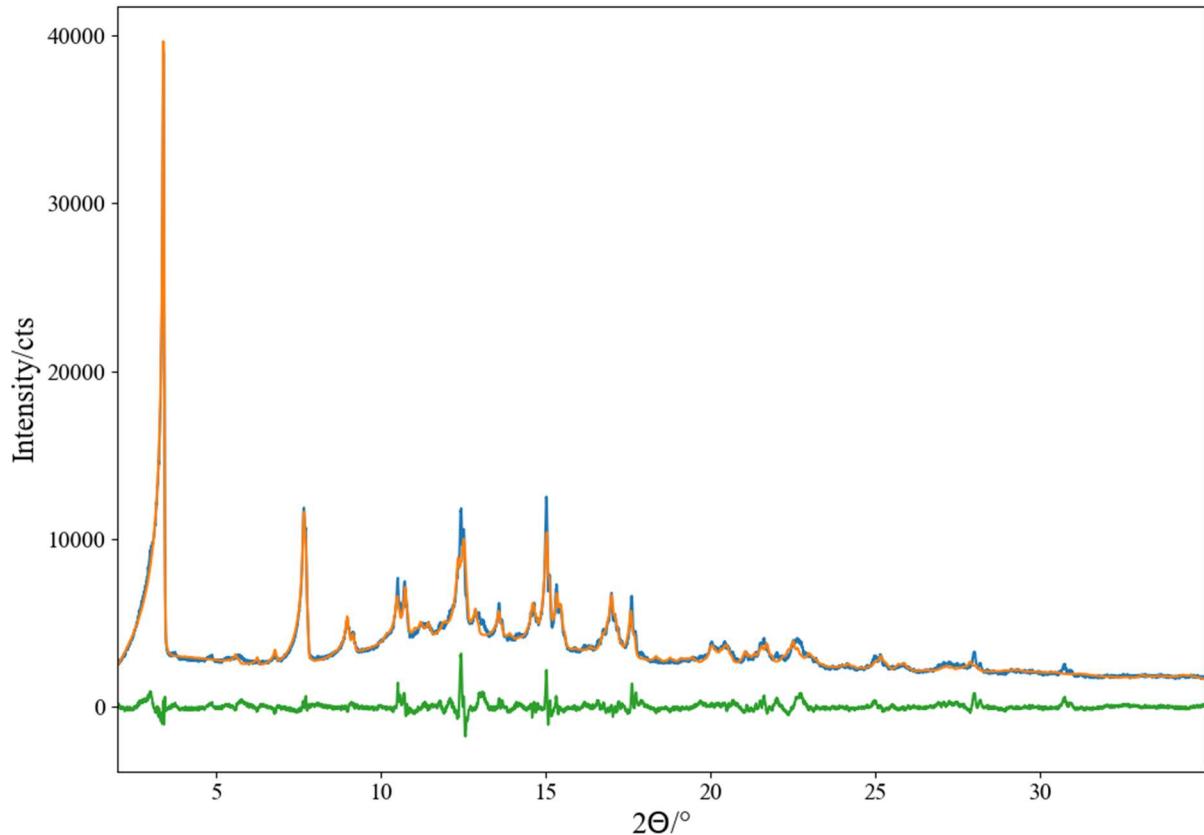
point_for_site Cu1 ux 0 uy 0 uz 0
point_for_site Cl1 ux =CuCl1;  uy 0 uz 0
point_for_site Cl2 ux 0 uy =CuCl2;  uz 0
rotate rottrans  357.30365`_0.09504 qa 1
rotate rottrans  133.10484`_0.11653 qb 1
rotate rottrans  262.26748`_0.10565 qc 1
translate ta 0.25 tb 0.25 tc 0
prm kut1  47.49648`_8.24535 _LIMIT_MIN_ 0 min 0 max 120

rigid

z_matrix N1
z_matrix C1 N1 1.453
z_matrix C2 C1 1.461 N1 113.6
z_matrix C3 C2 1.31 C1 120 N1 @ 122.90657`_0.73315
z_matrix H1 N1 0.86 C1 109.5 C2 =kut1;
z_matrix H2 N1 0.86 C1 109.5 C2 =kut1+120;
z_matrix H3 N1 0.86 C1 109.5 C2 =kut1+240;
z_matrix H4 C1 1.01 C2 108.5 N1 120
z_matrix H5 C1 1.01 C2 108.5 N1 -120
z_matrix H6 C2 1.01 C3 120 C1 -180
z_matrix H7 C3 1.01 C2 120 C1 0
z_matrix H8 C3 1.01 C2 120 C1 180
rotate rottrans  108.62379`_0.61646 qa 1
rotate rottrans  345.69211`_0.81851 qb 1
rotate rottrans  228.66159`_0.24698 qc 1
translate ta rottrans  0.17051`_0.00017 tb rottrans  0.70620`_0.00116 tc
rottrans  0.01188`_0.00084

```

## aa<sub>2</sub>CuBr<sub>4</sub>



**Figure S14.** PXRD data for aa<sub>2</sub>CuBr<sub>4</sub>(blue), calculated pattern (orange) and difference between observed and calculated pattern (green).

```

xdd aa2cubr4.xy
iters 1000
'Auto_T(50)
do_errors
macro rotrans { @ }
      r_wp 5.84359227 r_exp 1.68041644 r_p 4.24524614 r_wp_dash 17.1195536 r_p_dash
17.0901591 r_exp_dash 4.92299563 weighted_Durbin_Watson 0.203245305 gof 3.47746674
      bkg @ 2422.82553`_6.86073751 -488.880305`_8.34475864 -596.533717`_8.62603976
464.943279`_7.19327559 -62.3069883`_6.98650147 -154.037217`_6.47413595 8.39063793`_6.24733384
264.40059`_6.11691803 -301.762824`_6.27887818 134.787703`_6.86485886 41.4749531`_6.10894782
-117.902922`_6.08654077
      lam ymin_on_ymax 0.0001
      Lam_recs
{
      0.6533 0.709300 0.2695
      0.3467 0.713574 0.2795
}
Radius(240)

```

```

Zero_Error(@, 0.02402`_0.00074)
LP_Factor(0)
Full_Axial_Model(12, 15, 12,    43.31400_LIMIT_MIN_0.0001,    4.31758)
x_calculation_step 0.01
      xdd_out "aa2cubr4.txt" load out_record out_fmt out_eqn
{
  " %11.6f  " = X;
  " %11.6f  " = Yobs;
  " %11.6f  " = Ycalc;
  " %11.6f\n" = Yobs-Ycalc;
}

str
a @ 12.497126`_0.002507
b @ 7.767166`_0.001068
c @ 7.590787`_0.000729
be @ 105.99829`_0.01349
space_group "P21"
      CS_G(@, 132.16515`_4.14770)
      Strain_L(@, 0.34327`_0.01582)
      scale @ 8.33709585e-005`_0.0006767
      prm beq1 8.17460`_0.35629 min 1 max 10
      site Cu1 x 0.50588`_0.00160 y 0.00177`_0.00000 z 0.73580`_0.00173 occ Cu 1
beq =beq1;
      site Br1 x 0.50725`_0.00218 y 0.23394`_0.00199 z 0.51630`_0.00273 occ Br 1
beq =beq1;
      site Br2 x 0.69878`_0.00198 y -0.01731`_0.00326 z 0.80526`_0.00243 occ Br 1
beq =beq1;
      site Br3 x 0.50451`_0.00218 y -0.23040`_0.00199 z 0.95531`_0.00273 occ Br 1
beq =beq1;
      site Br4 x 0.31299`_0.00198 y 0.02085`_0.00326 z 0.66634`_0.00243 occ Br 1
beq =beq1;

      prm vez1 2.45846`_0.01620_LIMIT_MAX_2.5 min 2.3 max 2.5
      prm vez2 2.32605`_0.01386_LIMIT_MIN_2.3 min 2.3 max 2.5
      'prm kut1 84.12498 min 60 max 90
      'prm kut2 66.95192 min 60 max 90
      rigid
      point_for_site Cu1 ux 0 uy 0 uz 0
      point_for_site Br1 ux =vez1; uy 0 uz 0
      point_for_site Br2 ux 0 uy =vez2; uz 0
      point_for_site Br3 ux =-vez1; uy 0 uz 0

```

```

point_for_site Br4 ux 0 uy ==vez2; uz 0
rotate rotrans 184.60998`_0.40505 qa 1
rotate rotrans 26.81845`_0.33628 qb 1
rotate rotrans 89.47673`_0.56237 qc 1
translate ta rotrans 0.50588`_0.00160 tb 0.00177 tc rotrans 0.73580`_0.00173
prm beq3 1.00000`_0.74665 LIMIT_MIN_1 min 1 max 10

site      C3      x  0.08529`_0.01880   y  0.56093`_0.04924   z
0.36170`_0.03727    occ C  1 beq =beq3;

site      C1      x  0.21761`_0.00934   y  0.45935`_0.02304   z
0.63478`_0.02477    occ C  1 beq =beq3;

site      C2      x  0.11642`_0.00745   y  0.55260`_0.03477   z
0.54100`_0.03693    occ C  1 beq =beq3;

site      N1      x  0.31934`_0.00745   y  0.55229`_0.01503   z
0.63998`_0.01168    occ N  1 beq =beq3;

site      H1      x  0.35135`_0.03571   y  0.58337`_0.09030
z  0.75073`_0.02107    occ H  1 beq =beq3*1.5;

site      H2      x  0.36337`_0.02907   y  0.48663`_0.03806
z  0.60108`_0.10357    occ H  1 beq =beq3*1.5;

site      H3      x  0.30360`_0.01160   y  0.64196`_0.05746
z  0.57123`_0.08657    occ H  1 beq =beq3*1.5;

site      H4      x  0.21640`_0.01365   y  0.43724`_0.03073
z  0.76533`_0.02920    occ H  1 beq =beq3*1.5;

site      H5      x  0.21903`_0.01596   y  0.34699`_0.02117
z  0.56849`_0.03001    occ H  1 beq =beq3*1.5;

site      H6      x  0.07045`_0.01497   y  0.61064`_0.05079
z  0.61441`_0.04719    occ H  1 beq =beq3*1.5;

site      H7      x  0.13125`_0.03107   y  0.50288`_0.06578
z  0.28829`_0.02814    occ H  1 beq =beq3*1.5;

site      H8      x  0.01533`_0.01961   y  0.62539`_0.05703
z  0.29687`_0.04797    occ H  1 beq =beq3*1.5;

normalize_FCs

prm kut1 111.06743`_56.56944 LIMIT_MIN_0 min 0 max 120
rigid

z_matrix N1
z_matrix C1 N1 1.453
z_matrix C2 C1 1.461 N1 113.6
z_matrix C3 C2 1.31 C1 120 N1 @ 76.18973`_14.54713
z_matrix H1 N1 0.86 C1 109.5 C2 =kut1;
z_matrix H2 N1 0.86 C1 109.5 C2 =kut1+120;
z_matrix H3 N1 0.86 C1 109.5 C2 =kut1+240;
z_matrix H4 C1 1.01 C2 108.5 N1 120
z_matrix H5 C1 1.01 C2 108.5 N1 -120
z_matrix H6 C2 1.01 C3 120 C1 -180
z_matrix H7 C3 1.01 C2 120 C1 0
z_matrix H8 C3 1.01 C2 120 C1 180

```

```

rotate rotrans 103.28588`_7.17613 qa 1
rotate rotrans 142.60294`_5.42596 qb 1
rotate rotrans 305.49463`_5.11796 qc 1
translate ta rotrans 0.31934`_0.00745 tb rotrans 0.55229`_0.01503 tc
rotrans 0.63998`_0.01168

site      C31      x  0.95242`_0.00753  y  0.55142`_0.02745  z
0.94273`_0.05843    occ C  1 beq =beq3;

site      C11      x  0.75453`_0.00764  y  0.51496`_0.01471  z
0.87695`_0.02363    occ C  1 beq =beq3;

site      C21      x  0.85418`_0.00693  y  0.62260`_0.02043  z
0.91565`_0.03735    occ C  1 beq =beq3;

site      N11      x  0.65134`_0.00690  y  0.61254`_0.01204  z
0.82934`_0.01409    occ N  1 beq =beq3;

site      H11      x  0.61239`_0.03020  y  0.58416`_0.07409
z  0.72115`_0.04433    occ H  1 beq =beq3*1.5;

site      H21      x  0.61434`_0.03125  y  0.59051`_0.07755
z  0.90687`_0.06375    occ H  1 beq =beq3*1.5;

site      H31      x  0.66614`_0.00790  y  0.72079`_0.01260
z  0.83177`_0.10492    occ H  1 beq =beq3*1.5;

site      H41      x  0.75437`_0.01181  y  0.43707`_0.01906
z  0.77032`_0.02998    occ H  1 beq =beq3*1.5;

site      H51      x  0.75667`_0.01143  y  0.44458`_0.01987
z  0.98975`_0.02673    occ H  1 beq =beq3*1.5;

site      H61      x  0.84733`_0.00851  y  0.75191`_0.02001
z  0.92154`_0.04695    occ H  1 beq =beq3*1.5;

site      H71      x  0.95927`_0.01008  y  0.42211`_0.02821
z  0.93684`_0.07177    occ H  1 beq =beq3*1.5;

site      H81      x  1.02130`_0.00734  y  0.62583`_0.03254
z  0.96949`_0.07003    occ H  1 beq =beq3*1.5;

prm kut11 119.99683`_55.04315_LIMIT_MIN_0 min 0 max 120
rigid

z_matrix N11
z_matrix C11 N11 1.453
z_matrix C21 C11 1.461 N11 113.6
z_matrix C31 C21 1.31 C11 120 N11 @ 186.70714`_9.78553
z_matrix H11 N11 0.86 C11 109.5 C21 =kut11;
z_matrix H21 N11 0.86 C11 109.5 C21 =kut11+120;
z_matrix H31 N11 0.86 C11 109.5 C21 =kut11+240;
z_matrix H41 C11 1.01 C21 108.5 N11 120
z_matrix H51 C11 1.01 C21 108.5 N11 -120
z_matrix H61 C21 1.01 C31 120 C11 -180
z_matrix H71 C31 1.01 C21 120 C11 0
z_matrix H81 C31 1.01 C21 120 C11 180
rotate rotrans 269.76423`_5.62598 qa 1

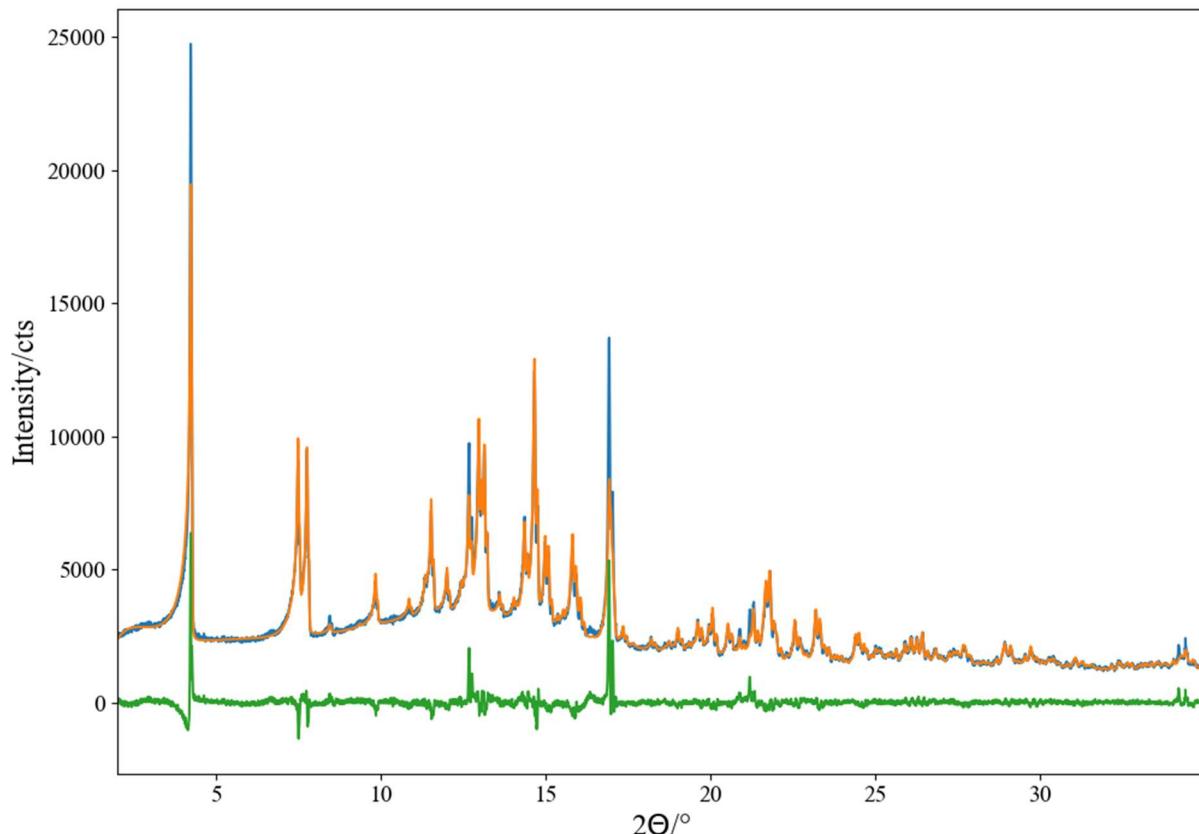
```

```

rotate rotrans 161.78410`_7.19099 qb 1
rotate rotrans 238.54743`_3.01179 qc 1
translate ta rotrans 0.65134`_0.00690 tb rotrans 0.61254`_0.01204 tc
rotrans 0.82934`_0.01409

```

### aacn<sub>2</sub>CuBr<sub>4</sub>



**Figure S15.** PXRD data for **aacn<sub>2</sub>CuBr<sub>4</sub>** (blue), calculated pattern (orange) and difference between observed and calculated pattern (green).

```

xdd aacn2cubr4.xy

macro rotrans { @ }

do_errors
randomize_on_errors
iters 10000

r_wp 6.16747841 r_exp 1.90352012 r_p 3.93435105 r_wp_dash 18.4734158 r_p_dash
15.3143446 r_exp_dash 5.70160386 weighted_Durbin_Watson 0.253414402 gof 3.24003846

bkg @ 1976.22544`_5.88978298 -881.726793`_7.69887091 -194.50276`_5.69114969
319.938392`_5.28550509 45.5993554`_5.19766738 -262.81402`_5.13724438 123.065113`_5.03579521
107.981978`_5.07216927 -142.686061`_4.97980239 25.2843412`_4.70161972 4.44953414`_4.73990428
-13.1589755`_4.66754017 -57.1616906`_5.2014443 69.553838`_4.88744362 -39.0164792`_4.77564132
-9.48991725`_4.66450975 -2.79184833`_4.41351636 14.1956173`_3.92547382
6.27250605`_3.78335322

lam ymin_on_ymax 0.0001
Lam_recs

```

```

{
  0.6533  0.709300  0.2695
  0.3467  0.713574  0.2795
}

Radius(240)

Zero_Error(@, 0.03275`_0.00042)
LP_Factor(0)

Full_Axial_Model(12, 15, 12, @ 3.34752`_0.80802, @ 10.28958`_6.19940)
x_calculation_step 0.01
xdd_out "aacn2cubr4.txt" load out_record out_fmt out_eqn

{
  " %11.6f  " = X;
  " %11.6f  " = Yobs;
  " %11.6f  " = Ycalc;
  " %11.6f\n" = Yobs-Ycalc;
}

str

CS_G(@, 174.23833`_7.84654)
Strain_L(@, 0.12971`_0.00907)
a @ 10.076857`_0.000497
b @ 8.290167`_0.000385
c @ 7.544772`_0.000345
be @ 106.67643`_0.00368
space_group "P21/c"
scale @ 5.50323936e-005`_4.736e-007
prm beq1 2.28346`_0.09832 min 1 max 10
site Cu1    x 0.00000`_0.00000 y 0.00000`_0.00000 z 0.50000`_0.00000 occ Cu
1 beq =beq1;
site Br1    x -0.01336`_0.00063 y -0.18045`_0.00060 z 0.23163`_0.00072 occ Br
1 beq =beq1;
site Br2    x -0.25077`_0.00049 y 0.02182`_0.00161 z 0.40104`_0.00115 occ Br
1 beq =beq1;
prm vezal 2.48982`_0.00537 min 2.2 max 2.6
prm vezal 2.42756`_0.00459 min 2.2 max 2.6
prm kut 89.20186`_0.18831 min 70 max 110
rigid
point_for_site Cu1 ux 0 uy 0 uz 0
point_for_site Br1 ux =vezal; uy 0 uz 0
point_for_site Br2 ux =vezal*Cos(kut*3.141592/180); uy =
vezal*Sin(kut*3.141592/180); uz 0
rotate rotrans 179.78385`_0.22782 min 0 max 359.99 qa 1

```

```

rotate rotrans 36.23442`_0.10876 min 0 max 359.99 qb 1
rotate rotrans 265.07330`_0.23097 min 0 max 359.99 qc 1
translate ta 0 tb 0 tc =1/2;

prm beq2 5.77188`_0.58615_LIMIT_MAX_10 min 1 max 10

site      N1      x  0.51805`_0.01705   y  0.79144`_0.02052   z
0.97352`_0.00641 occ N  1      beq  =beq2;

site      C1      x  0.59124`_0.01550   y  0.85612`_0.01898   z
0.90569`_0.00460 occ C  1      beq  =beq2;

site      C2      x  0.68389`_0.01373   y  0.93738`_0.01734   z
0.81782`_0.00333 occ C  1      beq  =beq2;

site      N2      x  0.75812`_0.01529   y  1.06854`_0.01857   z
0.93708`_0.00472 occ N  1      beq  =beq2;

site      H1      x  0.79680`_0.01651   y  1.03344`_0.01978   z
1.03404`_0.00403 occ H  1      beq  =beq2*1.2;

site      H2      x  0.70315`_0.01607   y  1.12909`_0.01908   z
0.95567`_0.00724 occ H  1      beq  =beq2*1.2;

site      H3      x  0.79806`_0.01449   y
1.10925`_0.01786 z  0.89145`_0.00503   occ H  1      beq
=beq2*1.2;

site      H4      x  0.62658`_0.01251   y
0.97718`_0.01625 z  0.69732`_0.00448   occ H  1      beq
=beq2*1.2;

site      H5      x  0.73848`_0.01297   y
0.85894`_0.01681 z  0.78726`_0.00439   occ H  1      beq
=beq2*1.2;

rigid

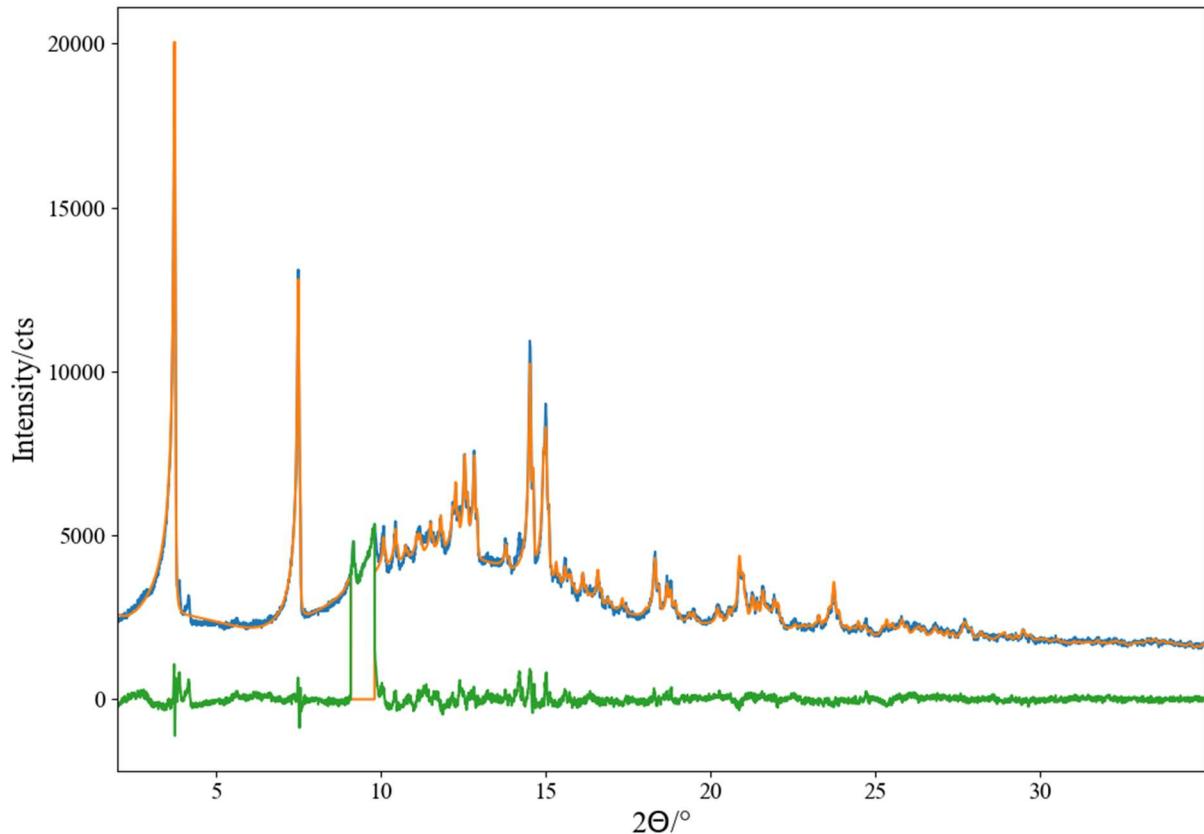
point_for_site N1      ux 1.2635 uy  2.9427 uz  3.8405
point_for_site C1      ux 1.2615 uy  2.9524 uz  2.6960
point_for_site C2      ux 1.2584 uy  2.9505 uz  1.2399
point_for_site N2      ux 1.2574 uy  4.3318 uz  0.7329
point_for_site H1      ux 1.8674 uy  4.7142 uz  1.0325
point_for_site H2      ux 0.6230 uy  4.7045 uz  1.0187
point_for_site H3      ux 1.2118 uy  4.3173 uz  0.0461
point_for_site H4      ux 0.4619 uy  2.4490 uz  0.9541
point_for_site H5      ux 1.9628 uy  2.4200 uz  0.9680

rotate rotrans 48.86664`_0.78290 min 0 max 359.99 qa 1
rotate rotrans 329.15650`_1.93310 min 0 max 359.99 qb 1
rotate rotrans 318.93791`_0.74839 min 0 max 359.99 qc 1

translate ta rotrans 0.57814`_0.01026 min 0 max 1 tb rotrans
0.88356`_0.01450 min 0 max 1 tc rotrans 0.34607`_0.00312 min 0 max 1

```

## cpa<sub>2</sub>CuBr<sub>4</sub>



**Figure S16.** PXRD data for **cpa<sub>2</sub>CuBr<sub>4</sub>** (blue), calculated pattern (orange) and difference between observed and calculated pattern (green). The region between 9.1 and 9.8 °2θ is excluded from fit.

```

xdd cpa2cubr4_2.xy
iters 50000
macro rotrans {@}

'Auto_T(50)
do_errors
r_wp 4.15452324 r_exp 1.82567102 r_p 3.14009576 r_wp_dash 16.6979934 r_p_dash 18.1564671
r_exp_dash 7.33779568 weighted_Durbin_Watson 0.446936477 gof 2.27561438

LP_Factor(0)
Zero_Error(, 0.02681)
Full_Axial_Model(12, 15, 12, 12.54022_1.17720, 2.16332_0.22014)
Radius(240)

lam ymin_on_ymax 0.0001
Lam_recs
{

```

```

0.6533  0.709300  0.2695
0.3467  0.713574  0.2795
}

xdd_out "cpa2cubr4_2.txt" load out_record out_fmt out_eqn
{
    " %11.6f  " = X;
    " %11.6f  " = Yobs;
    " %11.6f  " = Ycalc;
    " %11.6f\n" = Yobs-Ycalc;
}

bkg @ 2335.77842`_2.95440024 -630.883542`_4.49910149 -512.663914`_3.85848496
454.84835`_3.73423097 67.8298926`_3.46393095 -367.594261`_3.47563636 200.927858`_3.51012278
119.071507`_3.49905454 -251.740246`_3.53232696 102.812889`_3.37935809 83.5251763`_3.18372989
-137.342734`_2.90371 56.8793076`_2.88341949

x_calculation_step 0.01

exclude 9.1 9.8

str
'hkl_Is

CS_L(@, 206.96960`_6.44566)
Strain_G(@, 0.26589`_0.00780)
a @ 7.806465`_0.000453
b @ 8.085963`_0.000517
c @ 21.862873`_0.000901
space_group "Bmab"
scale @ 8.7384532e-006`_5.242e-008
prm beq1 2.31929`_0.10754 min 1 max 10
site Cu1 x 0.00000`_0.00000 y 0.00000`_0.00000 z 0.00000`_0.00000 occ Cu 1
beq =beq1;
site Br1 x -0.02072`_0.00096 y -0.04576`_0.00052 z 0.10994`_0.00020 occ Br 0.5
beq =beq1;
site Br2 x 0.22349`_0.00619 y 0.21199`_0.00592 z 0.01744`_0.00018 occ Br 0.5
beq =beq1;
prm vez1 2.43730`_0.00441 min 2 max 3
prm vez2 2.47539`_0.00599 min 2 max 3
'prm vez3 2.52641 min 2 max 3
'prm vez4 2.72481 min 2 max 3
normalize_FCs

rigid

```

```

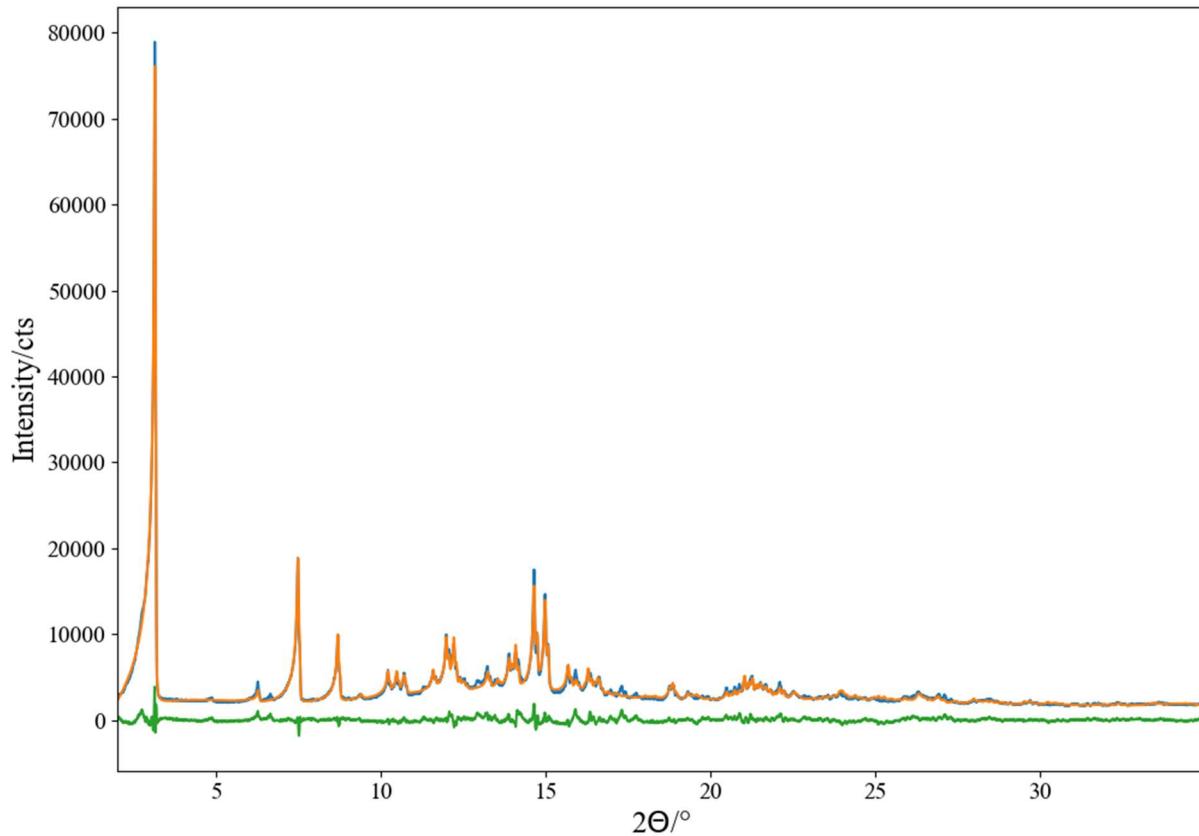
point_for_site Cu1 ux 0 uy 0 uz 0
point_for_site Br1 ux =vez1; uy 0 uz 0
point_for_site Br2 ux 0 uy =vez2; uz 0
rotate rotrans 68.37735`_1.08848 qa 1
rotate rotrans 279.53698`_0.06894 qb 1
rotate rotrans 246.39151`_1.14532 qc 1
translate ta 0 tb 0 tc 0

prm beq2 2.68750` min 1 max 10
site N1 x 0.49293`_0.00690 y 0.00110`_0.00328 z 0.10926`_0.00061 occ N 0.5
beq =beq1;
site C1 x 0.42362`_0.00843 y -0.02192`_0.00535 z 0.17268`_0.00090 occ C 0.5
beq =beq1;
site C2 x 0.40452`_0.01080 y 0.14422`_0.00684 z 0.20243`_0.00146 occ C 0.5
beq =beq1;
site C3 x 0.55153`_0.01063 y 0.03227`_0.00715 z 0.21979`_0.00086 occ C 0.5
beq =beq1;

rigid
z_matrix N1
z_matrix C1 N1 1.5
z_matrix C2 C1 1.5 N1 109
z_matrix C3 C1 1.5 N1 111 C2 -64.75
rotate rotrans 159.00694`_1.52026 qa 1
rotate rotrans 188.06810`_1.15152 qb 1
rotate rotrans 268.89474`_2.09522 qc 1
translate ta rotrans 0.49293`_0.00690 tb rotrans 0.00110`_0.00328 tc rotrans
0.10926`_0.00061

```

**cpma<sub>2</sub>CuBr<sub>4</sub>**



**Figure S17.** PXRD data for **cpma<sub>2</sub>CuBr<sub>4</sub>** (blue), calculated pattern (orange) and difference between observed and calculated pattern (green). The region between 9.1 and 9.8  $^\circ$ 2θ is excluded from fit.

```

xdd cpma2cubr4.xy
iters 20000
macro rotrans {@}
'Auto_T(100)
do_errors
r_wp 6.52331649 r_exp 1.68338677 r_p 4.99345988 r_wp_dash 14.1964309 r_p_dash 14.6879366
r_exp_dash 3.66348684 weighted_Durbin_Watson 0.17261235 gof 3.87511449

LP_Factor(0)
Zero_Error(@, 0.02220`_0.00034)
Full_Axial_Model(12, 15, 12, @ 8.58440`_0.49897, @ 3.87056`_0.12299)
Radius(240)

lam ymin_on_ymax 0.0001
Lam_recs
{
  0.6533 0.709300 0.2695

```

```

0.3467  0.713574  0.2795

}

xdd_out "cpma2cubr4.txt" load out_record out_fmt out_eqn

{
    " %11.6f  " = X;
    " %11.6f  " = Yobs;
    " %11.6f  " = Ycalc;
    " %11.6f\n" = Yobs-Ycalc;
}

bkg @ 2019.71473`_9.82206666 61.3242429`_15.9030023 -837.07247`_12.2894465
547.425597`_10.6945783 -117.311334`_9.86035952 77.8691445`_9.97456126 -174.129282`_8.64008443
314.000814`_8.22058772 -327.476179`_7.35794565 50.2648207`_7.07821717 80.9584211`_6.50657278
-55.7167419`_6.20074236 -51.7505296`_6.38691517

x_calculation_step 0.01

str

    CS_L(@, 555.93461`_74.51451)
    CS_G(@, 167.10131`_6.32446)
    Strain_G(@, 0.06936`_0.05066_LIMIT_MIN_0.0001)
    Strain_L(@, 0.09507`_0.02064)

    a @ 7.775261`_0.000371
    b @ 7.977310`_0.000449
    c @ 26.002141`_0.002189

    space_group "B2cb"
    scale @ 1.37598442e-005`_2.417e-007

    'lebail 1

    prm beq1 5.77675`_0.18459 min 1 max 10
    site Cu1 x 0.87334`_0.00000 y 0.00000`_0.00000 z 0.00000`_0.00000 occ Cu 1
beq =beq1;

    site Br1 x 0.84120`_0.00172 y 0.04392`_0.00140 z 0.09080`_0.00033 occ Br 1
beq =beq1;

    site Br2 x 1.08860`_0.01215 y -0.21927`_0.01148 z 0.01679`_0.00033 occ Br 1
beq =beq1;

    prm vez1 2.40000`_0.00852_LIMIT_MIN_2.4 min 2.40 max 2.46
    prm vez2 2.46000`_0.01438_LIMIT_MAX_2.46 min 2.40 max 2.46
    'prm vez3 2.35694 min 2.2 max 2.5
    'prm vez4 2.20024 min 2.2 max 2.5

    normalize_FCs

    rigid

    point_for_site Cu1 ux 0 uy 0 uz 0
    point_for_site Br1 ux =vez1; uy 0 uz 0
    point_for_site Br2 ux 0 uy =vez2; uz 0

```

```

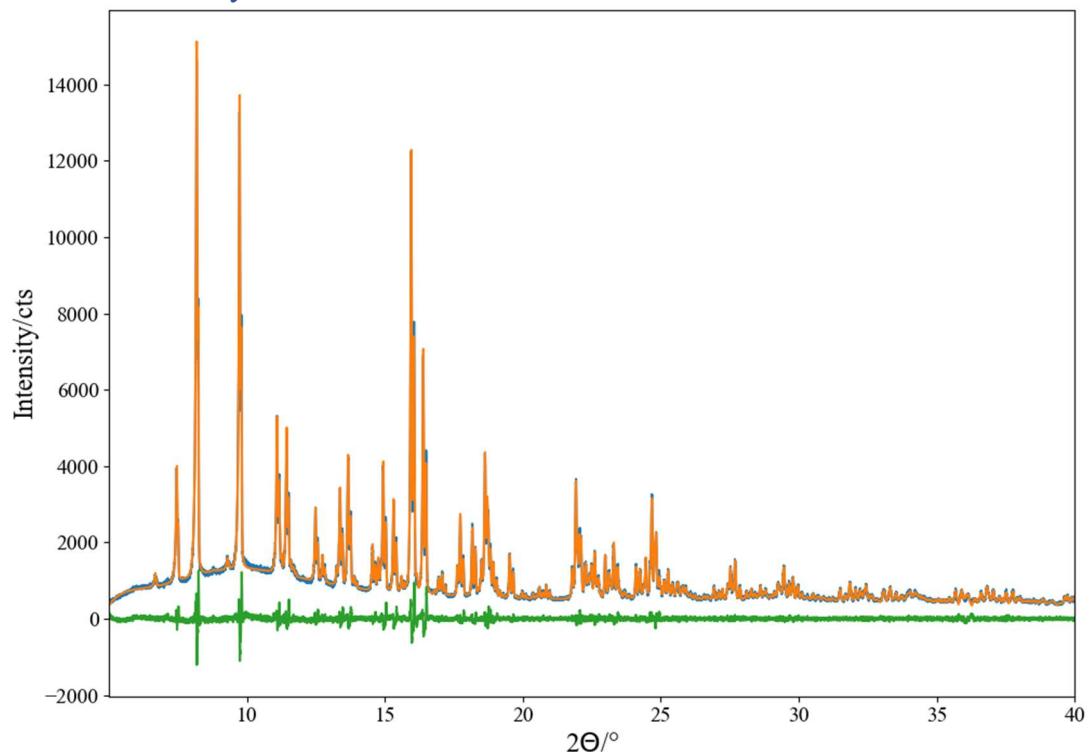
'point_for_site Br3 ux ==-vez3; uy 0 uz 0
'point_for_site Br4 ux 0 uy ==-vez4; uz 0
rotate rotrans 278.10852`_2.27088 qa 1
rotate rotrans 259.67027`_0.18788 qb 1
rotate rotrans 305.49552`_2.06415 qc 1
translate ta 0.87334 tb 0 tc 0
prm beq2 7.13855`_1.14110_LIMIT_MAX_10 min 1 max 10
site N1 x 0.30776`_0.00764 y 0.48661`_0.00656 z 0.41382`_0.00120 occ N 1
beq =beq2;
site C1 x 0.27610`_0.01147 y 0.40594`_0.00867 z 0.36432`_0.00141 occ C 1
beq =beq2;
site C2 x 0.35887`_0.01255 y 0.50017`_0.01119 z 0.32200`_0.00128 occ C 1
beq =beq2;
site C3 x 0.54738`_0.01257 y 0.53061`_0.02275 z 0.32635`_0.00364 occ C 1
beq =beq2;
site C4 x 0.47702`_0.02255 y 0.40474`_0.01664 z 0.28767`_0.00396 occ C 1
beq =beq2;
site H1 x 0.31507`_0.11567 y 0.59328`_0.01169 z 0.40957`_0.00534 occ H 1 beq
=beq2*1.5;
site H2 x 0.22446`_0.05712 y 0.46453`_0.09338 z 0.43450`_0.01112 occ H 1 beq
=beq2*1.5;
site H3 x 0.40245`_0.05920 y 0.44961`_0.08384 z 0.42660`_0.01622 occ H 1 beq
=beq2*1.5;
site H4 x 0.32474`_0.01717 y 0.28858`_0.00811 z 0.36519`_0.00224 occ H 1 beq
=beq2*1.5;
site H5 x 0.14802`_0.01208 y 0.40159`_0.01402 z 0.35797`_0.00199 occ H 1 beq
=beq2*1.5;
site H6 x 0.28962`_0.01509 y 0.59244`_0.01504 z 0.30530`_0.00288 occ H 1 beq
=beq2*1.5;
site H7 x 0.59227`_0.01803 y 0.64041`_0.02564 z 0.31243`_0.00349 occ H 1 beq
=beq2*1.5;
site H8 x 0.60687`_0.01117 y 0.48523`_0.03118 z 0.35795`_0.00524 occ H 1 beq
=beq2*1.5;
site H9 x 0.47984`_0.02715 y 0.43856`_0.01892 z 0.25025`_0.00354 occ H 1 beq
=beq2*1.5;
site H10 x 0.49224`_0.03162 y 0.28141`_0.01740 z 0.29519`_0.00609 occ H 1
beq =beq2*1.5;

prm kut 55.80683`_6.00924 min 0 max 360
prm kut2 31.96447`_64.23409_LIMIT_MIN_0 min 0 max 120
rigid
z_matrix N1
z_matrix C1 N1 1.46
z_matrix C2 C1 1.48 N1 111
z_matrix C3 C2 1.49 C1 117 N1 =kut;
z_matrix C4 C2 1.49 C1 117 N1 =kut+70;
z_matrix H1 N1 0.86 C1 109.5 C2 =kut2;

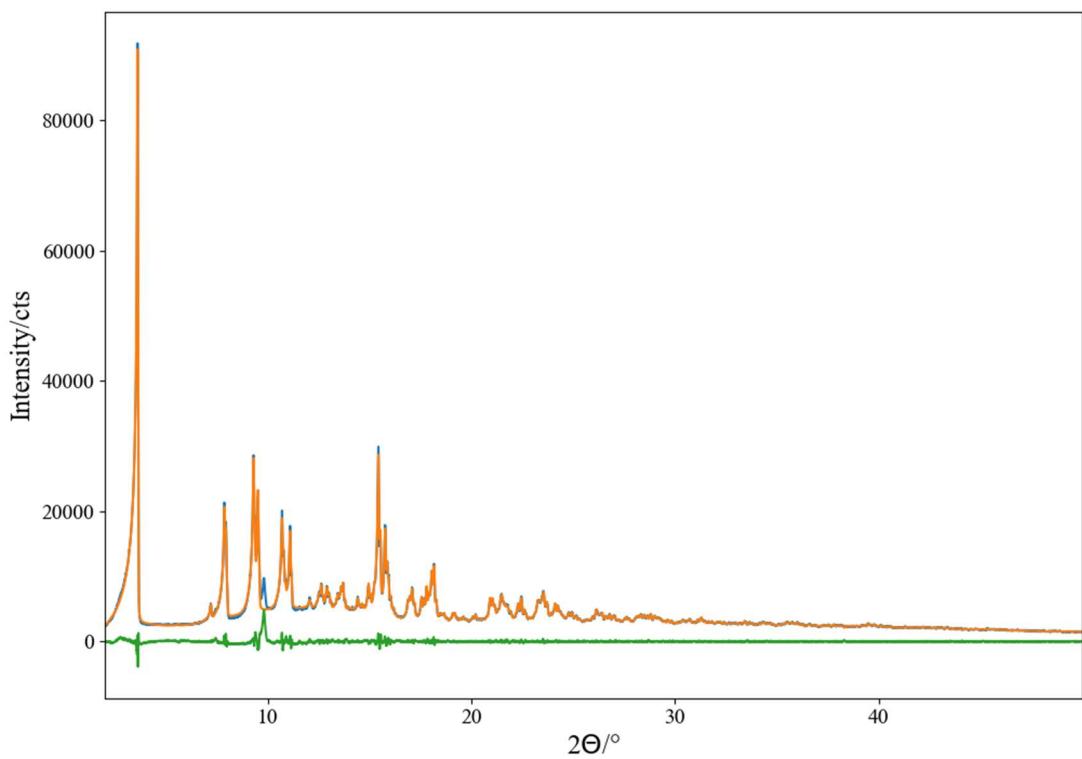
```

```
z_matrix H2 N1 0.86 C1 109.5 C2 =kut2+120;
z_matrix H3 N1 0.86 C1 109.5 C2 =kut2+240;
z_matrix H4 C1 1.01 N1 109      C2 120
z_matrix H5 C1 1.01 N1 109      C2 -120
z_matrix H6 C2 1.01 C3 116 C4 -107.25
z_matrix H7 C3 1.01 C2 117 H6 0
z_matrix H8 C3 1.01 C2 117 H6 145
z_matrix H9 C4 1.01 C2 117 H6 0
z_matrix H10 C4 1.01 C2 117 H6 -145
rotate rotrans 172.66073`_2.31806 qa 1
rotate rotrans 27.26163`_1.54523 qb 1
rotate rotrans 53.35634`_3.54816 qc 1
translate ta rotrans 0.30776`_0.00764 tb rotrans 0.48661`_0.00656 tc rotrans
0.41382`_0.00120
```

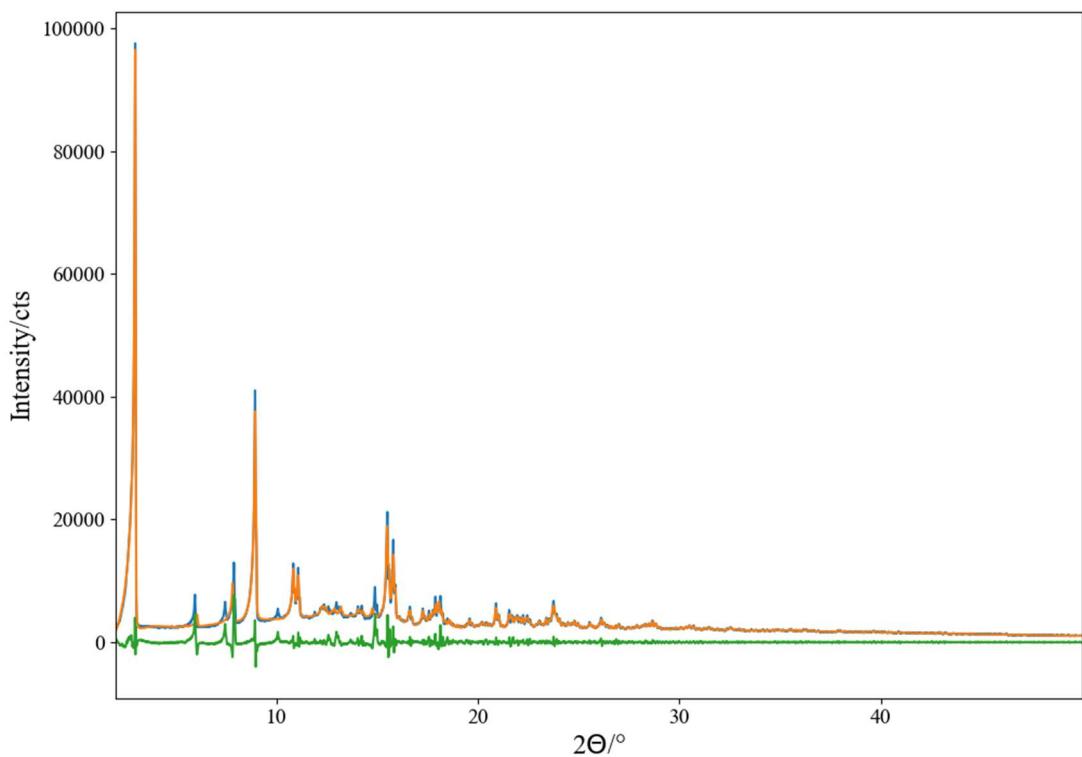
## Refinements with crystal structure from SCXRD data



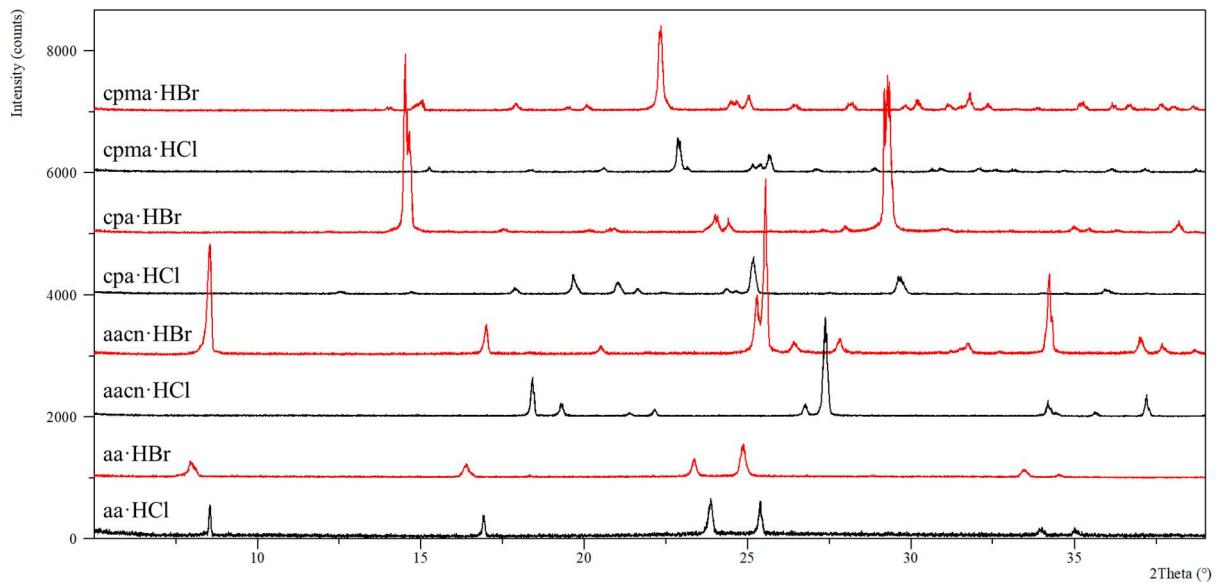
**Figure S18.** PXRD data (Mo K $\alpha$ ) for  $\text{aacn}_2\text{CuCl}_4$  (blue), calculated pattern (orange) and difference between observed and calculated pattern (green). The fit was done on crystal structure obtained from the SCXRD experiments.  $R_{\text{wp}} = 5.06\%$ .



**Figure S19.** PXRD data (Mo K $\alpha$ ) for  $\text{cpa}_2\text{CuCl}_4$  (blue), calculated pattern (orange) and difference between observed and calculated pattern (green). The fit was done on crystal structure obtained from the SCXRD experiments.  $R_{\text{wp}} = 4.84\%$ .

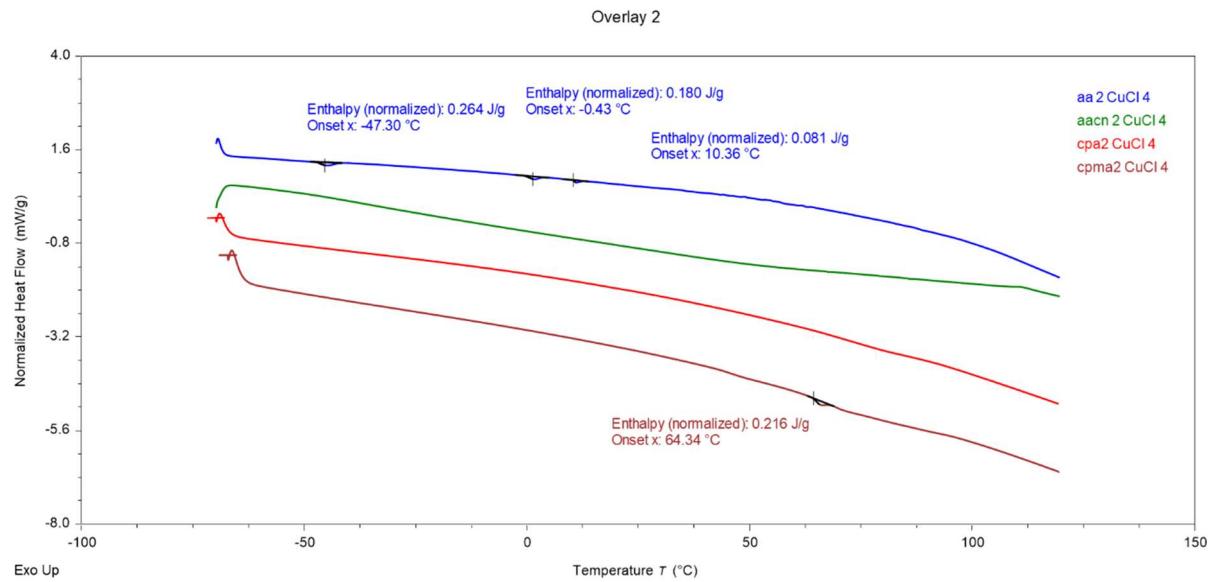


**Figure S20.** PXRD data (Mo K $\alpha$ ) for  $\text{cpma}_2\text{CuCl}_4$  (blue), calculated pattern (orange) and difference between observed and calculated pattern (green). The fit was done on crystal structure obtained from the SCXRD experiments.  $R_{\text{wp}} = 9.57\%$ .

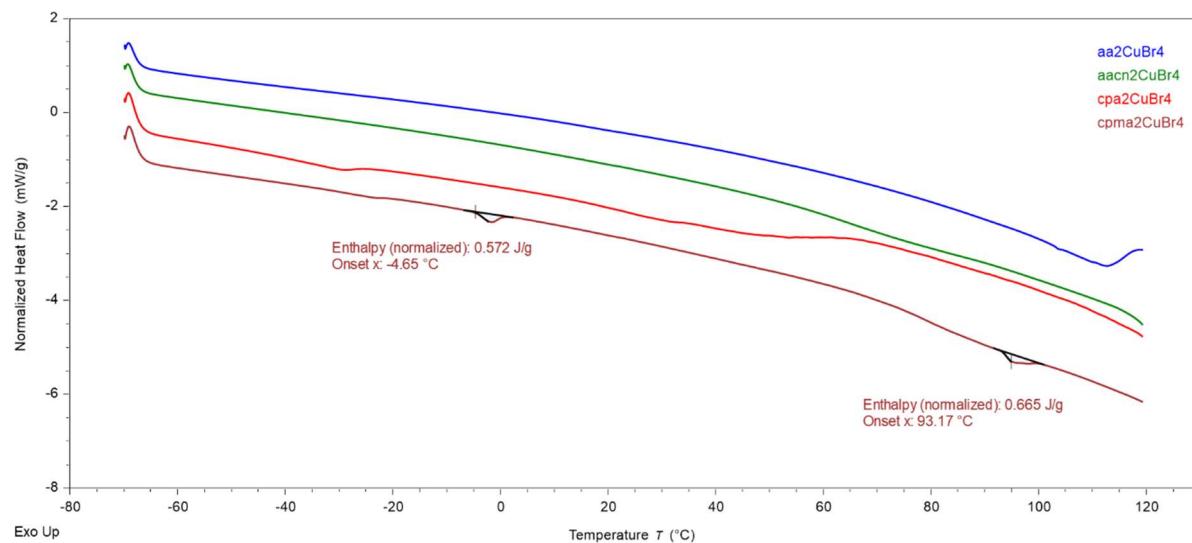


**Figure S21.** PXRD data (Cu K $\alpha$ ) of alkylammonium halogenides. Diffraction patterns of chloride salts are shown as black lines, while those of bromide salts are shown as red lines.

## Thermal analysis



**Figure S22.** DSC thermograms of **aa<sub>2</sub>CuCl<sub>4</sub>** (blue), **aacn<sub>2</sub>CuCl<sub>4</sub>** (green), **cpa<sub>2</sub>CuCl<sub>4</sub>** (red) and **cpma<sub>2</sub>CuCl<sub>4</sub>** (dark red). While **aacn<sub>2</sub>CuCl<sub>4</sub>** and **cpa<sub>2</sub>CuCl<sub>4</sub>** show no thermal events in the probed temperature range, **aa<sub>2</sub>CuCl<sub>4</sub>** and **cpma<sub>2</sub>CuCl<sub>4</sub>** show a few weak endothermic events indicating possible structural phase transitions, albeit the structural changes should be minimal considering the enthalpies of thermal events are minute (less than 1 kJ mol<sup>-1</sup>).



**Figure S23.** DSC thermograms of **aa<sub>2</sub>CuBr<sub>4</sub>** (blue), **aacn<sub>2</sub>CuBr<sub>4</sub>** (green), **cpa<sub>2</sub>CuBr<sub>4</sub>** (red) and **cpma<sub>2</sub>CuBr<sub>4</sub>** (dark red). As with chlorocuprates(II), no proper thermal events are observed except in **cpma<sub>2</sub>CuBr<sub>4</sub>** with two weak endothermal events with enthalpies less than 1 kJ mol<sup>-1</sup>.