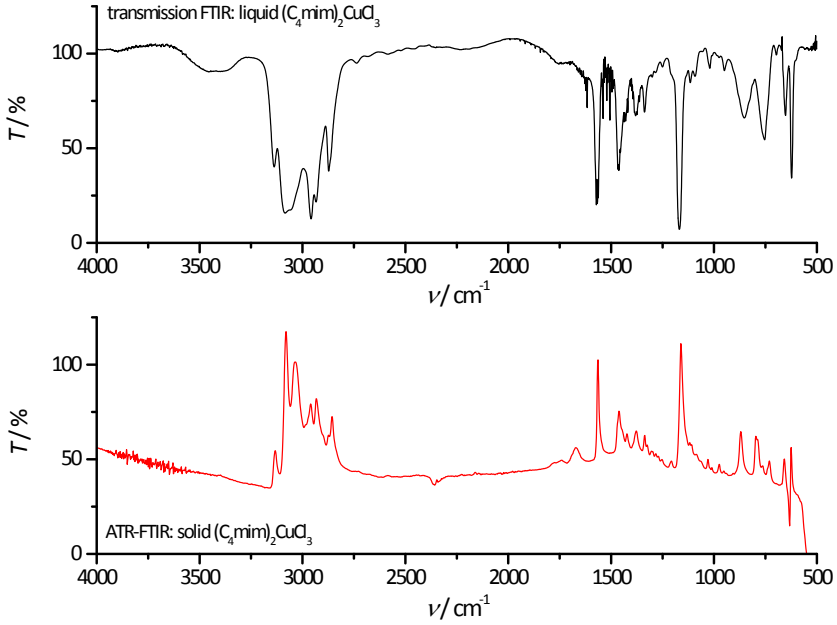
Electronic Supplementary Material (ESI) for Dalton Transactions.

Ionic Liquid, Glass or Crystalline Solid? Structures and Thermal Behaviour of $(C_4mim)_2CuCl_3$.

Philipp Zürner, Horst Schmidt, Sebastian Bette, Jörg Wagler and Gero Frisch*
TU Bergakademie Freiberg, Institut für Anorganische Chemie, Leipziger Str. 29, 09599 Freiberg, Germany
*gero.frisch@chemie.tu-freiberg.de

Supplementary information

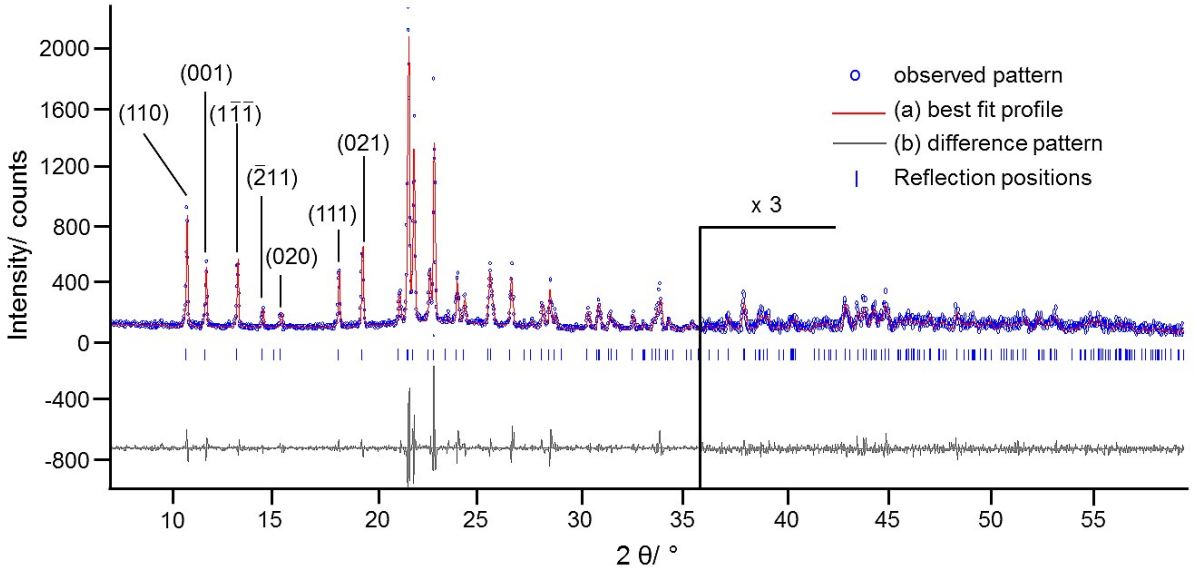


FTIR (transmission mode) of liquid and ATR-FTIR spectra of solid $(C_4mim)_2CuCl_3$ at 298 K.

Rietveld refinement data at ambient temperature.

R-F² /% *	1.801
gof /% *	1.381
Starting angle/ ° 2ϑ	7.0
Final angle/ ° 2ϑ	60.0
Step width/ ° 2ϑ	0.023
Time per step/ s	0.2
No. of variables	32

* *R-F²* and *gof* as defined in TOPAS (Bruker AXS)[1]



X-ray powder diffraction pattern of $(C_4mim)_2CuCl_3$ (Cu-K_α) at 298 K with selected reflection indices at ambient conditions compared to Rietveld fit profiles. The high angle part starting at 36° 2θ is enlarged for clarity.

Crystallographic data and experimental details for the three solid $(C_4mim)_2CuCl_3$ phases.

	high temperature phase	intermediate temperature phase	low temperature phase
Crystal data			
Chemical formula	$C_{16}H_{30}Cl_3CuN_4$		
M_r	448.33		
Crystal system, space group	Monoclinic, *C*2	Monoclinic, *C*2	Monoclinic, $P2_1$
Temperature (K)	233	213	90
a, *b*, *c* (Å)	12.990 (6), 11.404 (4), 8.386 (4)	12.983 (4), 11.352 (3), 15.982 (5)	12.854 (2), 11.2524 (13), 15.806 (4)
β (°)	116.30 (3)	110.11 (3)	109.355 (16)
V (Å^3)	1113.8 (9)	2212.1 (12)	2156.9 (7)
Z	2	4	4
Radiation type	Mo *K*α		
μ (mm^{-1})	1.35	1.36	1.39
Crystal size (mm)	0.3 × 0.2 × 0.1		
Data collection			
Diffractometer	STOE *IPDS* 2 diffractometer		
Absorption correction	Integration[2]		
T_{min}, T_{max}	0.803, 0.914	0.720, 0.797	0.645, 0.760
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3438, 2170, 1853	6529, 3932, 2931	19229, 8389, 7844
R_{int}	0.036	0.042	0.037
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.633	0.633	0.633
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.048, 0.111, 1.04	0.048, 0.131, 1.14	0.033, 0.084, 1.05
No. of reflections	2170	3932	8387
No. of parameters	145	280	479
No. of restraints	57	127	37
H-atom treatment	H-atom parameters constrained		
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.28	0.30, −0.34	0.58, −0.35
Absolute structure	Flack x determined using 694 quotients $[(I+)-(I-)]/[(I+)+(I-)]^3$	Flack x determined using 890 quotients $[(I+)-(I-)]/[(I+)+(I-)]^3$	Flack x determined using 3140 quotients $[(I+)-(I-)]/[(I+)+(I-)]^3$
Absolute structure parameter	0.00 (2)	−0.001 (16)	−0.014 (7)

Comparison of *measured* and calculated atom positions from the intermediate and low temperature crystal structure based on the high temperature phase. For clarification all hydrogen atoms and the carbon atoms of the butyl residue are omitted from the calculation.

C 1 2 1	No. 5	*a = 12.990(6) Å, b = 11.404(4) Å, c = 8.386(4) Å, β = 116.30(3)°, V = 1113.8(9) Å³, Z = 2*									
Atom	Wyck. Pos.	Site Sym.	x	y	z	Atom	Wyck. Pos.	Site Sym.	x	y	z
Cu (a)	2a	2	*1.0000*	*0.5571*	*0.0000*	*C (a)*	4c	1	*0.2053*	*0.8217*	*0.2967*
Cl (a)	4c	1	*0.9605*	*0.6633*	*0.1930*	*C (b)*	4c	1	*0.3463*	*0.9033*	*0.5215*
Cl (b)	2a	2	*1.0000*	*0.3625*	*0.0000*	*C (c)*	4c	1	*0.3453*	*0.9477*	*0.3739*
N (a)	4c	1	*0.2569*	*0.8265*	*0.4722*	*C (d)*	4c	1	*0.2269*	*0.7575*	*0.5941*
N (b)	4c	1	*0.2565*	*0.8949*	*0.2331*						

i 2 ↓

-1	0	1	0
0	-1	0	0
0	0	2	0.5
0	0	0	1

C 1 2 1	Nr. 5	a = 12.990 Å, b = 11.404 Å, c = 16.031 Å, β = 110.290° *a = 12.983(4) Å, b = 11.352(3) Å, c = 15.982(5) Å, β = 110.11(3)°, V = 2212.1(12) Å³, Z = 4*									
Atom	Wyck. Pos.	Site Sym.	x	y	z	Atom	Wyck. Pos.	Site Sym.	x	y	z
Cu (a1) *Cu (1)*	4c	1	0.7500 *0.7439*	0.4429 *0.4429*	0.7500 *0.7485*	C (a1) *C (9)*	4c	1	0.6931 *0.6909*	0.1783 *0.1809*	0.8984 *0.8989*
Cl (a1) *Cl (3)*	4c	1	0.8860 *0.8830*	0.3367 *0.3403*	0.8465 *0.8452*	C (a2) *C (1)*	4c	1	0.8070 *0.8047*	0.1783 *0.1752*	0.6017 *0.6045*
Cl (a2) *Cl (2)*	4c	1	0.6140 *0.6104*	0.3367 *0.3325*	0.6535 *0.6532*	C (b1) *C (10)*	4c	1	0.6645 *0.6723*	0.0967 *0.0906*	0.0108 *0.0131*
Cl (b1) *Cl (1)*	4c	1	0.7500 *0.7351*	0.6375 *0.6379*	0.7500 *0.7467*	C (b2) *C (2)*	4c	1	0.8356 *0.8419*	0.0967 *0.1005*	0.4893 *0.4921*
N (a1) *N (3)*	4c	1	0.7292 *0.7337*	0.1735 *0.1702*	0.9861 *0.9876*	C (c1) *C (11)*	4c	1	0.5917 *0.5933*	0.0523 *0.0514*	0.9370 *0.9405*
N (a2) *N (1)*	4c	1	0.7708 *0.7756*	0.1735 *0.1763*	0.5139 *0.5161*	C (c2) *C (3)*	4c	1	0.9084 *0.9107*	0.0523 *0.0520*	0.5631 *0.5663*
N (b1) *N (4)*	4c	1	0.6101 *0.6055*	0.1051 *0.1101*	0.8666 *0.8695*	C (d1) *C (12)*	4c	1	0.8202 *0.8300*	0.2425 *0.2319*	0.0471 *0.0458*
N (b2) *N (2)*	4c	1	0.8900 *0.8866*	0.1051 *0.1001*	0.6335 *0.6365*	C (d2) *C (4)*	4c	1	0.6799 *0.6898*	0.2425 *0.2505*	0.4530 *0.4558*

k 2 ↓

1	0	0	0.25

0	1	0	0
0	0	1	0
0	0	0	1

P 1 2_1 1 Nr. 4	a = 12.990Å, b = 11.404Å, c = 16.031Å, β = 110.290°
	a = 12.854(2) Å, b = 11.2524(13) Å, c = 15.806(4) Å, β = 109.355(16)°, V = 2156.9(7) Å^3, Z = 4

Atom	Wyck. Pos.	Site Sym.	x	y	z	Atom	Wyck. Pos.	Site Sym.	x	y	z
Cu (a11)	2a	1	0.5000	0.4429	0.7500	C (a11)	2a	1	0.4431	0.1783	0.8984
Cu (1)			*0.4984*	*0.4494*	*0.7528*	*C (25)*			*0.4242*	*0.2015*	*0.9026*
Cu (a21)	2a	1	0.0000	0.4429	0.2500	C (a12)	2a	1	0.0570	0.1783	0.1017
Cu (2)			*0.0204*	*0.4418*	*0.2587*	*C (1)*			*0.0416*	*0.1629*	*0.1028*
Cl (a11)	2a	1	0.6360	0.3367	0.8465	C (a21)	2a	1	0.5570	0.1783	0.6017
Cl (1)			*0.6309*	*0.3408*	*0.8525*	*C (9)*			*0.5362*	*0.1625*	*0.6094*
Cl (a12)	2a	1	0.8640	0.3367	0.1535	C (a22)	2a	1	0.9431	0.1783	0.3984
Cl (5)			*0.8696*	*0.3489*	*0.1633*	*C (17)*			*0.9251*	*0.2022*	*0.3969*
Cl (a21)	2a	1	0.3640	0.3367	0.6535	C (b11)	2a	1	0.4145	0.0967	0.0108
Cl (2)			*0.3551*	*0.3412*	*0.6642*	*C (26)*			*0.4141*	*0.0980*	*0.0182*
Cl (a22)	2a	1	0.1360	0.3367	0.3465	C (b12)	2a	1	0.0856	0.0967	0.9893
Cl (4)			*0.1428*	*0.3256*	*0.3587*	*C (2)*			*0.0583*	*0.0686*	*0.9856*
Cl (b11)	2a	1	0.5000	0.6375	0.7500	C (b21)	2a	1	0.5856	0.0967	0.4893
Cl (3)			*0.4952*	*0.6470*	*0.7428*	*C (10)*			*0.5863*	*0.0997*	*0.4969*
Cl (b12)	2a	1	0.0000	0.6375	0.2500	C (b22)	2a	1	0.9145	0.0967	0.5108
Cl (6)			*0.0401*	*0.6378*	*0.2518*	*C (18)*			*0.8949*	*0.1176*	*0.5125*
N (a11)	2a	1	0.4792	0.1735	0.9861	C (c11)	2a	1	0.3417	0.0523	0.9370
N (7)			*0.4711*	*0.1852*	*0.9910*	*C (27)*			*0.3309*	*0.0622*	*0.9445*
N (a12)	2a	1	0.0208	0.1735	0.0139	C (c12)	2a	1	0.1584	0.0523	0.0631
N (1)			*-0.0039*	*0.1486*	*0.0141*	*C (3)*			*0.1431*	*0.0344*	*0.0591*
N (a21)	2a	1	0.5208	0.1735	0.5139	C (c21)	2a	1	0.6584	0.0523	0.5631
N (3)			*0.5126*	*0.1690*	*0.5207*	*C (11)*			*0.6549*	*0.0513*	*0.5729*
N (a22)	2a	1	0.9792	0.1735	0.4861	C (c22)	2a	1	0.8417	0.0523	0.4370
N (6)			*0.9556*	*0.2025*	*0.4863*	*C (19)*			*0.8281*	*0.0659*	*0.4371*
N (b11)	2a	1	0.3601	0.1051	0.8666	C (d11)	2a	1	0.5702	0.2425	0.0471
N (8)			*0.3384*	*0.1282*	*0.8734*	*C (28)*			*0.5707*	*0.2444*	*0.0488*
N (b12)	2a	1	0.1400	0.1051	0.1335	C (d12)	2a	1	0.9299	0.2425	0.9530
N (2)			*0.1310*	*0.0947*	*0.1314*	*C (4)*			*0.8939*	*0.2054*	*0.9579*
N (b21)	2a	1	0.6400	0.1051	0.6335	C (d21)	2a	1	0.4299	0.2425	0.4530
N (4)			*0.6217*	*0.0907*	*0.6428*	*C (12)*			*0.4264*	*0.2425*	*0.4597*
N (b22)	2a	1	0.8601	0.1051	0.3666	C (d22)	2a	1	0.0702	0.2425	0.5471
N (5)			*0.8473*	*0.1205*	*0.3655*	*C (20)*			*0.0375*	*0.2814*	*0.5470*

References

1 Bruker AXS Topas, version 4.2. 2009.

2 P. Coppens, *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, Copenhagen: Munksggard, 1970, p. 255–270.

3 S. Parsons, H. D. Flack, T. Wagner, *Acta Crystallogr. Sect. B*, 2013, **69**, 249.