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Supporting information for article:

The square-planar to flattened-tetrahedral Cu*X*4^{2-} (*X* = Cl, Br) structural phase transition in 1,2,6-trimethylpyridinium salts

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Table S1 Experimental details

	(Cl100K)	(Cl295K)	(Cl350K)	(Br100K)
Crystal data				
Chemical formula	$2(C_8H_{12}N)\cdot Cl_4Cu$	$2(C_8H_{12}N)\cdot Cl_4Cu$	$2(C_8H_{12}N)\cdot Cl_4Cu$	$2(C_8H_{12}N)\cdot Br_4Cu$
M_r	449.74	449.74	449.74	627.55
Crystal system, space group	Monoclinic, *C*2/*m*	Monoclinic, *C*2/*m*	Triclinic, *P*1	Monoclinic, *C*2/*m*
Temperature (K)	100	295	350	100
a, *b*, *c* (Å)	12.9074 (4), 9.2262 (4), 8.6377 (3)	13.1910 (6), 9.2068 (4), 8.7242 (4)	7.9236 (4), 9.1502 (4), 16.1341 (8)	13.0879 (12), 9.4953 (10), 8.7957 (9)
α, β, γ (°)	90, 114.925 (2), 90	90, 114.595 (2), 90	75.409 (2), 86.964 (3), 64.493 (3)	90, 113.631 (6), 90
V (Å^3)	932.82 (6)	963.40 (7)	1019.63 (8)	1001.41 (17)
Z	2	2	2	2
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	1.74	1.69	1.60	9.07
Crystal size (mm)	0.21 × 0.18 × 0.12	0.30 × 0.27 × 0.11	0.30 × 0.27 × 0.11	0.25 × 0.17 × 0.13
Data collection				
Diffractometer	KappaCCD diffractometer	KappaCCD diffractometer	KappaCCD diffractometer	KappaCCD diffractometer
Absorption correction	Multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)	Multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)	Multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)	Multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.674, 0.787	0.605, 0.679	0.607, 0.708	0.140, 0.341

No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2151, 2151, 1935	5103, 2683, 2199	8596, 4665, 3361	2272, 1212, 1013
R_{int}	0.036	0.017	0.026	0.039
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.806	0.862	0.649	0.649
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.065, 1.08	0.038, 0.108, 1.03	0.062, 0.223, 1.07	0.060, 0.183, 1.21
No. of reflections	2151	2683	4665	1212
No. of parameters	80	63	214	62
No. of restraints	0	0	0	0
H-atom treatment	All H-atom parameters refined	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.44, −0.68	0.97, −0.65	1.15, −0.62	1.81, −1.24
	(Br295K)	(26lutcl100k)	(26lutclrt)	(26lutbr100k)
Crystal data				
Chemical formula	$2(C_8H_{12}N)\cdot Br_4Cu$	$2(C_7H_{10}N)\cdot Cl_4Cu$	$2(C_7H_{10}N)\cdot Cl_4Cu$	$2(C_7H_{10}N)\cdot Br_4Cu$
M_r	627.55	421.69	421.66	599.5
Crystal system, space	Triclinic, *P*1	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*

group				
Temperature (K)	295	100	295	100
a, *b*, *c* (Å)	8.0517 (2), 9.3247 (3), 16.4524 (5)	14.3451 (3), 7.5569 (2), 16.6038 (3)	14.4831 (3), 7.7267 (2), 16.6432 (3)	14.5510 (3), 7.8249 (2), 17.0624 (3)
α, β, γ (°)	75.997 (2), 88.567 (2), 65.757 (2)	90, 96.309 (1), 90	90, 95.840 (1), 90	90, 97.540 (1), 90
V (Å^3)	1088.97 (6)	1789.03 (7)	1852.82 (7)	1925.93 (7)
Z	2	4	4	4
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	8.34	1.81	1.75	9.43
Crystal size (mm)	0.18 × 0.13 × 0.09	0.34 × 0.17 × 0.13	0.33 × 0.28 × 0.17	0.34 × 0.23 × 0.05
Data collection				
Diffractometer	KappaCCD diffractometer	KappaCCD diffractometer	KappaCCD diffractometer	KappaCCD diffractometer
Absorption correction	Multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)	Multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)	Multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)	Multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.283, 0.441	0.677, 0.795	0.578, 0.653	0.094, 0.159
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9067, 4944, 3455	8345, 4334, 3401	5595, 2939, 2250	6496, 3356, 2453
R_{int}	0.034	0.029	0.020	0.044
$(\sin\theta/\lambda)_{max}$	0.649	0.833	0.725	0.747

($Å^{-1}$)				
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.089, 1.03	0.033, 0.078, 1.03	0.035, 0.094, 1.05	0.040, 0.098, 1.05
No. of reflections	4944	4334	2939	3356
No. of parameters	215	137	97	96
No. of restraints	0	0	0	0
H-atom treatment	H-atom parameters constrained	All H-atom parameters refined	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	1.02, −1.17	0.53, −0.71	0.55, −0.41	0.80, −1.15
	(26lutbrrt)	(26lut100kortho)	(26lutrtortho)	(123tmpcubr4)
Crystal data				
Chemical formula	$2(C_7H_{10}N)\cdot Br_4Cu$	$2(C_7H_{10}N)\cdot Cl_4Cu$	$2(C_7H_{10}N)\cdot Cl_4Cu$	$2(C_8H_{12}N)\cdot Br_4Cu$
M_r	599.5	421.66	421.66	627.55
Crystal system, space group	Monoclinic, *C*2/*c*	Orthorhombic, *Pbcn*	Orthorhombic, *Pbcn*	Monoclinic, *C*2/*c*
Temperature (K)	295	100	295	295
a, *b*, *c* (Å)	14.6041 (3), 7.9883 (2), 17.1986 (3)	16.9587 (3), 7.8858 (1), 13.8774 (3)	16.9411 (5), 8.2218 (2), 13.8212 (4)	17.6373 (5), 9.4076 (4), 14.7798 (5)
α, β, γ (°)	90, 97.345 (1), 90	90, 90, 90	90, 90, 90	90, 118.396 (2), 90
V ($Å^3$)	1989.96 (7)	1855.86 (6)	1925.10 (9)	2157.27 (13)

Z	4	4	4	4
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	9.13	1.75	1.68	8.42
Crystal size (mm)	0.25 × 0.21 × 0.13	0.33 × 0.25 × 0.13	0.29 × 0.25 × 0.10	0.21 × 0.20 × 0.18
Data collection				
Diffractometer	KappaCCD diffractometer	KappaCCD diffractometer	KappaCCD diffractometer	KappaCCD diffractometer
Absorption correction	Multi-scan (*DENZO*/*SCALEPACK* ; Otwinowski & Minor, 1997)	Multi-scan (*DENZO*/*SCALEPACK* ; Otwinowski & Minor, 1997)	Multi-scan (*DENZO*/*SCALEPACK* ; Otwinowski & Minor, 1997)	Multi-scan (*DENZO*/*SCALEPACK* ; Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.115, 0.176	0.629, 0.663	0.578, 0.699	0.164, 0.217
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4740, 2558, 2034	5525, 2952, 2386	4080, 2191, 1732	2461, 2461, 1686
R_{int}	0.020	0.019	0.012	0.022
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.676	0.725	0.648	0.650
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.030, 0.074, 1.06	0.031, 0.078, 1.08	0.033, 0.098, 1.06	0.028, 0.065, 0.95
No. of reflections	2558	2952	2191	2461
No. of parameters	98	120	97	109

No. of restraints	0	0	0	0
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.73, −0.79	0.51, −0.64	0.27, −0.56	0.49, −0.39

Computer programs: Collect (Nonius BV, 1997-2000), Collect (Bruker AXS BV, 1997-2004), *HKL SCALEPACK* (Otwinowski & Minor 1997), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997), *SIR92* (Giacovazzo *et al.*, 1993), *SHELXS86* (Sheldrick, 1986), *SHELXL97* (Sheldrick, 1997), *ORTEP-3 for Windows* (Farrugia, 1997), *WinGX* publication routines (Farrugia, 1999).

Table S2 Selected geometric parameters (Å, º)

Cl100K

Cu1—Cl1	2.2527 (3)	C11—H11F	0.96
Cu1—Cl2	2.2990 (3)	C2—C3	1.3868 (14)
N1—C2	1.3660 (11)	C2—C21	1.4949 (14)
N1—C11	1.4755 (19)	C21—H21A	0.982 (17)
C11—H11A	0.96	C21—H21B	0.992 (18)
C11—H11B	0.96	C21—H21C	0.963 (19)
C11—H11C	0.96	C3—C4	1.3852 (12)
C11—H11D	0.96	C3—H3	0.979 (17)
C11—H11E	0.96	C4—H4	0.96 (2)
C2—N1—C2^{i}	122.03 (12)	H11B—C11—H11F	56.3
C2—N1—C11	118.98 (6)	H11C—C11—H11F	141.1
C2^{i}—N1—C11	118.98 (6)	H11D—C11—H11F	109.5
N1—C11—H11A	109.5	H11E—C11—H11F	109.5
N1—C11—H11B	109.5	N1—C2—C3	119.07 (9)
H11A—C11—H11B	109.5	N1—C2—C21	119.91 (9)
N1—C11—H11C	109.5	C3—C2—C21	121.02 (9)
H11A—C11—H11C	109.5	C2—C21—H21A	111.9 (10)
H11B—C11—H11C	109.5	C2—C21—H21B	109.5 (10)
N1—C11—H11D	109.5	H21A—C21—H21B	106.8 (15)
H11A—C11—H11D	141.1	C2—C21—H21C	110.5 (11)
H11B—C11—H11D	56.3	H21A—C21—H21C	108.4 (15)
H11C—C11—H11D	56.3	H21B—C21—H21C	109.7 (15)
N1—C11—H11E	109.5	C4—C3—C2	120.12 (10)
H11A—C11—H11E	56.3	C4—C3—H3	122.3 (10)
H11B—C11—H11E	141.1	C2—C3—H3	117.6 (10)
H11C—C11—H11E	56.3	C3—C4—C3^{i}	119.58 (13)
H11D—C11—H11E	109.5	C3—C4—H4^{i}	120.21 (7)
N1—C11—H11F	109.5	C3—C4—H4	120.21 (7)
H11A—C11—H11F	56.3		

Cl295K

Cu1—Cl1	2.2510 (5)	C11—H11F	0.96
Cu1—Cl2	2.2916 (5)	C2—C3	1.380 (2)
N1—C2	1.3641 (16)	C2—C21	1.492 (2)
N1—C11	1.472 (3)	C21—H21A	0.96
C11—H11A	0.96	C21—H21B	0.96
C11—H11B	0.96	C21—H21C	0.96
C11—H11C	0.96	C3—C4	1.3760 (19)
C11—H11D	0.96	C3—H3	0.93
C11—H11E	0.96	C4—H4	0.93
C2—N1—C2^{i}	121.69 (17)	N1—C2—C3	119.04 (13)
C2—N1—C11	119.15 (9)	N1—C2—C21	119.95 (15)
N1—C11—H11A	109.5	C3—C2—C21	121.01 (14)
N1—C11—H11B	109.5	C2—C21—H21A	109.5
H11A—C11—H11B	109.5	C2—C21—H21B	109.5
N1—C11—H11C	109.5	H21A—C21—H21B	109.5
H11A—C11—H11C	109.5	C2—C21—H21C	109.5
H11B—C11—H11C	109.5	H21A—C21—H21C	109.5
N1—C11—H11D	109.5	H21B—C21—H21C	109.5
N1—C11—H11E	109.5	C2—C3—C4	120.36 (14)
H11D—C11—H11E	109.5	C2—C3—H3	119.8
N1—C11—H11F	109.5	C4—C3—H3	119.8
H11D—C11—H11F	109.5	C3^{i}—C4—C3	119.5 (2)
H11E—C11—H11F	109.5	C3—C4—H4	120.3

Cl350K

Cu1—Cl1	2.2433 (16)	C161—H16B	0.96
Cu1—Cl2	2.2369 (16)	C161—H16C	0.96
Cu1—Cl3	2.2578 (15)	N21—C26	1.365 (8)
Cu1—Cl4	2.2461 (15)	N21—C22	1.362 (8)
N11—C16	1.346 (8)	N21—C211	1.489 (8)
N11—C12	1.348 (7)	C211—H21A	0.96

N11—C111	1.483 (8)	C211—H21B	0.96
C111—H11A	0.96	C211—H21C	0.96
C111—H11B	0.96	C22—C23	1.359 (9)
C111—H11C	0.96	C22—C221	1.506 (9)
C12—C13	1.370 (9)	C221—H22A	0.96
C12—C121	1.513 (9)	C221—H22B	0.96
C121—H12A	0.96	C221—H22C	0.96
C121—H12B	0.96	C23—C24	1.356 (8)
C121—H12C	0.96	C23—H23	0.93
C13—C14	1.351 (9)	C24—C25	1.365 (9)
C13—H13	0.93	C24—H24	0.93
C14—C15	1.361 (9)	C25—C26	1.381 (8)
C14—H14	0.93	C25—H25	0.93
C15—C16	1.368 (10)	C26—C261	1.471 (10)
C15—H15	0.93	C261—H26A	0.96
C16—C161	1.503 (9)	C261—H26B	0.96
C161—H16A	0.96	C261—H26C	0.96
Cl1—Cu1—Cl2	99.02 (7)	H16A—C161—H16C	109.5
Cl1—Cu1—Cl3	140.46 (8)	H16B—C161—H16C	109.5
Cl1—Cu1—Cl4	96.66 (6)	C26—N21—C22	121.9 (5)
Cl2—Cu1—Cl3	95.36 (6)	C26—N21—C211	118.7 (6)
Cl2—Cu1—Cl4	139.43 (9)	C22—N21—C211	119.3 (6)
Cl3—Cu1—Cl4	95.84 (6)	N21—C211—H21A	109.5
C16—N11—C12	121.1 (5)	N21—C211—H21B	109.5
C16—N11—C111	120.5 (6)	H21A—C211—H21B	109.5
C12—N11—C111	118.5 (5)	N21—C211—H21C	109.5
N11—C111—H11A	109.5	H21A—C211—H21C	109.5
N11—C111—H11B	109.5	H21B—C211—H21C	109.5
H11A—C111—H11B	109.5	N21—C22—C23	119.1 (6)
N11—C111—H11C	109.5	N21—C22—C221	120.0 (6)
H11A—C111—H11C	109.5	C23—C22—C221	120.9 (7)

H11B—C111—H11C	109.5	C22—C221—H22A	109.5
N11—C12—C13	118.6 (6)	C22—C221—H22B	109.5
N11—C12—C121	120.7 (6)	H22A—C221—H22B	109.5
C13—C12—C121	120.7 (6)	C22—C221—H22C	109.5
C12—C121—H12A	109.5	H22A—C221—H22C	109.5
C12—C121—H12B	109.5	H22B—C221—H22C	109.5
H12A—C121—H12B	109.5	C22—C23—C24	120.7 (6)
C12—C121—H12C	109.5	C22—C23—H23	119.7
H12A—C121—H12C	109.5	C24—C23—H23	119.7
H12B—C121—H12C	109.5	C22—C23—H23	119.7
C12—C13—C14	121.5 (6)	C23—C24—C25	119.7 (6)
C12—C13—H13	119.3	C23—C24—H24	120.1
C14—C13—H13	119.3	C25—C24—H24	120.1
C13—C14—C15	118.8 (6)	C24—C25—C26	120.9 (6)
C13—C14—H14	120.6	C24—C25—H25	119.6
C15—C14—H14	120.6	C26—C25—H25	119.6
C14—C15—C16	120.1 (6)	N21—C26—C25	117.6 (6)
C14—C15—H15	120	N21—C26—C261	121.1 (7)
C16—C15—H15	120	C25—C26—C261	121.3 (7)
N11—C16—C15	119.9 (6)	C26—C261—H26A	109.5
N11—C16—C161	119.3 (7)	C26—C261—H26B	109.5
C15—C16—C161	120.7 (7)	H26A—C261—H26B	109.5
C16—C161—H16A	109.5	C26—C261—H26C	109.5
C16—C161—H16B	109.5	H26A—C261—H26C	109.5
H16A—C161—H16B	109.5	H26B—C261—H26C	109.5
C16—C161—H16C	109.5		

Br100K

Cu1—Br1	2.3903 (10)	C11—H11F	0.96
Cu1—Br2	2.4472 (10)	C2—C3	1.372 (11)
N1—C2	1.355 (8)	C2—C21	1.501 (9)
N1—C11	1.493 (14)	C21—H21A	0.96

C11—H11A	0.96	C21—H21B	0.96
C11—H11B	0.96	C21—H21C	0.96
C11—H11C	0.96	C3—C4	1.377 (9)
C11—H11D	0.96	C3—H3	0.93
C11—H11E	0.96	C4—H4	0.93
Br2^{ii}—Cu1—Br1	90.00 (1)	H11A—C11—H11F	56.3
C2—N1—C2^{iii}	121.6 (9)	H11B—C11—H11F	56.3
C2—N1—C11	119.1 (5)	H11C—C11—H11F	141.1
N1—C11—H11A	109.5	H11D—C11—H11F	109.5
N1—C11—H11B	109.5	H11E—C11—H11F	109.5
H11A—C11—H11B	109.5	N1—C2—C3	119.5 (7)
N1—C11—H11C	109.5	N1—C2—C21	120.2 (7)
H11A—C11—H11C	109.5	C3—C2—C21	120.3 (6)
H11B—C11—H11C	109.5	C2—C21—H21A	109.5
N1—C11—H11D	109.5	C2—C21—H21B	109.5
H11A—C11—H11D	141.1	H21A—C21—H21B	109.5
H11B—C11—H11D	56.3	C2—C21—H21C	109.5
H11C—C11—H11D	56.3	H21A—C21—H21C	109.5
N1—C11—H11E	109.5	H21B—C21—H21C	109.5
H11A—C11—H11E	56.3	C2—C3—C4	119.7 (7)
H11B—C11—H11E	141.1	C2—C3—H3	120.2
H11C—C11—H11E	56.3	C4—C3—H3	120.2
H11D—C11—H11E	109.5	C3^{iii}—C4—C3	119.9 (10)
N1—C11—H11F	109.5	C3—C4—H4	120

Br295K

Cu1—Br1	2.3881 (7)	C161—H16B	0.9600
Cu1—Br2	2.3717 (7)	C161—H16C	0.9600
Cu1—Br3	2.3958 (7)	N21—C26	1.358 (6)
Cu1—Br4	2.3957 (7)	N21—C22	1.370 (6)
N11—C16	1.370 (7)	N21—C211	1.475 (6)
N11—C12	1.353 (6)	C211—H21A	0.9600

N11—C111	1.488 (6)	C211—H21B	0.9600
C111—H11A	0.9600	C211—H21C	0.9600
C111—H11B	0.9600	C22—C23	1.366 (7)
C111—H11C	0.9600	C22—C221	1.492 (7)
C12—C13	1.366 (7)	C221—H22A	0.9600
C12—C121	1.498 (7)	C221—H22B	0.9600
C121—H12A	0.9600	C221—H22C	0.9600
C121—H12B	0.9600	C23—C24	1.362 (7)
C121—H12C	0.9600	C23—H23	0.9300
C13—C14	1.367 (7)	C24—C25	1.355 (7)
C13—H13	0.9300	C24—H24	0.9300
C14—C15	1.356 (7)	C25—C26	1.372 (7)
C14—H14	0.9300	C25—H25	0.9300
C15—C16	1.370 (7)	C26—C261	1.484 (7)
C15—H15	0.9300	C261—H26A	0.9600
C16—C161	1.499 (7)	C261—H26B	0.9600
C161—H16A	0.9600	C261—H26C	0.9600
Br1—Cu1—Br2	98.19 (3)	C16—C161—H16C	109.5
Br1—Cu1—Br3	141.67 (3)	H16A—C161—H16C	109.5
Br1—Cu1—Br4	96.79 (3)	H16B—C161—H16C	109.5
Br2—Cu1—Br3	95.14 (3)	C26—N21—C22	121.3 (4)
Br2—Cu1—Br4	140.58 (3)	C26—N21—C211	120.5 (5)
Br3—Cu1—Br4	95.25 (2)	C22—N21—C211	118.2 (5)
C16—N11—C12	121.1 (4)	N21—C211—H21A	109.5
C16—N11—C111	120.3 (4)	N21—C211—H21B	109.5
C12—N11—C111	118.6 (5)	H21A—C211—H21B	109.5
N11—C111—H11A	109.5	N21—C211—H21C	109.5
N11—C111—H11B	109.5	H21A—C211—H21C	109.5
H11A—C111—H11B	109.5	H21B—C211—H21C	109.5
N11—C111—H11C	109.5	N21—C22—C23	118.9 (4)
H11A—C111—H11C	109.5	N21—C22—C221	119.6 (5)

H11B—C111—H11C	109.5	C23—C22—C221	121.5 (5)
N11—C12—C13	119.0 (5)	C22—C221—H22A	109.5
N11—C12—C121	119.8 (5)	C22—C221—H22B	109.5
C13—C12—C121	121.2 (5)	H22A—C221—H22B	109.5
C12—C121—H12A	109.5	C22—C221—H22C	109.5
C12—C121—H12B	109.5	H22A—C221—H22C	109.5
H12A—C121—H12B	109.5	H22B—C221—H22C	109.5
C12—C121—H12C	109.5	C22—C23—C24	120.4 (5)
H12A—C121—H12C	109.5	C22—C23—H23	119.8
H12B—C121—H12C	109.5	C24—C23—H23	119.8
C12—C13—C14	121.0 (5)	C23—C24—H24	120.0
C12—C13—H13	119.5	C23—C24—C25	120.0 (5)
C14—C13—H13	119.5	C25—C24—H24	120.0
C13—C14—C15	119.2 (5)	C24—C25—C26	120.7 (5)
C13—C14—H14	120.4	C24—C25—H25	119.6
C15—C14—H14	120.4	C26—C25—H25	119.6
C14—C15—C16	120.8 (5)	C25—C26—N21	118.8 (4)
C14—C15—H15	119.6	C25—C26—C261	120.8 (5)
C16—C15—H15	119.6	N21—C26—C261	120.5 (5)
C15—C16—N11	118.9 (5)	C26—C261—H26A	109.5
C15—C16—C161	121.0 (6)	C26—C261—H26B	109.5
N11—C16—C161	120.2 (5)	H26A—C261—H26B	109.5
C16—C161—H16A	109.5	C26—C261—H26C	109.5
C16—C161—H16B	109.5	H26A—C261—H26C	109.5
H16A—C161—H16B	109.5	H26B—C261—H26C	109.5

26lutcl100k

Cu1—Cl1	2.2749 (3)	C3—C4	1.386 (2)
Cu1—Cl2	2.2379 (3)	C3—H3	0.967 (19)
N1—C6	1.3534 (17)	C4—C5	1.394 (2)
N1—C2	1.3491 (17)	C4—H4	0.953 (19)
N1—H1	0.862 (18)	C5—C6	1.3784 (19)

C2—C3	1.3833 (18)	C5—H5	0.951 (19)
C2—C21	1.493 (2)	C6—C61	1.4942 (19)
C21—H21A	0.93 (3)	C61—H61A	0.98 (2)
C21—H21B	0.91 (2)	C61—H61B	0.91 (3)
C21—H21C	0.90 (3)	C61—H61C	0.91 (3)
Cl1—Cu1—Cl1^{iv}	137.10 (2)	C2—C3—H3	119.3 (11)
Cl1—Cu1—Cl2	95.640 (12)	C4—C3—H3	121.0 (11)
Cl1—Cu1—Cl2^{iv}	97.116 (12)	C3—C4—C5	120.15 (12)
Cl2—Cu1—Cl2^{iv}	144.63 (2)	C3—C4—H4	119.5 (12)
C6—N1—C2	124.31 (11)	C5—C4—H4	120.3 (12)
C6—N1—H1	119.8 (12)	C4—C5—C6	119.39 (13)
C2—N1—H1	115.9 (12)	C4—C5—H5	121.3 (12)
N1—C2—C3	118.14 (12)	C6—C5—H5	119.3 (12)
N1—C2—C21	117.28 (12)	C5—C6—N1	118.31 (12)
C3—C2—C21	124.57 (12)	C5—C6—C61	124.03 (13)
C2—C21—H21A	114.0 (18)	N1—C6—C61	117.63 (12)
C2—C21—H21B	110.6 (15)	C6—C61—H61A	108.6 (14)
H21A—C21—H21B	109 (2)	C6—C61—H61B	112.7 (16)
C2—C21—H21C	110.3 (16)	H61A—C61—H61B	110 (2)
H21A—C21—H21C	108 (2)	C6—C61—H61C	111.3 (17)
H21B—C21—H21C	104 (2)	H61A—C61—H61C	107 (2)
C2—C3—C4	119.62 (12)	H61B—C61—H61C	108 (2)

(26lutclrt)

Cu1—Cl1	2.2736 (5)	C3—C4	1.372 (3)
Cu1—Cl2	2.2312 (6)	C3—H3	0.9300
N1—C6	1.352 (2)	C4—C5	1.387 (3)
N1—C2	1.342 (2)	C4—H4	0.9300
N1—H1	0.8600	C5—C6	1.371 (3)
C2—C3	1.381 (3)	C5—H5	0.9300
C2—C21	1.490 (3)	C6—C61	1.495 (3)
C21—H21A	0.9600	C61—H61A	0.9600

C21—H21B	0.9600	C61—H61B	0.9600
C21—H21C	0.9600	C61—H61C	0.9600
C21—H21D	0.9600	C61—H61D	0.9600
C21—H21E	0.9600	C61—H61E	0.9600
C21—H21F	0.9600	C61—H61F	0.9600
Cl1—Cu1—Cl1^{iv}	134.96 (4)	C2—C3—H3	120.1
Cl1—Cu1—Cl2	96.52 (2)	C4—C3—H3	120.1
Cl1—Cu1—Cl2^{iv}	97.34 (2)	C3—C4—C5	120.35 (18)
Cl2—Cu1—Cl2^{iv}	143.27 (4)	C3—C4—H4	119.8
C6—N1—C2	124.43 (16)	C5—C4—H4	119.8
C6—N1—H1	117.8	C4—C5—C6	119.53 (19)
C2—N1—H1	117.8	C4—C5—H5	120.2
N1—C2—C3	117.93 (18)	C6—C5—H5	120.2
N1—C2—C21	117.54 (18)	C5—C6—N1	118.00 (18)
C3—C2—C21	124.53 (19)	C5—C6—C61	124.25 (19)
C2—C21—H21A	109.5	N1—C6—C61	117.73 (18)
C2—C21—H21B	109.5	C6—C61—H61A	109.5
H21A—C21—H21B	109.5	C6—C61—H61B	109.5
C2—C21—H21C	109.5	H61A—C61—H61B	109.5
H21A—C21—H21C	109.5	C6—C61—H61C	109.5
H21B—C21—H21C	109.5	H61A—C61—H61C	109.5
C2—C21—H21D	109.5	H61B—C61—H61C	109.5
C2—C21—H21E	109.5	C6—C61—H61D	109.5
H21D—C21—H21E	109.5	C6—C61—H61E	109.5
C2—C21—H21F	109.5	H61D—C61—H61E	109.5
H21D—C21—H21F	109.5	C6—C61—H61F	109.5
H21E—C21—H21F	109.5	H61D—C61—H61F	109.5
C2—C3—C4	119.71 (19)	H61E—C61—H61F	109.5

26lutbr100k

Cu1—Br1	2.4034 (4)	C3—C4	1.385 (5)
Cu1—Br2	2.3768 (4)	C3—H3	0.93

N1—C6	1.356 (5)	C4—C5	1.392 (5)
N1—C2	1.339 (5)	C4—H4	0.93
N1—H1	0.86	C5—C6	1.376 (5)
C2—C3	1.382 (5)	C5—H5	0.93
C2—C21	1.484 (5)	C6—C61	1.500 (5)
C21—H21A	0.96	C61—H61A	0.96
C21—H21B	0.96	C61—H61B	0.96
C21—H21C	0.96	C61—H61C	0.96
C21—H21D	0.96	C61—H61D	0.96
C21—H21E	0.96	C61—H61E	0.96
C21—H21F	0.96	C61—H61F	0.96
Br1—Cu1—Br1^{iv}	135.40 (3)	C2—C3—H3	120.2
Br1—Cu1—Br2	96.261 (12)	C4—C3—H3	120.2
Br1—Cu1—Br2^{iv}	97.538 (13)	C3—C4—C5	120.3 (3)
Br2—Cu1—Br2^{iv}	143.09 (4)	C3—C4—H4	119.9
C6—N1—C2	124.8 (3)	C5—C4—H4	119.9
C6—N1—H1	117.6	C4—C5—C6	119.3 (3)
C2—N1—H1	117.6	C4—C5—H5	120.4
N1—C2—C3	118.0 (3)	C6—C5—H5	120.4
N1—C2—C21	117.6 (3)	C5—C6—N1	118.0 (3)
C3—C2—C21	124.4 (3)	C5—C6—C61	123.8 (3)
C2—C21—H21A	109.5	N1—C6—C61	118.1 (3)
C2—C21—H21B	109.5	C6—C61—H61A	109.5
H21A—C21—H21B	109.5	C6—C61—H61B	109.5
C2—C21—H21C	109.5	H61A—C61—H61B	109.5
H21A—C21—H21C	109.5	C6—C61—H61C	109.5
H21B—C21—H21C	109.5	H61A—C61—H61C	109.5
C2—C21—H21D	109.5	H61B—C61—H61C	109.5
C2—C21—H21E	109.5	C6—C61—H61D	109.5
H21D—C21—H21E	109.5	C6—C61—H61E	109.5
C2—C21—H21F	109.5	H61D—C61—H61E	109.5

H21D—C21—H21F	109.5	C6—C61—H61F	109.5
H21E—C21—H21F	109.5	H61D—C61—H61F	109.5
C2—C3—C4	119.6 (3)	H61E—C61—H61F	109.5

(26lutbrrt)

Cu1—Br1	2.4016 (4)	C3—C4	1.371 (5)
Cu1—Br2	2.3724 (3)	C3—H3	0.9300
N1—C6	1.354 (4)	C4—C5	1.377 (5)
N1—C2	1.342 (4)	C4—H4	0.9300
N1—H1	0.8600	C5—C6	1.375 (4)
C2—C3	1.375 (4)	C5—H5	0.9300
C2—C21	1.486 (5)	C6—C61	1.493 (5)
C21—H21A	0.9600	C61—H61A	0.9600
C21—H21B	0.9600	C61—H61B	0.9600
C21—H21C	0.9600	C61—H61C	0.9600
C21—H21D	0.9600	C61—H61D	0.9600
C21—H21E	0.9600	C61—H61E	0.9600
C21—H21F	0.9600	C61—H61F	0.9600
Br1—Cu1—Br1^{iv}	134.28 (3)	C2—C3—H3	119.9
Br1—Cu1—Br2	96.790 (11)	C4—C3—H3	119.9
Br1—Cu1—Br2^{iv}	97.627 (12)	C3—C4—C5	120.4 (3)
Br2—Cu1—Br2^{iv}	142.32 (3)	C3—C4—H4	119.8
C6—N1—C2	124.7 (3)	C5—C4—H4	119.8
C6—N1—H1	117.7	C4—C5—C6	119.6 (3)
C2—N1—H1	117.7	C4—C5—H5	120.2
N1—C2—C3	117.5 (3)	C6—C5—H5	120.2
N1—C2—C21	117.6 (3)	C5—C6—N1	117.7 (3)
C3—C2—C21	124.9 (3)	C5—C6—C61	124.7 (3)
C2—C21—H21A	109.5	N1—C6—C61	117.6 (3)
C2—C21—H21B	109.5	C6—C61—H61A	109.5
H21A—C21—H21B	109.5	C6—C61—H61B	109.5
C2—C21—H21C	109.5	H61A—C61—H61B	109.5

H21A—C21—H21C	109.5	C6—C61—H61C	109.5
H21B—C21—H21C	109.5	H61A—C61—H61C	109.5
C2—C21—H21D	109.5	H61B—C61—H61C	109.5
C2—C21—H21E	109.5	C6—C61—H61D	109.5
H21D—C21—H21E	109.5	C6—C61—H61E	109.5
C2—C21—H21F	109.5	H61D—C61—H61E	109.5
H21D—C21—H21F	109.5	C6—C61—H61F	109.5
H21E—C21—H21F	109.5	H61D—C61—H61F	109.5
C2—C3—C4	120.2 (3)	H61E—C61—H61F	109.5

26lut100kortho

Cu1—Cl1	2.2619 (4)	C3—C4	1.388 (3)
Cu1—Cl2	2.2409 (4)	C3—H3	0.95 (2)
N1—C6	1.346 (2)	C4—C5	1.379 (3)
N1—C2	1.351 (2)	C4—H4	0.93 (2)
N1—H1	0.88 (2)	C5—C6	1.385 (2)
C2—C3	1.386 (2)	C5—H5	0.90 (2)
C2—C21	1.493 (2)	C6—C61	1.494 (2)
C21—H21A	0.9600	C61—H61A	0.9600
C21—H21B	0.9600	C61—H61B	0.9600
C21—H21C	0.9600	C61—H61C	0.9600
Cl1—Cu1—Cl1^{iv}	126.65 (3)	C2—C3—H3	118.0 (13)
Cl1—Cu1—Cl2	100.259 (15)	C4—C3—H3	122.4 (13)
Cl2—Cu1—Cl1^{iv}	100.094 (15)	C3—C4—C5	120.27 (16)
Cl2—Cu1—Cl2^{iv}	133.65 (3)	C3—C4—H4	119.1 (14)
C6—N1—C2	124.93 (15)	C5—C4—H4	120.6 (14)
C6—N1—H1	115.4 (14)	C4—C5—C6	119.82 (17)
C2—N1—H1	119.7 (14)	C4—C5—H5	122.7 (14)
N1—C2—C3	117.66 (15)	C6—C5—H5	117.5 (14)
N1—C2—C21	117.85 (14)	C5—C6—N1	117.72 (16)
C3—C2—C21	124.47 (15)	C5—C6—C61	124.51 (16)
C2—C21—H21A	109.5	N1—C6—C61	117.77 (15)

C2—C21—H21B	109.5	C6—C61—H61A	109.5
H21A—C21—H21B	109.5	C6—C61—H61B	109.5
C2—C21—H21C	109.5	H61A—C61—H61B	109.5
H21A—C21—H21C	109.5	C6—C61—H61C	109.5
H21B—C21—H21C	109.5	H61A—C61—H61C	109.5
C2—C3—C4	119.56 (16)	H61B—C61—H61C	109.5

(26lutrtortho)

Cu1—Cl1	2.2628 (6)	C3—C4	1.374 (5)
Cu1—Cl2	2.2306 (5)	C3—H3	0.9300
N1—C6	1.342 (3)	C4—C5	1.364 (5)
N1—C2	1.344 (3)	C4—H4	0.9300
N1—H1	0.8600	C5—C6	1.377 (4)
C2—C3	1.374 (3)	C5—H5	0.9300
C2—C21	1.486 (4)	C6—C61	1.489 (4)
C21—H21A	0.9600	C61—H61A	0.9600
C21—H21B	0.9600	C61—H61B	0.9600
C21—H21C	0.9600	C61—H61C	0.9600
C21—H21D	0.9600	C61—H61D	0.9600
C21—H21E	0.9600	C61—H61E	0.9600
C21—H21F	0.9600	C61—H61F	0.9600
Cl1—Cu1—Cl1^{iv}	123.89 (5)	C2—C3—H3	120.2
Cl1—Cu1—Cl2	101.06 (2)	C4—C3—H3	120.2
Cl1—Cu1—Cl2^{iv}	100.85 (2)	C3—C4—C5	120.7 (3)
Cl2—Cu1—Cl2^{iv}	132.35 (4)	C3—C4—H4	119.7
C6—N1—C2	125.5 (2)	C5—C4—H4	119.7
C6—N1—H1	117.3	C4—C5—C6	120.0 (3)
C2—N1—H1	117.3	C4—C5—H5	120.0
N1—C2—C3	117.2 (2)	C6—C5—H5	120.0
N1—C2—C21	117.8 (2)	C5—C6—N1	117.0 (3)
C3—C2—C21	125.0 (2)	C5—C6—C61	125.2 (3)
C2—C21—H21A	109.5	N1—C6—C61	117.8 (2)

C2—C21—H21B	109.5	C6—C61—H61A	109.5
H21A—C21—H21B	109.5	C6—C61—H61B	109.5
C2—C21—H21C	109.5	H61A—C61—H61B	109.5
H21A—C21—H21C	109.5	C6—C61—H61C	109.5
H21B—C21—H21C	109.5	H61A—C61—H61C	109.5
C2—C21—H21D	109.5	H61B—C61—H61C	109.5
C2—C21—H21E	109.5	C6—C61—H61D	109.5
H21D—C21—H21E	109.5	C6—C61—H61E	109.5
C2—C21—H21F	109.5	H61D—C61—H61E	109.5
H21D—C21—H21F	109.5	C6—C61—H61F	109.5
H21E—C21—H21F	109.5	H61D—C61—H61F	109.5
C2—C3—C4	119.6 (3)	H61E—C61—H61F	109.5

123tmpcubr4

Cu1—Br1	2.3646 (4)	C21—H21A	0.96
Cu1—Br2	2.3916 (4)	C3—C4	1.385 (5)
N1—C6	1.352 (4)	C3—C31	1.497 (4)
N1—C2	1.358 (4)	C31—H31A	0.96
N1—C11	1.479 (4)	C31—H31B	0.96
C11—H11B	0.96	C31—H31C	0.96
C11—H11A	0.96	C4—C5	1.379 (5)
C11—H11C	0.96	C4—H4	0.93
C2—C3	1.390 (4)	C5—C6	1.348 (5)
C2—C21	1.496 (4)	C5—H5	0.93
C21—H21B	0.96	C6—H6	0.93
C21—H21C	0.96		
Br1—Cu1—Br1^{v}	105.23 (3)	H21B—C21—H21A	109.5
Br1—Cu1—Br2	123.933 (12)	H21C—C21—H21A	109.5
Br1—Cu1—Br2^{v}	100.999 (12)	C2—C3—C4	119.1 (3)
Br2—Cu1—Br2^{v}	103.84 (2)	C2—C3—C31	121.4 (3)
C6—N1—C2	121.4 (3)	C4—C3—C31	119.4 (3)
C6—N1—C11	118.3 (3)	C3—C31—H31A	109.5

C2—N1—C11	120.3 (3)	C3—C31—H31B	109.5
N1—C11—H11B	109.5	H31A—C31—H31B	109.5
N1—C11—H11A	109.5	C3—C31—H31C	109.5
H11B—C11—H11A	109.5	H31A—C31—H31C	109.5
N1—C11—H11C	109.5	H31B—C31—H31C	109.5
H11B—C11—H11C	109.5	C3—C4—C5	120.1 (3)
H11A—C11—H11C	109.5	C3—C4—H4	119.9
N1—C2—C3	119.0 (3)	C5—C4—H4	119.9
N1—C2—C21	118.1 (3)	C4—C5—C6	119.4 (3)
C3—C2—C21	122.9 (3)	C4—C5—H5	120.3
C2—C21—H21B	109.5	C6—C5—H5	120.3
C2—C21—H21C	109.5	C5—C6—N1	121.0 (3)
H21B—C21—H21C	109.5	C5—C6—H6	119.5
C2—C21—H21A	109.5	N1—C6—H6	119.5

Symmetry code(s): (i) *x*, −*y*+1, *z*; (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*, −*y*, *z*; (iv) −*x*+1, *y*, −*z*+3/2; (v) −*x*+1, *y*, −*z*+1/2.

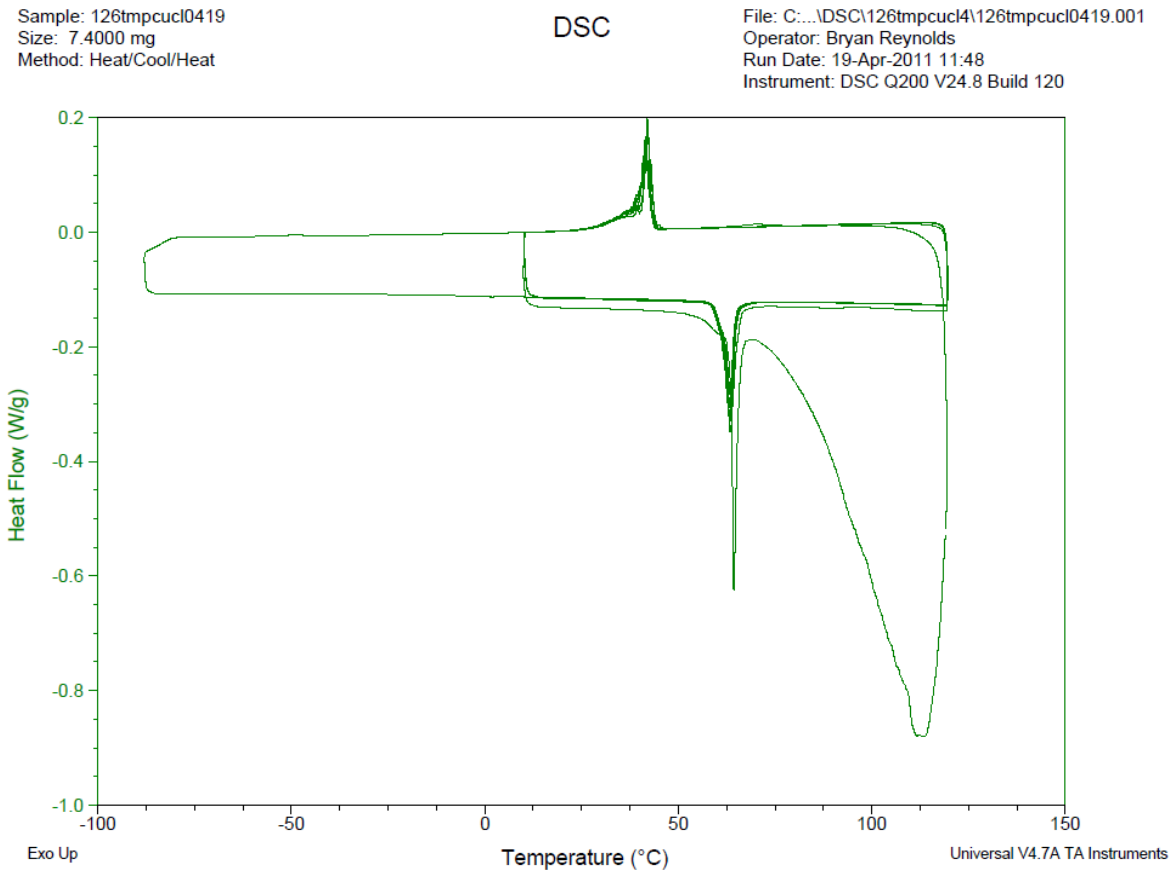

Figure S1 DSC thermogram for a single crystal sample of **I** scanned at 5º C. The first heating scan shows an anomaly after the transition peak that is not present in the later peaks, and we interpret this as due to the initial fracturing of the crystal. Four successive heat/cool/heat cycles are shown.

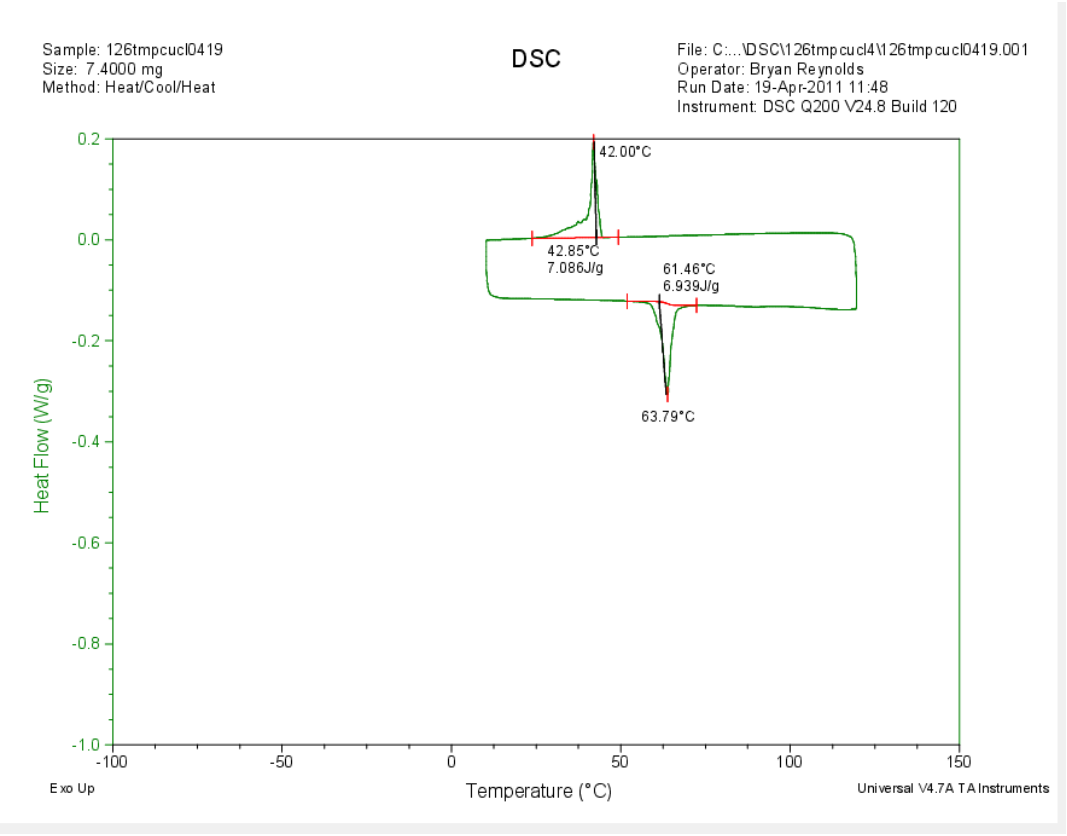

Figure S2 View of the second cool/heat cycle from Figure S1 showing peak integration.

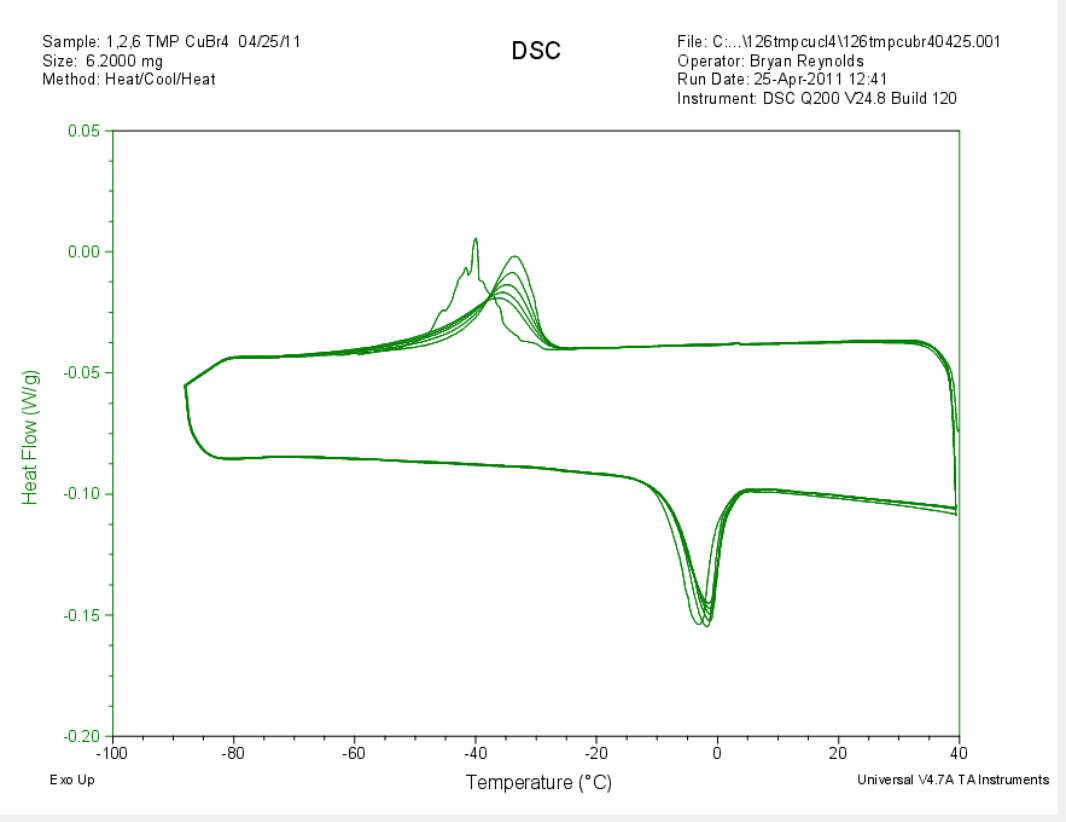

Figure S3 DSC thermogram for **II** showing five successive heat/cool cycles after the initial cooling. The irregular transition peak on cooling occurs with initial cooling and we postulate occurs due to initial fracturing of the crystal. Successive cool cycles result in a broadening of the cooling peak.

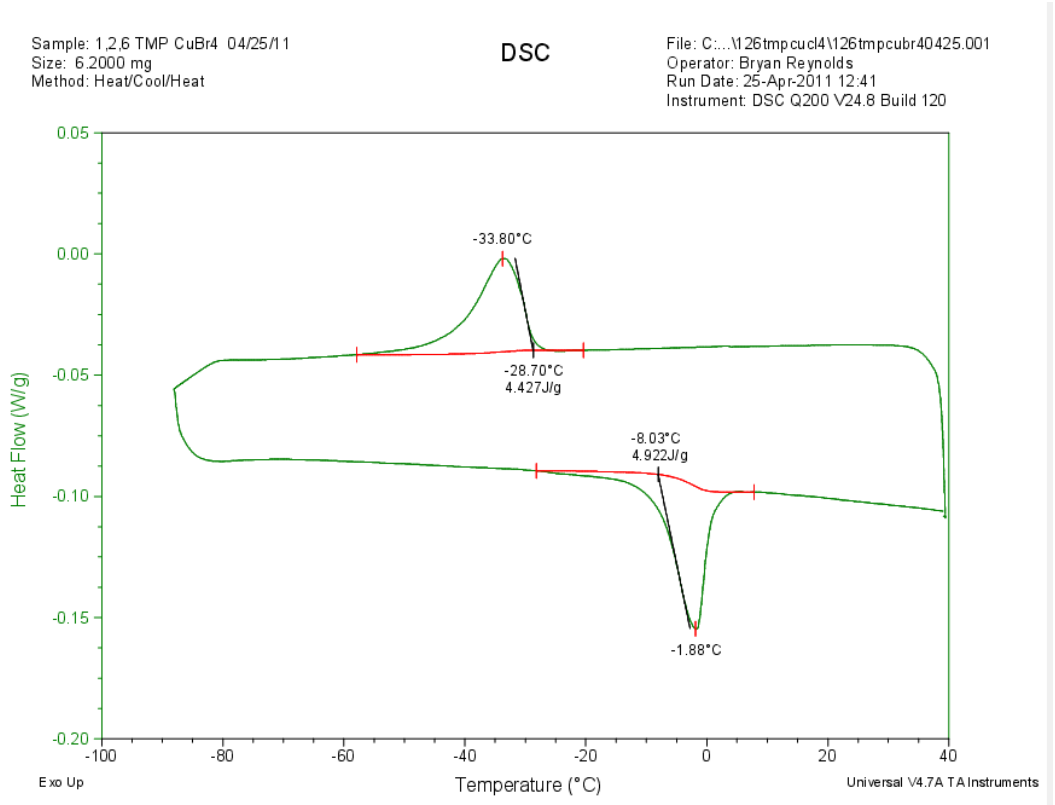

Figure S4 View of the second heat/cool cycle in the thermogram in Figure S3 with peak integration.

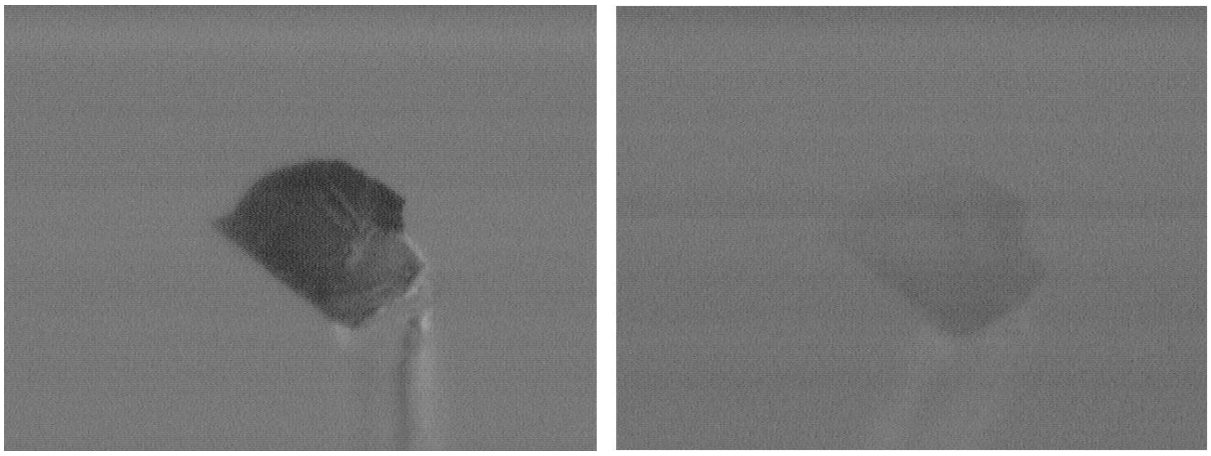

Figure S5 . Microscope photograph of the single crystal of **I** at the start of the ambient temperature data collection (left) and the 350 K data collection (right) illustrating the similar orientation and morphology of the sample I both β- and α-phases.