Supplemental Material

- Crystal Structure Investigations –
- Temperature dependent X-ray powder diffraction -

Synthesis, Crystal Structures, Thermal and Thermodynamic Properties of Dimorphic Copper(I) Coordination Polymers

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Single Crystal Structure Determination of Catena[CuCl(Pyidazine-N,N) (I)

Tab. 1 Protocol

Crystal data:

Compound:	CuCl-(Pyridazine)
Formula:	$C_4H_4N_2CuCl$
Crystal colour/habit:	red needle
Crystal size:	0.03 mm · 0.04 mm · 0.15 mm
Molecular weight:	179.08 g/mol
Space group:	triclinic P-1; IT – Nr.: 2
Calculated density:	2.125 g · cm^{-3}
F(000):	176
Lattice parameters:	Least-Squares refinement of 76 reflections in the range of $28° \leq 2\theta \leq 40°$
	a = 3.7512 (6) Å α= 90.43 (1)°
	b = 8.412 (1) Å β= 94.04 (1) °
	c = 8.900(1) Å γ = 92.27 (1) °
	V = 279.88 (7) $Å^3$
	Z = 2

Data collection

Device:	AED2- 4-circle diffractometer
Radiation:	Mo-Kα; 71.073 pm; Graphite monochromator
Temperature:	RT
Orientation matrix:	26 Reflections in the range of $21° \leq 2\theta \leq 26°$
Scan range:	$3° \leq 2\theta \leq 54°$
	$-4 \leq h \leq 4$
	$0 \leq k \leq 10$
	$-11 \leq l \leq 11$
scan mode:	ω-θ-Scan
Scan time:	min.: 1.0 s / max.: 6.0 s ($1 \leq I / \sigma (I) \leq 30$)
Scan width:	(1.05 + 0.35 · tan θ)°, (35 Steps a 0.03°)
Intensity control:	4 reflections every 2h
Intensity correction:	None
Orientation control:	if peak-shift of a control reflection is more than 0.15° or every 6 standard reflections

Structure solution and refinement:

Reflections:	1306 measured reflections
	0 systematically absent reflections
	1222 independent reflections
	0 suppressed reflections
	1222 independent reflections used for refinement
	966 independent reflections with Fo>4σ(Fo)
Average I/σ(I)	22.07
$R_{int.}$:	$\Sigma \lvert F_o^2 - (F_o^2)\text{mean}\rvert / [\Sigma F_o^2] = 0.0467$
Absorption correction:	face-indexed; min./max. trans.: 0.4001, 0.6833; μ = 4.25 mm^{-1}
Structure solution:	Direct methods (SHELXS-97)
Structure refinement:	Full-Matrix Least-Squares against F^2 (SHELXL-97)

Parameters:	In the asymmetric unit:	
	4 C-, 2 N-, 1Cu-, 1 Cl-atom(s)	anisotropic displacement parameters
	4 H atoms	isotropic displacement parameters
	74 Parameter full matrix refined	
Reflections / parameter:	16.5	
Hydrogen atoms:	The hydrogen atoms were positioned with idealised geometry (d_{C-H} (aromatic)= 0.93 Å) and refined with fixed isotropic displacement parameters according to the riding model [$U_{iso} = 1.2 \times U_{eq}(C_{aromatic})$].	
Scattering factors:	For neutral atoms	
LP corrections	yes	
Extinction correction:	$F^* = F_c (k[1 + 0.001 \cdot x \cdot F_c^2 \cdot \lambda^3 / \sin(2\theta)]^{-0.25})$ x = 0.062 (8)	
Weight:	$w = 1/[\sigma^2(F_o^2) + (0.0574 \cdot P)^2 + 0.13 \cdot P]$; $P = (\mathrm{Max}(F_o^2,0) + 2 \cdot F_c^2) / 3$	
Shift/Error:	≤ 0.001 in the last cycle	
Residual electron density:	Max.: 0.45 / Min.: -0.57e/Å^3	
R1 for 966 Fo>4σ(Fo)	$R1 = \Sigma \lvert \lvert Fo \rvert - \lvert Fc \rvert \rvert / \Sigma \lvert Fo \rvert$	= 0.0362
R1 for all 1222 reflections		= 0.0565
wR2 for 966 Fo>4σ(Fo)	$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{½}$	= 0.0893
wR2 for all 1222 reflections		= 0.0952
Goodness of fit (all refl.)	$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{½}$	= 1.037
Restrained GoF (all refl.)		= 1.037
Restraints		= 0

Remarks:

Data collection: STOE DIF4; Data reduction: STOE REDU4; Graphics: SHELXTL PC XP;

Tables: SHELXL-97 CIFTAB

Tab. 2 Atomic coordinates [$\cdot 10^4$] and equivalent isotropic displacement parameters [$Å^2 \cdot 10^3$]

	X	Y	Z	U_{eq}
Cu(1)	9302 (1)	6515 (1)	1132 (1)	41 (1)
Cl(1)	4723 (2)	7778 (1)	2261 (1)	40 (1)
N(1)	9228 (8)	4260 (3)	1917 (3)	32 (1)
N(2)	10440 (8)	3080 (4)	1075 (3)	32 (1)
C(1)	10844 (11)	1657 (4)	1681 (5)	38 (1)
C(2)	10101 (12)	1302 (5)	3145 (5)	46 (1)
C(3)	8851 (12)	2488 (5)	3989 (5)	45 (1)
C(4)	8443 (10)	3949 (5)	3318 (4)	37 (1)

Equivalent isotropic U calculated as a third of the trace of the orthogonalised U_{ij} tensors

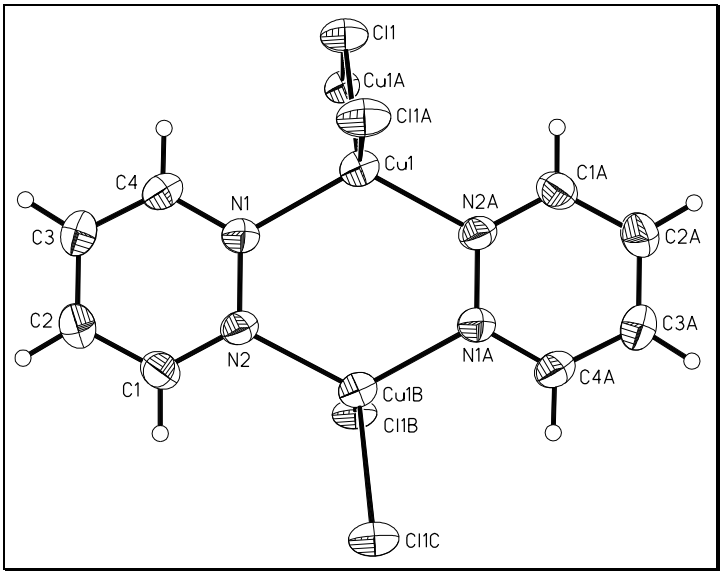
Tab. 3 Anisotropic displacement parameters [$Å^2 \cdot 10^3$]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	56 (1)	37 (1)	33 (1)	0 (1)	12 (1)	10 (1)
Cl(1)	35 (1)	42 (1)	45 (1)	-12 (1)	8 (1)	7 (1)
N(1)	33 (2)	31 (1)	31 (2)	-1 (1)	5 (1)	5 (1)
N(2)	38 (2)	33 (2)	26 (1)	-4 (1)	3 (1)	6 (1)
C(1)	46 (2)	31 (2)	37 (2)	-1 (1)	-2 (2)	7 (2)
C(2)	61 (3)	37 (2)	40 (2)	8 (2)	2 (2)	8 (2)
C(3)	55 (2)	47 (2)	33 (2)	9 (2)	9 (2)	4 (2)
C(4)	42 (2)	41 (2)	29 (2)	-4 (2)	7 (2)	4 (2)

The temperature factor exponent has the form: $-2\pi^2(h^2 \cdot a^{*2} U_{11}+...+2hka^*b^*U_{12})$

Tab. 4 H-Atomic coordinates [$\cdot 10^4$] and isotropic displacement factors [$Å^2 \cdot 10^3$]

	X	Y	Z	U_{eq}
H(1)	11672	854	1090	45
H(2)	10442	293	3537	55
H(3)	8294	2319	4978	54
H(4)	7566	4764	3881	45



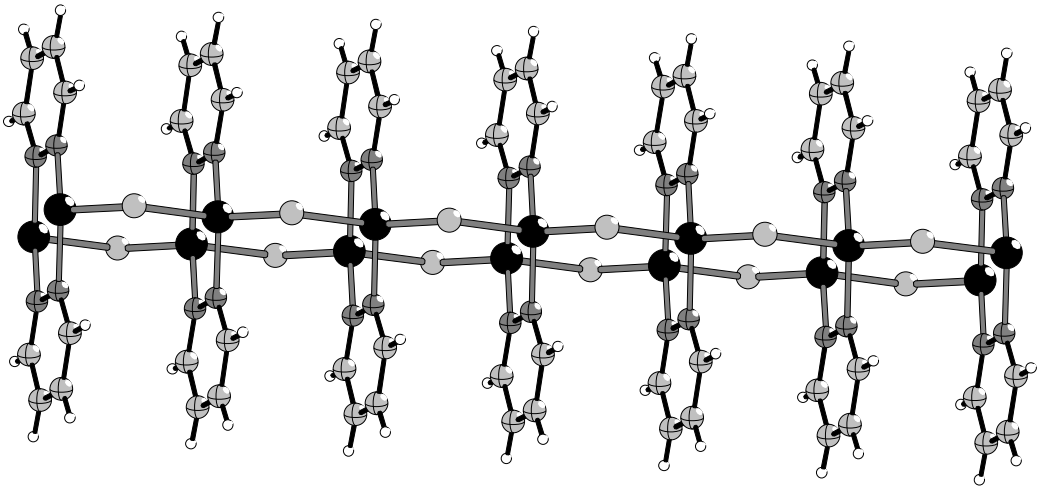
Tab. 5 Geometric parameters

Bond lengths [**Å**]

Cu(1) - N(2A)	2.004	(3)	Cu(1) - N(1)	2.026	(3)
Cu(1) - Cl(1)	2.337	(1)	Cu(1) - Cl(1A)	2.408	(2)
Cl(1) - Cu(1A)	2.408	(2)	N(2) - Cu(1B)	2.004	(3)
N(1) - C(4)	1.327	(5)	N(1) - N(2)	1.352	(4)
N(2) - C(1)	1.326	(5)	C(1) - C(2)	1.384	(6)
C(2) - C(3)	1.361	(6)	C(3) - C(4)	1.379	(5)

Angles [°]

N(2A) - Cu(1) - N(1)	120.4	(2)	N(2A) - Cu(1) - Cl(1)	115.1	(1)
N(1) - Cu(1) - Cl(1)	105.9	(1)	N(2A) - Cu(1) - Cl(1A)	103.9	(1)
N(1) - Cu(1) - Cl(1A)	105.5	(1)	Cl(1) - Cu(1) - Cl(1A)	104.5	(1)
Cu(1) - Cl(1) - Cu(1A)	104.5	(1)	C(1) - N(2) - Cu(1A)	123.1	(3)
N(1) - N(2) - Cu(1A)	117.0	(2)			
C(4) - N(1) - N(2)	118.8	(3)	C(4) - N(1) - Cu(1)	121.1	(2)
N(2) - N(1) - Cu(1)	119.5	(2)	C(1) - N(2) - N(1)	118.9	(3)
N(2) - C(1) - C(2)	123.7	(4)	C(3) - C(2) - C(1)	117.4	(4)
C(2) - C(3) - C(4)	117.4	(4)	N(1) - C(4) - C(3)	123.9	(3)



Single Crystal Structure Determination of Poly[Cu_2Cl_2(Pyidazine-N,N) (II)

Tab. 1 Protocol

Crystal data:

Compound:	Cu_2Cl_2-(Pyridazine)
Formula:	$C_4H_4N_2Cu_2Cl_2$
Crystal colour/habit:	orange block
Crystal size:	0.12 mm · 0.09 mm · 0.06 mm
Molecular weight:	278.07 g/mol
Space group:	triclinic P-1; IT – Nr.: 2
Calculated density:	2.579 g · cm^{-3}
F(000):	268
Lattice parameters:	Least-Squares refinement of 96 reflections in the range of $20° \le 2\theta \le 30°$ a = 3.7757 (8) Å α= 106.03 (2)° b = 8.687 (2) Å β= 95.69 (2) ° c = 11.537 (3) Å γ = 96.36 (2) ° V = 358.1 (1) $Å^3$ Z = 2

Data collection

Device:	CAD4 4-circle diffractometer
Radiation:	Mo-Kα; 71.073 pm; Graphite monochromator
Temperature:	RT
Orientation matrix:	24 Reflections in the range of $20° \le 2\theta \le 30°$
Scan range:	$3° \le 2\theta \le 54°$ $-4 \le h \le 4$ $-11 \le k \le 11$ $-14 \le l \le 14$
scan mode:	ω-Scan
Scan time:	Prescan 3.0 s ; / max.: 240 s ($1 \le I / \sigma(I) \le 30$)
Scan width:	$(1.10 + 0.35 \cdot \tan\theta)°$
Intensity control:	3 reflections every 4h
Intensity correction:	None
Orientation control:	3 reflections every 400 reflections

Structure solution and refinement:

Reflections:	3122 measured reflections 0 systematically absent reflections 1561 independent reflections 0 suppressed reflections 1561 independent reflections used for refinement 1180 independent reflections with $Fo>4\sigma(Fo)$
Average $I/\sigma(I)$	23.55
$R_{int.}$:	$\Sigma \lvert F_o^2 - (F_o^2)\text{mean}\rvert / [\Sigma F_o^2] = 0.0171$
Absorption correction:	face-indexed; min./max. trans.: 0.3609, 0.4811; μ = 6.59 mm^{-1}
Structure solution:	Direct methods (SHELXS-97)
Structure refinement:	Full-Matrix Least-Squares against F^2 (SHELXL-97)

Parameters:	In the asymmetric unit:	
	4 C-, 2 N-, 2Cu-, 2 Cl-atom(s)	anisotropic displacement parameters
	4 H atoms	isotropic displacement parameters
	92 Parameter full matrix refined	
Reflections / parameter:	17.0	
Hydrogen atoms:	The hydrogen atoms were positioned with idealised geometry (d_{C-H} (aromatic)= 0.93 Å) and refined with fixed isotropic displacement parameters according to the riding model [$U_{iso} = 1.2 \times U_{eq}(C_{aromatic})$].	
Scattering factors:	For neutral atoms	
LP corrections	yes	
Extinction correction:	$F^* = F_c (k[1 + 0.001 \cdot x \cdot F_c^2 \cdot \lambda^3 / \sin(2\theta)]^{-0.25})$ x = 0.012 (8)	
Weight:	$w = 1/[\sigma^2(F_o^2) + (0.0366 \cdot P)^2 + 0.58 \cdot P]$; $P = (\mathrm{Max}(F_o^2,0) + 2 \cdot F_c^2) / 3$	
Shift/Error:	≤ 0.001 in the last cycle	
Residual electron density:	Max.: 0.71 / Min.: -0.86e/Å^3	
R1 for 1180 Fo>4σ(Fo)	$R1 = \Sigma \lvert \lvert Fo \rvert - \lvert Fc \rvert \rvert / \Sigma \lvert Fo \rvert$	= 0.0291
R1 for all 1561 reflections		= 0.0490
wR2 for 1180 Fo>4σ(Fo)	$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{½}$	= 0.0728
wR2 for all 1561 reflections		= 0.0788
Goodness of fit (all refl.)	$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{½}$	= 1.019
Restrained GoF (all refl.)		= 1.019
Restraints		= 0

Remarks:

Data collection: CAD4 Version5; Data reduction: XCAD4; Graphics: SHELXTL PC XP;

Tables: SHELXL-97 CIFTAB

Tab. 2 Atomic coordinates [$\cdot 10^4$] and equivalent isotropic displacement parameters [$Å^2 \cdot 10^3$]

	X	Y	Z	U_{eq}
Cu(1)	6236 (1)	9140 (1)	6003 (1)	41 (1)
Cu(2)	11855 (2)	8995 (1)	9005 (1)	54 (1)
Cl(1)	11061 (2)	8199 (1)	6923 (1)	33 (1)
Cl(2)	6895 (2)	8104 (1)	9891 (1)	32 (1)
N(1)	5234 (8)	7790 (3)	4267 (3)	28 (1)
N(2)	3750 (8)	8476 (3)	3454 (2)	28 (1)
C(1)	2768 (10)	7591 (5)	2313 (3)	35 (1)
C(2)	3162 (11)	5966 (5)	1897 (3)	42 (1)
C(3)	4682 (11)	5282 (4)	2711 (4)	40 (1)
C(4)	5714 (10)	6256 (4)	3890 (3)	33 (1)

Equivalent isotropic U calculated as a third of the trace of the orthogonalised U_{ij} tensors

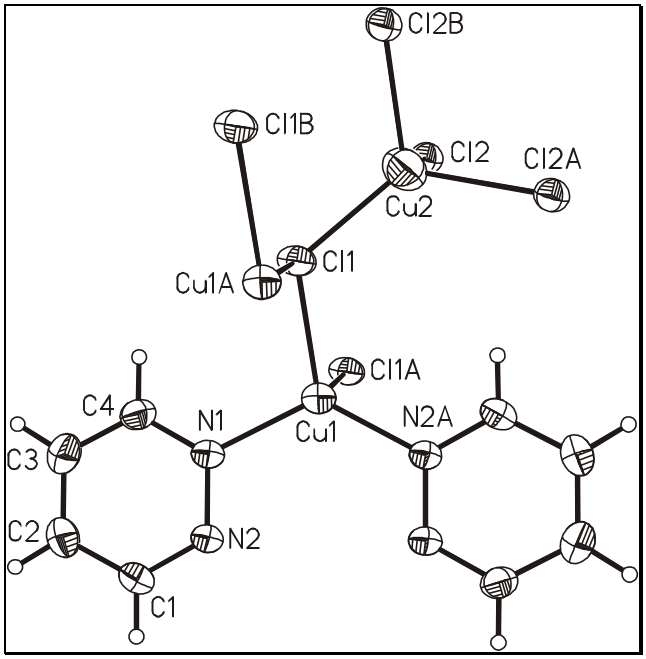
Tab. 3 Anisotropic displacement parameters [$Å^2 \cdot 10^3$]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	60 (1)	34 (1)	30 (1)	10 (1)	-1 (1)	16 (1)
Cu(2)	55 (1)	66 (1)	41 (1)	13 (1)	4 (1)	14 (1)
Cl(1)	31 (1)	43 (1)	29 (1)	16 (1)	3 (1)	10 (1)
Cl(2)	31 (1)	36 (1)	29 (1)	9 (1)	2 (1)	8 (1)
N(1)	32 (2)	29 (1)	25 (1)	12 (1)	3 (1)	7 (1)
N(2)	33 (2)	29 (1)	23 (1)	10 (1)	3 (1)	7 (1)
C(1)	40 (2)	40 (2)	24 (2)	10 (1)	-1 (1)	8 (2)
C(2)	51 (2)	36 (2)	31 (2)	1 (2)	0 (2)	4 (2)
C(3)	46 (2)	29 (2)	44 (2)	7 (2)	8 (2)	7 (2)
C(4)	38 (2)	33 (2)	34 (2)	15 (1)	5 (2)	11 (1)

The temperature factor exponent has the form: $-2\pi^2(h^2 \cdot a^{*2} U_{11}+...+2hka^*b^*U_{12})$

Tab. 4 H-Atomic coordinates [$\cdot 10^4$] and isotropic displacement factors [$Å^2 \cdot 10^3$]

	X	Y	Z	U_{eq}
H(1)	1763	8078	1761	42
H(2)	2411	5369	1090	50
H(3)	5015	4200	2483	48
H(4)	6809	5807	4451	40



Tab. 5 Geometric parameters

Bond lengths [**Å**]

Cu(1)	- N(2A)	1.990	(3)	Cu(1) - N(1)		1.997	(3)
Cu(1)	- Cl(1)	2.354	(1)	Cu(1) - Cl(1A)		2.480	(2)
Cu(2)	- Cl(1)	2.287	(2)	Cu(2) - Cl(2B)		2.376	(2)
Cu(2)	- Cl(2)	2.376	(2)	Cu(2) - Cl(2A)		2.458	(2)
Cl(1)	- Cu(1A)	2.480	(2)	N(1) - C(4)		1.322	(4)
N(1)	- N(2)	1.352	(4)	N(2) - C(1)		1.320	(4)
C(1)	- C(2)	1.390	(5)	C(2) - C(3)		1.357	(6)
C(3)	- C(4)	1.379	(5)				

Angles [°]

N(2A)	- Cu(1)	- N(1)	124.06	(11)	N(2A)	- Cu(1)	- Cl(1)	115.50	(9)
N(1)	- Cu(1)	- Cl(1)	106.83	(9)	N(2A)	- Cu(1)	- Cl(1A)	100.92	(9)
N(1)	- Cu(1)	- Cl(1A)	103.70	(9)	Cl(1)	- Cu(1)	- Cl(1A)	102.69	(4)
Cl(1)	- Cu(2)	- Cl(2B)	113.93	(4)	Cl(1)	- Cu(2)	- Cl(2)	114.58	(4)
Cl(2A)	- Cu(2)	- Cl(2)	105.22	(4)	Cl(1)	- Cu(2)	- Cl(2B)	119.42	(4)
Cl(2B)	- Cu(2)	- Cl(2B)	99.56	(4)	Cl(2)	- Cu(2)	- Cl(2A)	102.05	(4)
C(4)	- N(1)	- N(2)	118.9	(3)	C(1)	- N(2)	- N(1)	119.2	(3)
N(2)	- C(1)	- C(2)	123.2	(3)	C(3)	- C(2)	- C(1)	117.6	(3)
C(2)	- C(3)	- C(4)	117.4	(3)	N(1)	- C(4)	- C(3)	123.7	(3)

Single Crystal Structure Determination of Poly[Cu_2Br_2(Pyidazine-N,N) (III)

Tab. 1 Protocol

Crystal data:

Compound:	Cu_2Br_2-(Pyridazine)
Formula:	$C_4H_4N_2Cu_2Br_2$
Crystal colour/habit:	orange block
Crystal size:	0.12 mm · 0.09 mm · 0.06 mm
Molecular weight:	278.07 g/mol
Space group:	triclinic P-1; IT – Nr.: 2
Calculated density:	3.114 g · cm^{-3}
F(000):	340
Lattice parameters:	Least-Squares refinement of 96 reflections in the range of $20° \le 2\theta \le 30°$ a = 3.9577 (9) Å α= 105.439 (2)° b = 8.7868 (2) Å β= 94.710 (2) ° c = 11.8227(3) Å γ = 96.165 (2) ° V = 391.37 (1) $Å^3$ Z = 2

Data collection

Device:	AED2- 4-circle diffractometer
Radiation:	Mo-Kα; 71.073 pm; Graphite monochromator
Temperature:	RT
Orientation matrix:	26 Reflections in the range of $21° \le 2\theta \le 26°$
Scan range:	$3° \le 2\theta \le 56°$ $-5 \le h \le 4$ $-11 \le k \le 11$ $-15 \le l \le 15$
scan mode:	ω-θ-Scan
Scan time:	min.: 0.7 s / max.: 4.0 s ($1 \le I / \sigma(I) \le 30$)
Scan width:	(1.08 + 0.35 · tan θ)°, (36 Steps a 0.03°)
Intensity control:	4 reflections every 2h
Intensity correction:	None
Orientation control:	if peak-shift of a control reflection is more than 0.15° or every 6 standard reflections

Structure solution and refinement:

Reflections:	3680 measured reflections 0 systematically absent reflections 1899 independent reflections 0 suppressed reflections 1899 independent reflections used for refinement 1436 independent reflections with Fo>4σ(Fo)
Average I/σ(I)	22.09
$R_{int.}$:	$\Sigma \lvert F_o^2 - (F_o^2)\text{mean} \rvert / [\Sigma F_o^2] = 0.0565$
Absorption correction:	face-indexed; min./max. trans.: 0.0816, 0.1456; μ = 17.12 mm^{-1}
Structure solution:	Direct methods (SHELXS-97)
Structure refinement:	Full-Matrix Least-Squares against F^2 (SHELXL-97)

Parameters:	In the asymmetric unit:	
	4 C-, 2 N-, 2Cu-, 2 Br-atom(s)	anisotropic displacement parameters
	4 H atoms	isotropic displacement parameters
	92 Parameter full matrix refined	
Reflections / parameter:	20.64	
Hydrogen atoms:	The hydrogen atoms were positioned with idealised geometry (d_{C-H} (aromatic)= 0.93 Å) and refined with fixed isotropic displacement parameters according to the riding model [$U_{iso} = 1.2 \times U_{eq}(C_{aromatic})$].	
Scattering factors:	For neutral atoms	
LP corrections	yes	
Extinction correction:	$F^* = F_c (k[1 + 0.001 \cdot x \cdot F_c^2 \cdot \lambda^3 / \sin(2\theta)]^{-0.25})$ x = 0.016 (1)	
Weight:	$w = 1/[\sigma^2(F_o^2) + (0.0126 \cdot P)^2 + 0.48 \cdot P]$; $P = (\text{Max}(F_o^2,0) + 2 \cdot F_c^2) / 3$	
Shift/Error:	≤ 0.001 in the last cycle	
Residual electron density:	Max.: 0.81 / Min.: -0.82e/Å^3	
R1 for 1436 Fo>4σ(Fo)	$R1 = \Sigma \lvert \lvert Fo \rvert - \lvert Fc \rvert \rvert / \Sigma \lvert Fo \rvert$	= 0.0273
R1 for all 1899 reflections		= 0.0472
wR2 for 1436 Fo>4σ(Fo)	$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{½}$	= 0.0623
wR2 for all 1899 reflections		= 0.0674
Goodness of fit (all refl.)	$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{½}$	= 1.003
Restrained GoF (all refl.)		= 1.003
Restraints		= 0

Remarks:

Data collection: STOE DIF4; Data reduction: STOE REDU4; Graphics: SHELXTL PC XP;

Tables: SHELXL-97 CIFTAB

Tab. 2 Atomic coordinates [· 10^4] and equivalent isotropic displacement parameters [$Å^2$· 10^3]

	X	Y	Z	U_{eq}
Cu(1)	6282 (2)	9126 (1)	5957 (1)	43 (1)
Cu(2)	11862 (2)	9048 (1)	9079 (1)	55 (1)
Br(1)	11106 (1)	8179 (1)	6915 (1)	36 (1)
Br(2)	6828 (1)	7987 (1)	9920 (1)	35 (1)
N(1)	5198 (9)	7810 (4)	4270 (3)	32 (1)
N(2)	3623 (9)	8507 (4)	3517 (3)	32 (1)
C(1)	2500 (13)	7644 (5)	2426 (4)	41 (1)
C(2)	2840 (14)	6052 (5)	2005 (4)	47 (1)
C(3)	4438 (13)	5350 (5)	2759 (4)	44 (1)
C(4)	5624 (12)	6305 (5)	3891 (4)	39 (1)

Equivalent isotropic U calculated as a third of the trace of the orthogonalised U_{ij} tensors

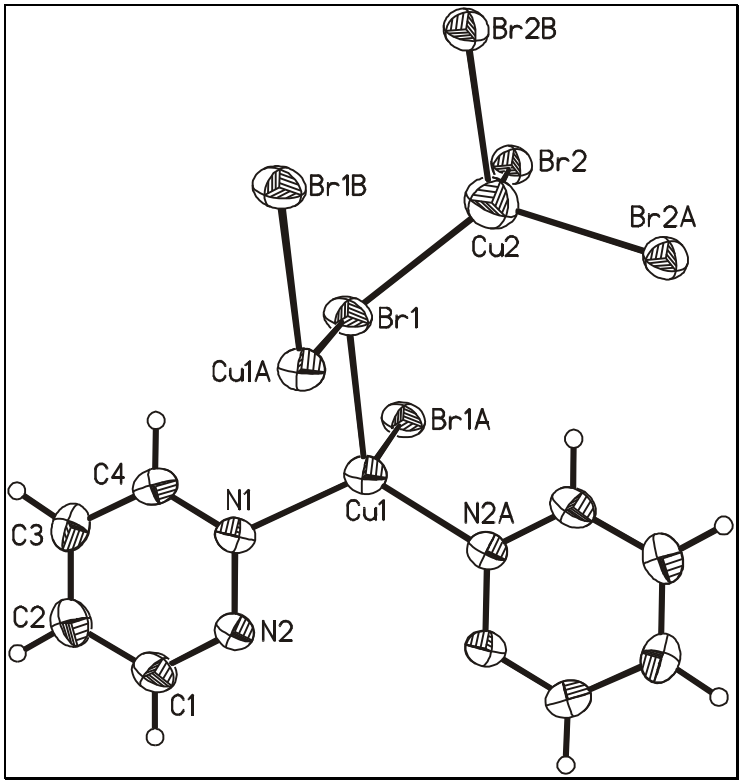
Tab. 3 Anisotropic displacement parameters [$Å^2$· 10^3]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	58 (1)	38 (1)	34 (1)	10 (1)	-4 (1)	15 (1)
Cu(2)	53 (1)	62 (1)	49 (1)	14 (1)	2 (1)	12 (1)
Br(1)	30 (1)	47 (1)	33 (1)	16 (1)	1 (1)	11 (1)
Br(2)	32 (1)	40 (1)	33 (1)	9 (1)	0 (1)	8 (1)
N(1)	36 (2)	34 (2)	28 (2)	12 (1)	2 (1)	8 (1)
N(2)	35 (2)	33 (2)	28 (2)	9 (1)	0 (1)	6 (1)
C(1)	46 (3)	43 (2)	32 (2)	10 (2)	-7 (2)	6 (2)
C(2)	59 (3)	41 (2)	34 (2)	1 (2)	-3 (2)	3 (2)
C(3)	55 (3)	32 (2)	43 (2)	3 (2)	7 (2)	9 (2)
C(4)	47 (3)	34 (2)	40 (2)	16 (2)	3 (2)	10 (2)

The temperature factor exponent has the form: $-2\pi^2(h^2 \cdot a^{*2} U_{11}+...+2hka^*b^*U_{12})$

Tab. 4 H-Atomic coordinates [· 10^4] and isotropic displacement factors [$Å^2$· 10^3]

	X	Y	Z	U_{eq}
H(1)	1426	8135	1917	49
H(2)	2008	5478	1234	57
H(3)	4722	4278	2526	53
H(4)	6783	5854	4409	47



Tab. 5 Geometric parameters

Bond lengths [**Å**]

Cu(1) - N(2A)	2.001	(3)	Cu(1) - N(1)	2.006	(3)
Cu(1) - Br(1)	2.472	(1)	Cu(1) - Br(1A)	2.586	(1)
Cu(2) - Br(1)	2.449	(1)	Cu(2) - Br(2)	2.500	(1)
Cu(2) - Br(2B)	2.508	(1)	Cu(2) - Br(2A)	2.535	(1)
Br(1) - Cu(1A)	2.586	(1)			
N(1) - C(4)	1.313	(5)	N(1) - N(2)	1.355	(4)
N(2) - C(1)	1.323	(5)	C(1) - C(2)	1.379	(6)
C(2) - C(3)	1.364	(6)	C(3) - C(4)	1.389	(6)

Angles [°]

N(2A) - Cu(1) - N(1)	123.86	(12)	N(2A) - Cu(1) - Br(1)	113.45	(9)
N(1) - Cu(1) - Br(1)	109.53	(10)	N(2A) - Cu(1) - Br(1A)	101.50	(11)
N(1) - Cu(1) - Br(1A)	102.25	(11)	Br(1) - Cu(1) - Br(1A)	102.95	(3)
Br(1) - Cu(2) - Br(2)	111.61	(3)	Br(1) - Cu(2) - Br(2B)	111.83	(3)
Br(2) - Cu(2) - Br(2B)	104.45	(3)	Br(1) - Cu(2) - Br(2A)	117.80	(3)
Br(2) - Cu(2) - Br(2A)	107.64	(3)	Br(2B) - Cu(2) - Br(2A)	102.35	(3)
C(4) - N(1) - N(2)	119.2	(3)	C(4) - N(1) - Cu(1)	124.2	(3)
N(2) - N(1) - Cu(1)	116.3	(2)	C(1) - N(2) - N(1)	119.1	(3)
N(2) - C(1) - C(2)	123.3	(4)	C(3) - C(2) - C(1)	117.7	(4)
C(2) - C(3) - C(4)	117.1	(4)	N(1) - C(4) - C(3)	123.6	(4)

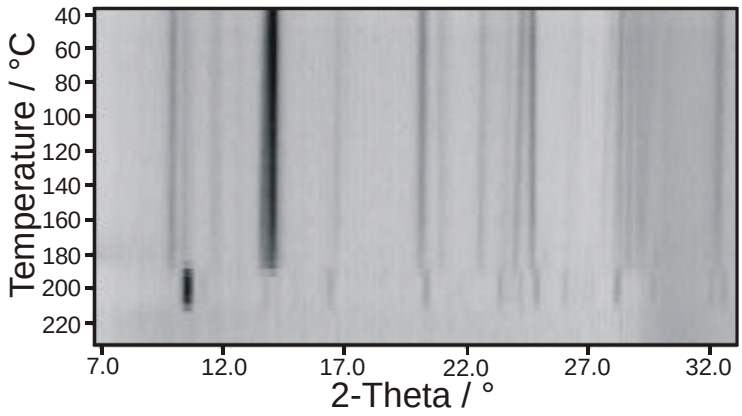


Figure 1. Results of the temperature resolved X-ray powder diffraction experiments on catena[CuCl(μ_2-pyridazine-N,N)] (**LI**).

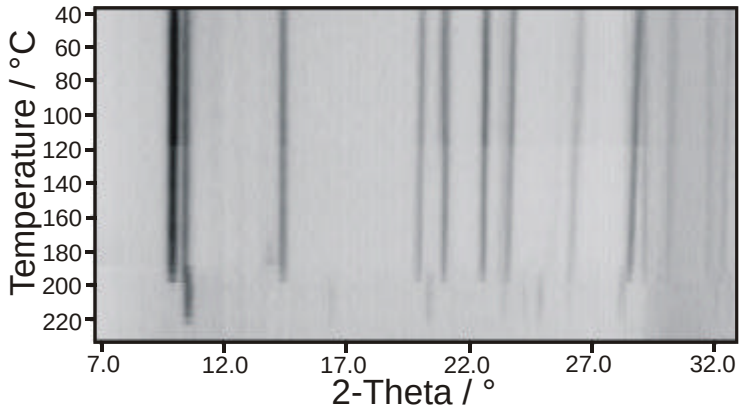


Figure 2. Results of the temperature resolved X-ray powder diffraction experiments on catena[CuCl(μ_2-pyridazine-N,N)] (**I**).

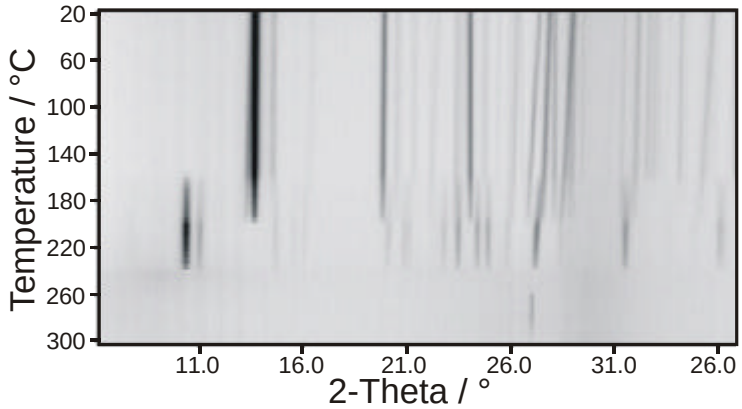


Figure 3. Results of the temperature resolved X-ray powder diffraction experiments on catena[CuBr(μ_2-pyridazine-N,N)] (**LII**).