

# Synthesis, Thermal Properties and Crystal Structure of Twinned Crystals of the New Coordination Polymer Poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')]

Christian Näther<sup>a</sup>, Inke Jeß<sup>a</sup>, and Michael Bolte<sup>b</sup>

<sup>a</sup> Institut für Anorganische Chemie der Christian-Albrechts-Universität zu Kiel, Olshausenstraße 40, D-24098 Kiel, Germany

<sup>b</sup> Institut für Organische Chemie, Johann-Wolfgang-Goethe-Universität Frankfurt, Marie-Curie-Straße 11, D-60439 Frankfurt am Main, Germany

Reprint requests to Dr. Christian Näther. E-mail: cnaether@ac.uni-kiel.de

Z. Naturforsch. **58b**, 1105 – 1111 (2003); received August 11, 2003

*Dedicated to Professor Hans Bock on the occasion of his 75th birthday*

Reaction of copper(I) bromide with pyrimidine in acetonitrile leads to the formation of crystals of the new coordination polymer poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')]. Indexing of the reflections yields a monoclinic primitive cell with  $a = 3.9119(2)$ ,  $b = 13.525(1)$ ,  $c = 15.346(1)$  Å,  $\beta = 97.29(1)^\circ$  and  $V = 805.4(1)$  Å<sup>3</sup>. Inspection of the reciprocal space shows weak reflections which might be indicative of a superstructure leading to a doubling of the crystallographic  $c$ -axis. The structure can be solved in space group  $P2_1/m$  but the refinement leads to very poor reliability factors ( $wR2$  for all refl.: 62.57%,  $R_1$  for all  $F_o > 4\sigma(F_o) = 27.84\%$ ). A twin refinement assuming merohedral twinning drastically reduces the  $R$ -values ( $wR2$  for all refl.: 7.27%,  $R_1$  for all  $F_o > 4\sigma(F_o) = 2.64\%$ ) and a structure model is obtained which consists of two crystallographically independent copper and bromine atoms and two pyrimidine ligands in the asymmetric unit. However, careful inspection of this structure shows that the two crystallographically independent layers formed by the connection of the building blocks are very similar and that they are related by a translation by half of the crystallographic  $c$ -axis. As a result of that, the crystal is just a partial merohedral twin and the reflections which led to the assumption that the  $c$ -axis is twice as long are generated by the second twin domain. The structure was refined with the correct twin law ( $wR2$  for all refl.: 6.70%,  $R_1$  for all  $F_o > 4\sigma(F_o) = 2.57\%$ ). By this procedure a reasonable structure model is obtained which consists of one crystallographically independent copper and bromine atom and one pyrimidine ligand. In the crystal structure CuBr double chains are formed which are connected into layers *via*  $\mu$ -N,N' coordination by the N-donor ligands. On heating, the compound loses all of the ligands and transforms into CuBr within only one single step in an exothermic reaction.

*Key words:* Coordination Polymers, Crystal Structures, Partial Merohedral Twinning

## Introduction

Recently, we have become interested in the synthesis, crystal structures and properties of coordination polymers based on copper(I) halides or pseudo halides and aromatic nitrogen donor ligands. Several of such compounds with interesting structural features are known [1 – 31], some also with inorganic building units other than amine ligands [33, 34]. These compounds consist of typical CuX substructures like 4- or 6-membered rings, “zig-zag” or helical single chains or “ladder-like” double chains which are connected by the N donor ligands into 1-, 2- or 3-dimensional coordination polymers. The dimensionality of these compounds depends predominantly on the coordination behaviour of the organic ligands, the nature of the

halide atom and the ratio between the organic and inorganic part. For one definite copper(I) halide or pseudo halide and one specific nitrogen donor ligand frequently several compounds are found, which contain a different CuX : ligand ratio like, *e. g.* 1:2, 1:1, 3:2, 2:1 or 4:1. We have found that most of the ligand-rich copper(I) halide or pseudo halide compounds can be transformed into ligand poorer compounds by thermal decomposition, which therefore, is an alternative route for the preparation of new CuX (X = Cl, Br, I) coordination polymers which cannot be prepared in solution or which are always obtained as phase mixtures [21, 32]. In some cases several amine poorer intermediates can be isolated. In order to investigate the influence of the organic ligands on the structure of these coordination polymers we have prepared and

structurally characterised several of these compounds. In most cases we have used small 6-membered nitrogen heterocycles like *e.g.* pyrazine. To investigate the influence of the position of the nitrogen donor atoms on the structure we were also interested in the pyridazine or pyrimidine coordination compounds. With pyrimidine only the 1:1 compound CuBr(pyrimidine) [4] and the 2:1 compound (CuCN)<sub>2</sub>(pyrimidine) [13, 19] are known. Some other compounds were only characterised by elemental analysis [20]. The crystal structure of CuBr(pyrimidine) consists of alternating CuBr single chains and (CuBr)<sub>2</sub> dimers which are connected into layers by the pyrimidine ligands [4]. The structures of the amine poorer compound with copper(I) bromide are unknown. Here we report on the synthesis and the crystal structure determination of twinned crystals of the new 2:1 coordination polymer poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')].

## Results and Discussion

### Crystal structure investigations

Search for reflections and indexing of these reflections yield a monoclinic primitive cell with  $a = 3.9119(2)$ ,  $b = 13.525(1)$ ,  $c = 15.346(1)$  Å,  $\beta = 97.288(7)$  and  $V = 805.4(1)$  Å<sup>3</sup> which can be transformed into an orthorhombic C-centred cell with  $a = 3.912$ ,  $b = 30.444$ ,  $c = 13.525$  Å, and  $V = 1610.8$  Å<sup>3</sup>. However, analysis of the intensities of symmetry equivalent reflections clearly shows that the true symmetry should be monoclinic ( $R_{\text{int}}(\text{monoclinic}) = 3.7\%$ ,  $R_{\text{int}}(\text{orthorhombic}) = 15.6\%$ ). The ratio ( $I/\sigma(I) = 26.6$ ) was high but inspection of the reciprocal space using RECIPE [36] shows some weak reflections indicative of a super structure leading to a doubling of the crystallographic  $c$ -axis (Table 1). All reflections with  $h$  even and  $l$  odd are weak. Determination of the space group was straightforward, because the systematic absence conditions show a 2<sub>1</sub> screw axis parallel to  $b$  and the  $|E^2 - 1|$  value points to the centrosymmetric space group  $P2_1/m$ . However, the structure could only be solved with great difficulty by direct methods using SHELXS-97 [37]. Anisotropic refinement with SHELXL-97 [38] by full-matrix least-squares leads to poor reliability factors and large residual electron densities in the difference map (Table 2). Since the data looked reasonable, it was suspected that the crystal was merohedrally twinned.

In order to derive a twin law, a picture of the reciprocal space has been drawn showing the  $a^*/c^*$  plane

Table 1. Intensity statistics for different groups of reflections for the data set measured for the large unit cell of poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')].

	I/σ max	I/σ min	I/σ mean	n	n > 3σ
all	360.5	-3.5	26.6	8523	4929
uuu	257.4	-1.7	23.6	1050	750
uug	238.0	-2.2	32.7	1033	807
ugu	192.0	-2.5	25.8	1051	745
ugg	262.9	-2.3	39.5	1051	811
guu	2.9	-3.3	0.1	1097	0
gug	360.5	-2.6	50.5	1091	906
ggu	3.7	-3.5	0.0	1082	4
ggg	353.7	-2.2	41.5	1068	906
0uu	2.8	-3.3	0.1	334	0
0ug	360.5	-2.6	67.2	322	253
0gu	3.7	-3.5	0.0	320	2
0gg	230.2	-2.0	56.4	317	255
u0u	169.3	-2.5	41.5	103	77
g0u	1.2	-1.4	-0.1	67	0
u0g	239.3	-0.1	63.4	105	90
g0g	353.7	2.2	53.6	63	58
uu0	180.4	-0.4	29.3	66	42
ug0	131.1	-0.9	36.2	70	61
gu0	134.5	2.9	45.5	64	63
gg0	287.5	-2.2	33.0	55	41
u00	53.8	7.0	23.7	8	8
g00	49.1	39.8	44.4	2	2
0u0	1.8	-0.9	0.3	16	0
0g0	230.2	0.3	94.1	14	12
00u	3.7	-1.9	0.0	23	1
00g	80.6	1.1	35.7	20	15

Table 2. Selected results of some structure refinements for poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')].

Refinement	without twinning	with merohedral twinning	with partial merohedral twinning
$a$ / Å	3.9119(2)	3.9119(2)	3.9119(2)
$b$ / Å	13.525(1)	13.525(1)	13.525(1)
$c$ / Å	15.346(1)	15.346(1)	7.6733(5)
$\beta$ / °	97.288(7)	97.288(7)	97.288(7)
$V$ [Å <sup>3</sup> ]	805.4(1)	805.4(1)	402.70(4)
Refl. collected	8523	8523	4243
Independent refl.	1982	1982	987
Refl. $F_o < 4\sigma(F_o)$	1312	1312	900
$R_{\text{int}}$ [%]	0.0373	0.0373	0.0313
Parameters	98	99	50
$R1$ ( $F_o < 4\sigma(F_o)$ )	0.2784	0.0264	0.0257
$wR2$ (all refl.)	0.6257	0.0727	0.0670
GOOF	1.259	0.991	1.057
$\delta F$ [eÅ <sup>-3</sup> ]	15.03 / -10.79	0.53 / -0.71	0.55 / -0.79

(Fig. 1). From this diagram it can be seen that the original  $b^*/c^*$  plane acts as a mirror plane and transforms the reciprocal cell into its twin counterpart. The twin law for this operation is  $(-1 \ 0 \ 1 / 0 \ 1 \ 0 / 0 \ 0 \ 1)$ . In order to refine the structure, this twin law for the reciprocal cell parameters has to be inverted and transposed

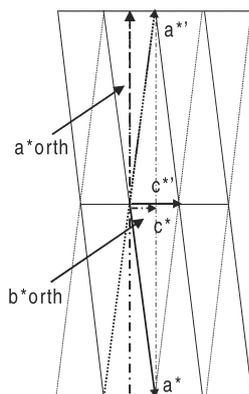


Fig. 1. Reciprocal space plot with view onto the  $a^*/c^*$  plane showing the relationship between both twin domains in the large unit cell. Full lines:  $a^*$ ,  $c^*$  prime component, dotted lines:  $a^{*'}$ ,  $c^{*'}$  twin component ( $c^*$  and  $c^{*'}$  are identical), dot-dashed lines:  $a^*$ orth,  $b^*$ orth orthorhombic C-centred setting.

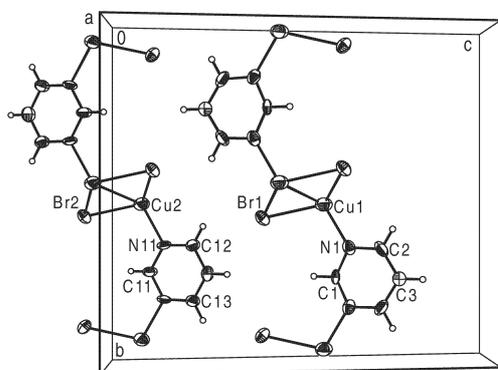


Fig. 2. Crystal structure of poly[(CuBr) $_2$ ( $\mu_2$ -pyrimidine-N,N')] with labelling and displacement ellipsoids drawn at the 50% probability level (The plot originates from a twin refinement in the large unit cell assuming merohedral twinning.).

to obtain the twin law for the reflection indices. The result of this matrix operation is  $(-1\ 0\ 0 / 0\ 1\ 0 / 1\ 0\ 1)$ . Applying this twin law all reliability factors drop down dramatically leading to a reasonable structure model (Table 2).

For this unit cell the asymmetric unit consists of two crystallographically independent CuBr(pyrimidine) units with the copper and bromine atom in general positions and the pyrimidine ligands located on a crystallographic mirror plane (Fig. 2). The crystal structure consist of CuBr double chains which are connected into layers by the pyrimidine ligands. In this model two crystallographically independent layers are found. In-

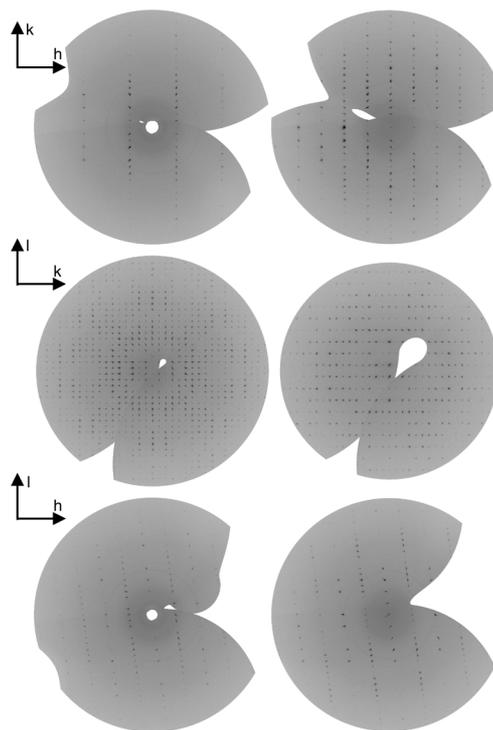


Fig. 3. View of the HK1 (top: left), HK2 (top: right), 1KL (middle: left), 2KL (middle: right), H1L (bottom: left) and H2L (bottom: right) layers calculated with SPACE [36] the data set measured on a crystal of [(CuBr) $_2$ ( $\mu_2$ -pyrimidine-N,N')].

terestingly no structural differences can be found for both layer units and analysis of the positional parameters reveals that for any atom, there was a second atom on  $x, y, z + 0.5$ . This means that the  $c$ -axis is too long by a factor of 2.

When the  $c$ -axis is halved the space group remains the same, but unfortunately, the twin law is no longer valid, because now only some of the reflections of the two domains overlap, while others are not affected by the twinning. This means that the crystal is not a merohedral twin, but a non-merohedral twin. From Table 1 it is obvious that all reflections with  $h = 2n$  and  $l = 2n + 1$  are not observed, which is a quarter of all measured reflections. This is also obvious from diffraction images calculated with SPACE [36] from the data set measured (Fig. 3). From these images it is obvious that some zones have twice as much reflections than others, which is an indication for a twinning of the crystal. Therefore, a second diagram of the reciprocal space was drawn which shows the relationship

Cu(1) - N(1)	2.033(3)	Cu(1) - Br(1A)	2.460(1)
Cu(1) - Br(1)	2.530(1)	Cu(1) - Br(1B)	2.545(1)
Cu(1) - Cu(1B)	2.820(2)	Cu(1) - Cu(1A)	2.838(2)
N(1) - Cu(1) - Br(1A)	119.47(10)	N(1) - Cu(1) - Br(1)	106.85(9)
Br(1A) - Cu(1) - Br(1)	111.20(2)	N(1) - Cu(1) - Br(1B)	104.31(9)
Br(1A) - Cu(1) - Br(1B)	102.79(2)	Br(1) - Cu(1) - Br(1B)	112.00(3)
N(1) - Cu(1) - Cu(1B)	133.58(9)	Br(1A) - Cu(1) - Cu(1B)	56.77(2)
Br(1) - Cu(1) - Cu(1B)	54.44(2)	Br(1B) - Cu(1) - Cu(1B)	121.95(3)
N(1) - Cu(1) - Cu(1A)	118.70(10)	Br(1A) - Cu(1) - Cu(1A)	121.39(3)
Br(1) - Cu(1) - Cu(1A)	56.25(2)	Br(1B) - Cu(1) - Cu(1A)	55.75(2)
Cu(1B) - Cu(1) - Cu(1A)	87.48(3)	Cu(1B) - Br(1) - Cu(1)	68.80(2)
Cu(1B) - Br(1) - Cu(1A)	102.79(2)	Cu(1) - Br(1) - Cu(1A)	68.00(3)

Table 3. Selected bond lengths (Å) and angles (°) for poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')].

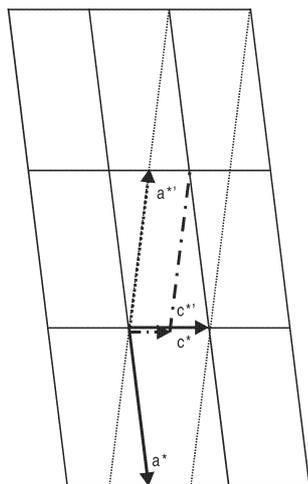


Fig. 4. Reciprocal space plot with view onto the  $a^*/c^*$  plane showing the relationship between the original cell (dotted lines) the correct cell (full lines) and the twin component (dashed lines). The correct cell and its twin counterpart are related via a mirror plane in the  $b^*/c^*$  plane.

between the original cell (which is actually too big) and the correct cell (Fig. 4). This shows that the crystal is in fact twinned by a mirror plane located in the  $b^*/c^*$  plane. However, the correct twin law describing the relationship of the two reciprocal cells is  $(-1\ 0\ 0.5\ /\ 0\ 1\ 0\ /\ 0\ 0\ 1)$ . Inverting and transposing this matrix leads to  $(-1\ 0\ 0\ /\ 0\ 1\ 0\ /\ 0.5\ 0\ 1)$ , which is the matrix for the transformation of the reflection indices of the two domains. As can be seen from Fig. 4, reflections with  $h = 2n$  overlap, whereas reflections with  $h = 2n + 1$  do not overlap. Therefore, refinement with SHELXL must be performed using the HKLF 5 option and a modified data set (see exp. part). This procedure leads to a reasonable structure model and very good reliability factors (Table 2 and 4).

A further interesting feature of the data (which can be a warning sign that a structure may possibly be

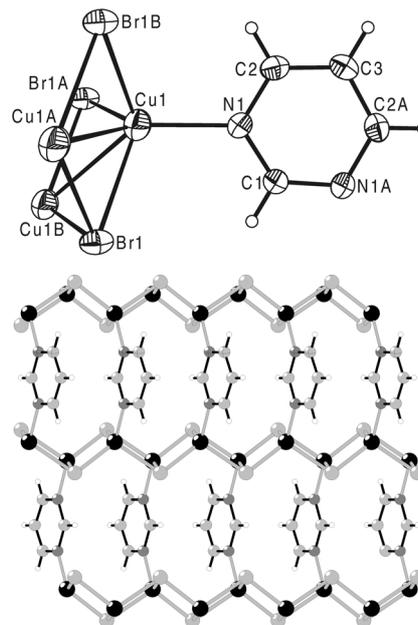


Fig. 5. Crystal structure of poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')] with labelling and displacement ellipsoids drawn at the 50% probability level (top) and with view in the direction of the crystallographic  $c$ -axis (bottom) (The plot originates from a twin refinement in the correct unit cell using the HKLF 5 option).

twinned) is, that the cell can be transformed to a cell of higher symmetry with an only slightly worse  $R(\text{int})$  value. In the present case the monoclinic cell can be transformed into an orthorhombic C-centred one (Fig. 1).

#### Crystal structure

The asymmetric unit of poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')] contains one crystallographically independent copper and bromine atom in general positions as well as one pyrazine ligand which is located on

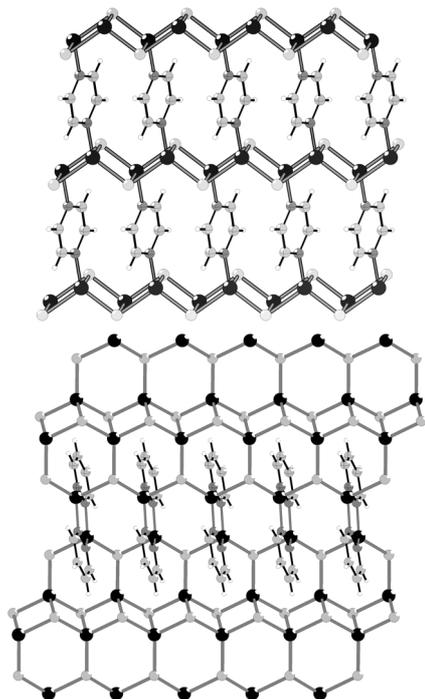


Fig. 6. Crystal structures of poly[(CuBr)<sub>2</sub>( $\mu_2$ -pyrazine-N,N')] with view along the *c*-axis (top) and of poly[(CuBr)<sub>2</sub>( $\mu_2$ -pyridazine-N,N')] with view along the *b*-axis (bottom).

a crystallographic mirror plane. Each copper atom is coordinated by three symmetry related bromine atoms and one nitrogen atom of the pyrimidine ligand within a strongly distorted tetrahedron (Fig. 5). The Cu-N bond length of 2.033(3) Å and the Cu-Br bond lengths between 2.460(1) and 2.545(1) Å are in the range observed in other CuBr(amine) compounds with similar structures (Table 3). There are two additional short contacts to neighbouring copper atoms of 2.820 and 2.838 Å (Table 3). The copper atoms in the double chains are connected by the bromine atoms into double chains along the direction of the crystallographic *a*-axis. These double chains are connected by the pyrimidine ligands *via*  $\mu$ -N,N' coordination into layers parallel to the *a/b* plane (Fig. 5: bottom).

In this context it is interesting to compare the structures of the 2:1 compounds with the different diazine ligands pyrimidine, pyrazine and pyridazine (Fig. 6). The 2:1 CuBr compound with pyrazine in which the nitrogen donor atoms are located in the 1- and 4-position exhibit a similar structure like the title compound [6]. CuBr double chains occur, which are connected into

layers by the pyrazine ligands (Fig. 6: top). For sterical reasons this connection is no longer possible if the nitrogen donor atoms are located in the 1- and 2-position like in pyridazine [29]. In this compound a novel and interesting CuBr substructure occurs. The actual motif of CuBr double chains remains the same but these double chains are expanded by two CuBr single chains (Fig. 6: bottom). These CuBr tetra-chains are connected to layers by two pyridazine ligands (Fig. 6: bottom). This comparison clearly shows the influence of the position of the nitrogen donor atoms onto the topology and the structure of such coordination polymers.

### Thermal properties

The thermal properties of the title compound were investigated in order to find out if amine poorer intermediates are formed during the thermal decomposition as it is observed in many other CuX coordination polymers. If poly[(CuBr)<sub>2</sub>( $\mu_2$ -pyrimidine-N,N')] is heated in a thermobalance an endothermic event occurs at a peak temperature of about 247 °C which is accompanied with a strong mass loss in the TG curve (Fig. 7). The experimental mass loss of 21.9% is in perfect agreement with that calculated for the removal of all ligands ( $\Delta m_{\text{theo.}} = 21.9\%$ ). The DTG curve shows only one single step and from mass spectroscopic investigations it is obvious that only pyrimidine ( $m/z = 80$ ) is emitted (Fig. 7). From these investigations there is no hint for the occurrence of amine poorer intermediate phases. It must be pointed out that the decomposition of poly[(CuBr)<sub>2</sub>( $\mu_2$ -pyrimidine-N,N')] into CuBr proceeds via a strong exothermic reaction. This is in contrast to the decomposition reactions of all copper(I)

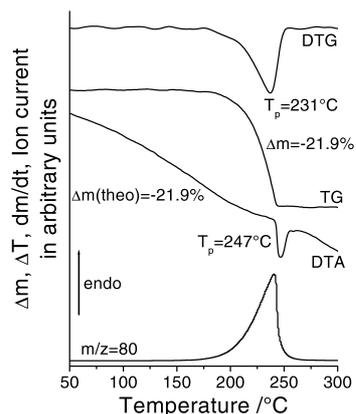


Fig. 7. DTA, TG, DTG and MS trend scan curve for poly[(CuBr)<sub>2</sub>( $\mu_2$ -pyrimidine-N,N')].

halide coordination polymers investigated previously. However, to be sure that the decomposition reaction is not more complex, experiments using temperature resolved X-ray powder diffraction were performed. In agreement with the DTA-TG-MS investigations there is no hint for additional intermediate phases.

## Experimental Section

### *Synthesis of poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')]:*

1.0 mmol of CuBr and 0.5 mmol of pyrimidine and 2 ml acetonitrile were filled into a glass ampoule which was sealed and heated for 1 week at 120 °C. The reaction mixture was cooled to r.t. and the residue filtered off and washed with ethanol and diethylether. Yield: 83%. Elemental analysis (%): calcd. C 13.09, H 1.10, N 7.63; found C 13.02, H 1.04, N 7.60.

Single crystal structure analysis: The data were measured using an Imaging Plate Diffraction System IPDS-1. The structure solution was performed with direct methods using SHELXS-97 [37]. Structure refinement was performed against  $F^2$  using SHELXL-97 [38]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C-H hydrogen atoms were positioned with idealised geometry ( $d_{C-H} = 0.93 \text{ \AA}$ ) and were refined with fixed isotropic displacement parameters ( $U_{eq}(H) = 1.2 \cdot U_{eq}(C)$ ) using the riding model. In order to refine the structure as a non-merohedral twin using the HKLF 5 option in SHELXL-97, the reflection file was modified using the program HKLF 5 [39]. For every overlapped reflection the reflection of the second twin domain calculated by the twin law has to be inserted before the prime reflection. Because this reflection is generated by a second domain its batch number has to be set to  $-2$ . The negative sign informs the program that contributions from other twin components follow. The intensity and the standard deviation of the second reflection are set to the same value as for the prime reflection. The refinement is finally performed adding a BASF instruction in order to refine the ratio of the two twin components and the data are read in by the HKLF 5 instruction BASF = 0.376(2). By this procedure equivalent reflections were not merged. The internal R-values given in this manuscript were calculated from the original data. Details of the structure determination, atomic coordinates and isotropic displacement parameters are given in Table 4 and 5.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 221254. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.ca.ac.uk).

*X-ray powder diffraction:* X-Ray powder diffraction experiments were performed using a STOE STADI P trans-

Table 4. Selected crystal data and details of the structure determination for poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')].

Formula	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> Cu <sub>2</sub> Br <sub>2</sub>
MG [g/mol]	366.99
Crystal colour/shape	yellow needle
Crystal size / mm	0.1 × 0.04 × 0.04
<i>a</i> / Å	3.9119(2)
<i>b</i> / Å	13.525(1)
<i>c</i> / Å	7.6733(5)
$\beta$ / °	97.288(7)
<i>V</i> / Å <sup>3</sup>	402.70(4)
Temperature	room-temperature
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>m</i>
<i>Z</i>	2
Scan range	3° ≤ 2θ ≤ 56°
$d_{\text{calc.}}$ / g·cm <sup>-3</sup>	3.027
$\mu$ / mm <sup>-1</sup>	15.12
Index range	−5 ≤ <i>h</i> ≤ 5 −17 ≤ <i>k</i> ≤ 17 −10 ≤ <i>l</i> ≤ 10
Refl. collected	4243
Independent refl.	987
Refl. $F_o < 4\sigma(F_o)$	900
$R_{\text{int}}$ [%]	0.0313
Parameters	50
$R1(F_o < 4\sigma(F_o))$	0.0257
$wR2$ (all refl.)	0.0660
GOOF	1.057
$\delta F$ [eÅ <sup>-3</sup> ]	0.55 / −0.79

Table 5. Atomic coordinates [ $\cdot 10^4$ ] and isotropic displacement parameters [ $\text{\AA}^2 \cdot 10^3$ ] for poly[(CuBr)<sub>2</sub>(μ<sub>2</sub>-pyrimidine-N,N')].

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Cu(1)	2785(2)	327(1)	1211(1)	43(1)
Br(1)	1872(1)	731(1)	−2034(1)	33(1)
N(1)	3879(8)	1622(2)	2507(4)	30(1)
C(1)	3074(17)	2500	1774(6)	31(1)
C(2)	5603(11)	1628(3)	4141(5)	35(1)
C(3)	6529(19)	2500	5007(7)	39(1)

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

mission powder diffractometer equipped with a 4° and 44° PSD (position sensitive detector) using CuK $\alpha$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ). For the temperature dependent X-ray powder measurements the instrument is equipped with a graphite furnace.

*Differential thermal analysis, thermogravimetry and mass spectrometry:* DTA-TG-MS measurements were performed using the STA-409CD with Skimmer coupling from Netzsch, which is equipped with a quadrupole mass spectrometer QMA 400 (max. 512 amu) from Balzers. The MS measurements were performed in analog and trend scan mode, in Al<sub>2</sub>O<sub>3</sub> crucibles under helium atmosphere (purity: 4.6) using

heating rates of 4 °C/min. All measurements were performed with a flow rate of 75 ml/min. and were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

*CHN analysis:* CHN-O-RAPID combustion analyser from Heraeus.

#### Acknowledgements

This work was supported by the State of Schleswig-Holstein. We are very thankful to Professor Dr. Wolfgang Bensch for financial support and for access to equipment.

- 
- [1] A. J. Blake, N. R. Brooks, N. R. Champness, L. R. Hanton, P. Hubberstey, M. Schröder, *Pure Appl. Chem.* **70**, 2351 (1998).
- [2] A. J. Blake, N. R. Brooks, N. R. Champness, P. A. Cook, A. M. Deveson, D. Fenske, P. Hubberstey, W.-S. Li, M. Schröder, *J. Chem. Soc. Dalton Trans.* 2103 (1999).
- [3] B. Roßenbeck, W. S. Sheldrick, *Z. Naturforsch.* **55b**, 467 (2000).
- [4] T. Kromp, W. S. Sheldrick, *Z. Naturforsch.* **54b**, 1175 (1999).
- [5] A. J. Blake, N. R. Brooks, N. R. Champness, P. A. Cooke, M. Crew, A. M. Deveson, L. R. Hanton, P. Hubberstey, D. Fenske, M. Schröder, *Crystal Engineering* **2**, 181 (1999).
- [6] N. S. Persky, J. M. Chow, K. A. Poschmann, N. N. Lacuesta, S. L. Stoll, *Inorg. Chem.* **40**, 29 (2001).
- [7] O. M. Yaghi, G. Li, *Angew. Chem.* **107**, 232 (1995) and *Angew. Chem. Int. Ed.* **34**, 207 (1995).
- [8] S. R. Batten, J. C. Jeffery, M. D. Ward, *Inorg. Chim. Acta* **292**, 231 (1999).
- [9] Y. L. Jack, B. R. Cabrera, R.-J. Wang, J. Li, *Inorg. Chem.* **38**, 4608 (1999).
- [10] P. M. Graham, R. D. Pike, M. Sabat, R. D. Bailey, W. T. Pennington, *Inorg. Chem.* **39**, 5121 (2001).
- [11] O. Teichert, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **626**, 1509 (2000).
- [12] O. Teichert, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **625**, 1860 (1999).
- [13] O. Teichert, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **626**, 2196 (2000).
- [14] T. Röttgers, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **627**, 1976 (2001).
- [15] C. Näther, I. Jeß, *Acta Crystallogr.* **C58**, m190 (2002).
- [16] K. Wasielewski, R. Mattes, *Z. Naturforsch.* **47b**, 1795 (1992).
- [17] K. Nieminen, *Acta Chem. Scand.* **A35**, 753 (1981).
- [18] M. D. Vaira, F. Mani, *J. Chem. Soc. Dalton Trans.* 2327 (1985).
- [19] S. A. Barnett, A. J. Blake, N. R. Champness, C. Wilson, *Cryst. Eng. Comm.* **5**, (2000).
- [20] J. T. Maeyer, T. J. Johnson, A. K. Smith, B. D. Borne, R. D. Pike, W. T. Pennington, M. Krawiec, *Polyhedron* **22**, 419 (2003).
- [21] C. Näther, J. Greve, I. Jeß, *Polyhedron* **20**, 1017 (2001).
- [22] C. Näther, I. Jeß, *Monatsh. Chem.* **132**, 897 (2001).
- [23] C. Näther, I. Jeß, H. Studzinski, *Z. Naturforsch.* **56b**, 997 (2001).
- [24] C. Näther, M. Wriedt, I. Jeß, *Z. Anorg. Allg. Chem.* **628**, 394 (2002).
- [25] C. Näther, J. Greve, I. Jeß, *Solid State Sciences* **4**, 813 (2002).
- [26] C. Näther, I. Jeß, *J. Solid State Chem.* **169**, 103 (2002).
- [27] C. Näther, I. Jeß, *Z. Naturforsch.* **57b**, 1133 (2002).
- [28] C. Näther, I. Jeß, *Inorg. Chem.* **42**, 2391 (2003).
- [29] C. Näther, I. Jeß, *Inorg. Chem.* **42**, 2968 (2003).
- [30] C. Näther, I. Jeß, *Solid State Sci.* (2003), in press.
- [31] C. Näther, J. Greve, I. Jeß, C. Wickleder, *Solid State Sci.* **5**, 1167 (2003).
- [32] T. Kromp, W. S. Sheldrick, C. Näther, *Z. Anorg. Allg. Chem.* **629**, 45 (2003).
- [33] A. Pfitzner, S. Reiser, H.-J. Deiseroth, *Z. Anorg. Allg. Chem.* **625**, 2196 (1999).
- [34] A. Pfitzner, *Chem. Eur. J.* **6**, 1891 (2000).
- [35] E. Freudenthaler, A. Pfitzner, *Solid State Ionics* **101**, 1053 (1997).
- [36] STOE & CIE, RECIPE and SPACE: Programs for exploring the reciprocal space and to calculate undistorted diffraction images, STOE & CIE GmbH, Darmstadt, Germany (1998).
- [37] G. M. Sheldrick, SHELXS 97: Program for Crystal Structure Solution, University of Göttingen, Germany (1997).
- [38] G. M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Germany (1997).
- [39] M. Bolte, HKLF 5: program for modifying HKL files using the twin law in the case of partial or non merohedral twinning.