

# Synthesis, Crystal Structures and Investigations on the Thermal Properties of New CuBr(2-Ethylpyrazine) Coordination Polymers

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Coordination Polymers, Crystal Structures, Thermal Properties

The new 3:2 coordination polymer catena[Cu<sub>3</sub>Br<sub>3</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')<sub>2</sub>] (**I**) was prepared by the reaction of CuBr with 2-ethylpyrazine in acetonitrile at room temperature. Its crystal structure consists of Cu<sub>3</sub>Br<sub>3</sub> rings which are connected by the 2-ethylpyrazine ligands to chains. The 2:1 compound poly[Cu<sub>2</sub>Br<sub>2</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')] (**II**) was only obtained phase pure if the reaction was performed at 100 °C. In this compound CuBr single chains occur, which are connected to sheets by the 2-ethylpyrazine ligands. If compound **I** is heated it decomposes in two separate steps as shown by thermogravimetry (TG), differential thermoanalysis (DTA) and mass spectroscopy (MS). *Ex situ* and temperature dependent *in situ* X-ray powder diffraction experiments prove that in the first step the 2:1 coordination polymer **II** has formed as the phase pure compound which decomposes to CuBr in the second step. From heating rate dependent TG measurements there is no hint for the occurrence of additional intermediates during the thermal decomposition reaction.

## Introduction

Recently we became interested in the synthesis, crystal structures and properties of coordination polymers based on copper(I) halides or pseudohalides and aromatic amine ligands. Several of these compounds are known and have been structurally characterised [1 - 15]. For one definite organic ligand and one definite copper(I) halide or pseudohalide mostly several compounds are found which differ in the ratio between the organic and inorganic part and compounds with a ratio between CuX and ligand of 4:1, 3:1, 2:1, 3:2, 1:1 and 1:2 being observed. We have found that most of the amine rich compounds decompose to amine poorer compounds on heating, whereas some others transform directly to the pure copper(I) halides or pseudohalides [16 - 22], and the occurrence of such amine poorer intermediate compounds does not necessarily depend on the structure of the starting compound. Whereas the 1:1 compounds of CuCl with pyrazine [17], 2-methylpyrazine [18] or 4,4'-bipyridine [19], *e. g.*, form the corresponding 2:1 coordination polymers on heating, the compound with 2-chloropyrazine [20] transforms directly to CuCl.

However, while the structures of the 1:1 compounds with 2-methylpyrazine and 2-chloropyrazine are very similar, the structure of the 4,4'-bipyridine compound is completely different. In further work we have demonstrated that the occurrence of the amine poorer compounds depends on the heating rate used in the experiment, and therefore the kinetics of all reactions involved may play an important role [22]. Starting from these findings we have initiated systematic investigations on the preparation, structure and properties of variety coordination polymers. Here we report on our investigations on new CuBr(2-ethylpyrazine) compounds.

## Results and Discussion

### *Crystal structures*

The 3:2 compound catena[Cu<sub>3</sub>Br<sub>3</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')<sub>2</sub>] (**I**) crystallises in the triclinic space group  $P\bar{1}$  with 2 formula units per cell and all atoms in general positions. The compound is not isotopic to the previously reported 3:2 compound with CuCl and 2-ethylpyrazine, but the topology of the structure is identical. The CuX substructure consists of 6-membered Cu<sub>3</sub>Br<sub>3</sub> rings in an

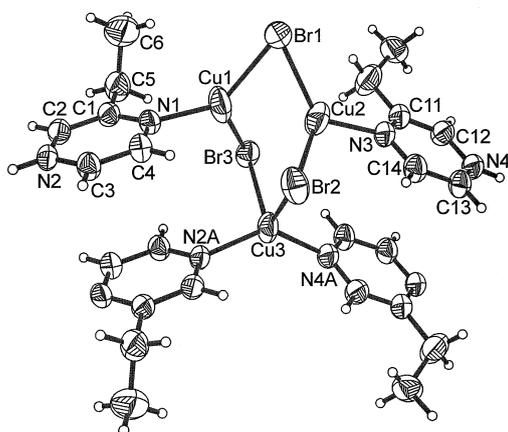


Fig. 1. Part of the crystal structure of catena[Cu<sub>3</sub>Br<sub>3</sub>( $\mu_2$ -2-ethylpyrazine-N,N')<sub>2</sub>] (**I**) showing the copper coordination with labelling (displacement ellipsoids are drawn at the 50% probability level; the disorder of C16 is not shown).

irregular conformation (Fig. 1). The copper atom Cu3 is fourfold coordinated by two crystallographically independent bromide atoms and two nitrogen atoms of two crystallographically independent 2-ethylpyrazine ligands within a strongly distorted tetrahedron (Fig. 1). The N-Cu-N angle is widened to 133.2° due to the bulky 2-ethylpyrazine ligand. The copper atoms Cu2 and Cu3 are only three-coordinated by two crystallographically independent bromide atoms and one nitrogen atom of a 2-ethylpyrazine ligand (Fig. 1). The coordination sphere of the copper atoms is formally completed by one Cu-Cu contact of 2.549 Å and therefore d<sup>10</sup>-d<sup>10</sup> interactions may play a role in the stabilisation of these rings [23]. However, there is one additional long contact between Cu2 and Br3 of 2.881 Å (Table 4). The CuBr bond lengths within the 6-membered rings vary between 2.358 and 2.550 Å with the shorter ones to the copper atoms which are coordinated by only one nitrogen atom of the 2-ethylpyrazine ligand. The Cu-N bond lengths are comparable to those found in other CuX coordination polymers.

The Cu<sub>3</sub>Br<sub>3</sub> rings are connected by the organic ligands *via*  $\mu$ -N,N' coordination forming Cu<sub>3</sub>Br<sub>3</sub>(-2-ethylpyrazine)<sub>2</sub> chains which run parallel to the crystallographic *c*-axis (Fig. 2). Between the chains no pronounced interaction can be found.

The 2:1 compound poly[Cu<sub>2</sub>Br<sub>2</sub>( $\mu_2$ -2-ethylpyrazine-N,N')] (**III**) crystallises in the triclinic space

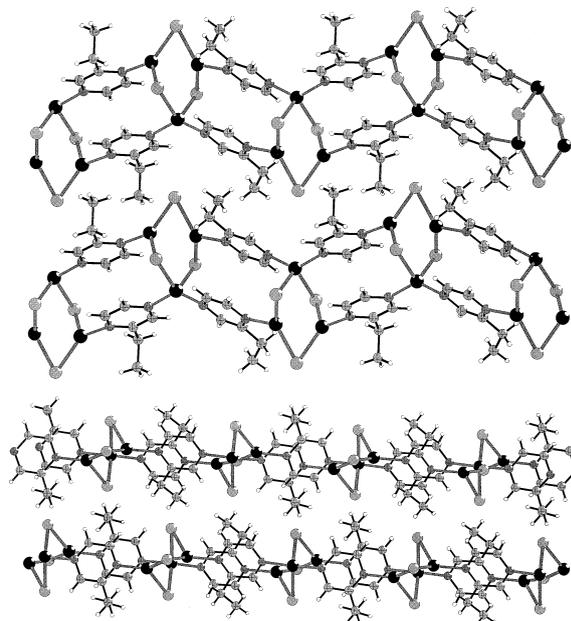


Fig. 2. Crystal structure of catena[Cu<sub>3</sub>Br<sub>3</sub>( $\mu_2$ -2-ethylpyrazine-N,N')<sub>2</sub>] (**I**) viewed along [100] (top) and [010] (bottom).

group  $P\bar{1}$  with 2 formula units in the unit cell and all atoms in general positions. The compound is not isotypic to the previously reported coordination polymer poly[Cu<sub>2</sub>Cl<sub>2</sub>( $\mu_2$ -2-ethylpyrazine-N,N')] which crystallizes in the monoclinic space group  $P2_1/c$  [22]. Each copper atom is connected to three bromine atoms and one nitrogen atom of a 2-ethylpyrazine ligand within a distorted tetrahedron (Fig. 3 and Table 4). The Cu-N bond length of 2.015 Å and the Cu-Br bond lengths between 2.358 and 2.505 Å are comparable to those in similar coordination compounds. The Cu-Cu distance of 2.846 Å is significantly longer than that in compound **I** of 2.549 Å indicating the absence of direct interactions between the copper atoms.

The CuX substructure consists of CuBr double chains formed by the connection of CuNBr<sub>3</sub> tetrahedra sharing common edges which are parallel to the crystallographic *a*-axis (Fig. 4: top). The CuBr double chains are connected by the 2-ethylpyrazine *via*  $\mu$ -N,N' coordination into sheets which are parallel to (001). This CuX substructure is frequently found in CuX coordination polymers of the general composition Cu<sub>2</sub>X<sub>2</sub> (base). Only if organic ligands are used which exhibit only one coordinating nitrogen atom such double chains can be found in 1:1

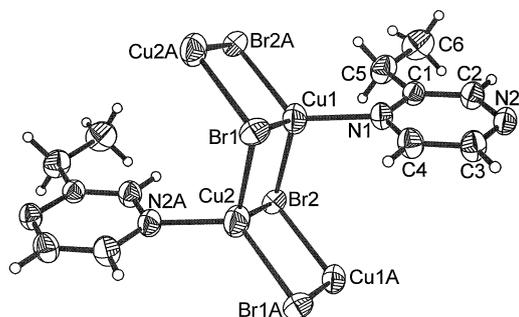


Fig. 3. Part of the crystal structure of poly[Cu<sub>2</sub>Br<sub>2</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')] (II) showing the copper coordination with labelling (displacement ellipsoids are drawn at the 50% probability level).

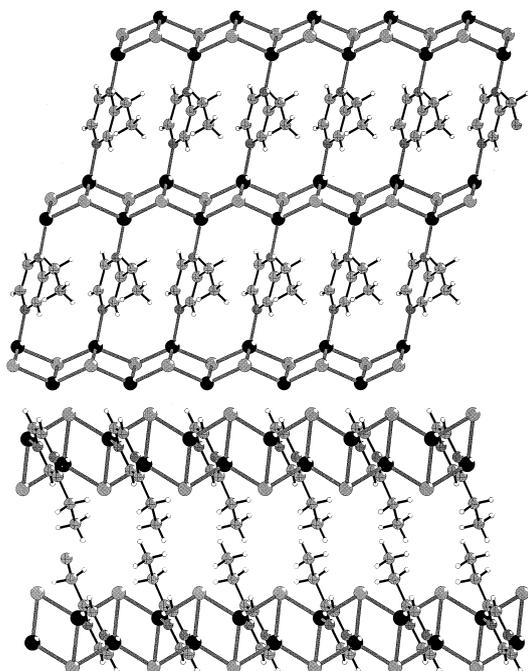


Fig. 4. Crystal structure of poly[Cu<sub>2</sub>Br<sub>2</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')] (II) viewed on (001) (top) and along (010) (bottom).

coordination polymers. The sheets are stacked in the direction of the crystallographic *c*-axis. As it is obvious from Fig. 4 (bottom) the sheets are oriented in a way that the non-polar ethyl ligands of different sheets are pointing to each other.

#### Thermoanalytical investigations

On heating the 3:2 compound **I** in a thermobalance with simultaneous differential thermoanalysis

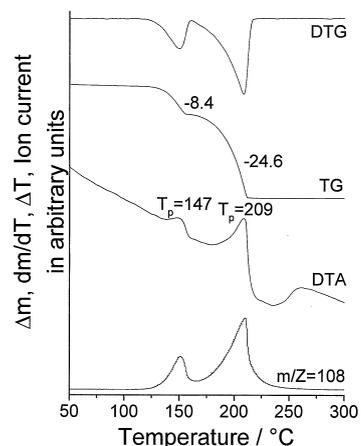


Fig. 5. DTA, TG, DTG and MS trend scan curve for catena[Cu<sub>3</sub>Br<sub>3</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')]<sub>2</sub> (I) (simultaneous measurement; powder; weight: 36.9 mg; heating rate: 4 °C/min; dynamic helium atmosphere; flow rate: 75 ml/min; *m/z* = 108 (2-ethylpyrazine); Al<sub>2</sub>O<sub>3</sub>-crucible; given are the mass changes (%) and the peak temperatures *T<sub>p</sub>* in °C; †: endo).

(DTA) and mass spectroscopy (MS) under a dynamic helium atmosphere an endothermic signal is observed in the DTA curve which is accompanied with a mass loss in the TG curve (Fig. 5). The experimental mass loss of 8.4% is in good agreement with that calculated for the removal of half of the 2-pyrazine ligands ( $\Delta m_{\text{theo}} - 0.5$  2-ethylpyrazine = 8.4%). On further heating a second TG step of 24.6% is observed in which the remaining organic ligands are removed ( $\Delta m_{\text{theo}} - 1.5$  2-ethylpyrazine = 25.2%). This is in agreement with simultaneous mass spectroscopic investigations which show that in both TG steps only 2-ethylpyrazine is emitted (*m/z* = 108) (Fig. 5). Therefore, it can be assumed that in the first reaction a 2:1 coordination polymer and in the second step CuBr are formed. From the DTG curve its obvious that both thermal events are well separated (Fig. 5). The final product of this reaction was identified as CuBr by X-ray powder diffraction.

Because we have shown in recent investigations that the product formation in such thermal decomposition reactions can depend on the heating rate of the experiment [22], we made additional heating rate dependent TG measurements under a dynamic nitrogen atmosphere (Fig. 6). However, from these measurements there are no hints for any further intermediates in this thermal decomposition reaction. The decomposition temperature of compound **I** is significantly lower than that measured in the DTA-

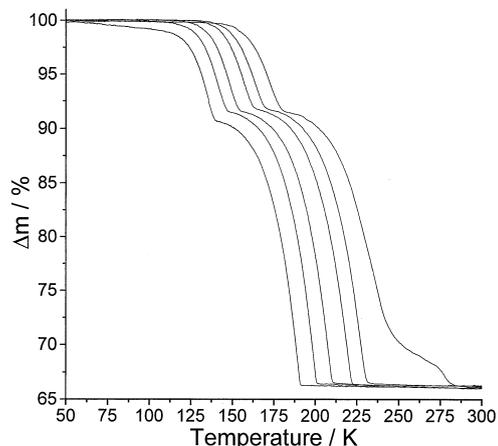


Fig. 6. Heating rate dependent TG curves for catena[Br<sub>3</sub>Br<sub>3</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')<sub>2</sub>] (I) (Al<sub>2</sub>O<sub>3</sub> crucibles without cap; dynamic nitrogen atmosphere; flow rate: 75 ml/min; heating rates (from left to right): 0.5, 1, 2, 4, 8, 16 °C/min).

TG-MS experiment shown in Fig. 5. It is also obvious that the change of the heating rate does not influence the resolution of the thermal events (Fig. 6).

To investigate which compound has formed as an intermediate we made additional TG experiments which were stopped when the first transformation had finished. If this residue is investigated by X-ray powder diffraction it can be shown that the 2:1 compound **II** has formed (Fig. 7). Elemental analysis proves that this intermediate is obtained in very pure form (see Experimental Section).

To prove the sequence of the reaction and to exclude the formation of any additional intermediates we performed experiments using temperature dependent X-ray powder diffraction under a static air atmosphere (Fig. 8). On heating of compound **I** a dramatic change of the diffraction pattern is observed at about 160 °C which corresponds to the transformation of the 3:2 compound **I** into the 2:1 compound **II** (Fig. 8). Because thin glass capillaries and a static air atmosphere were used in the experiment the transition temperature is significantly higher than that measured in the DTA-TG-MS experiments. On further heating the organic ligands were completely removed at about 220 °C and the diffraction pattern of CuBr occurred.

#### Synthetic aspects

In previous investigations we have shown that from the reaction of 2-ethylpyrazine with copper(I)

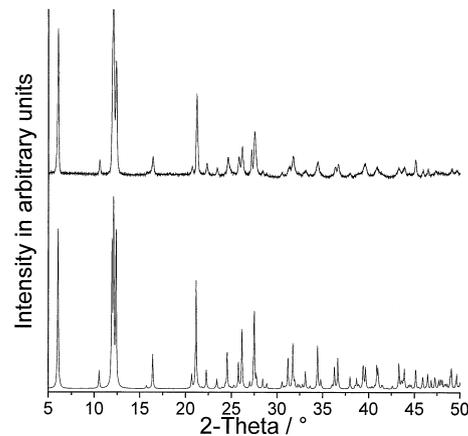


Fig. 7. X-ray powder pattern of the residue obtained with a heating rate of 4 °C/min at 185 °C from the thermal decomposition of catena[Cu<sub>3</sub>Br<sub>3</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')<sub>2</sub>] (I) (top) and calculated powder pattern for the 2:1 compound poly[Cu<sub>2</sub>Br<sub>2</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')<sub>2</sub>] (II) from single crystal data (bottom).

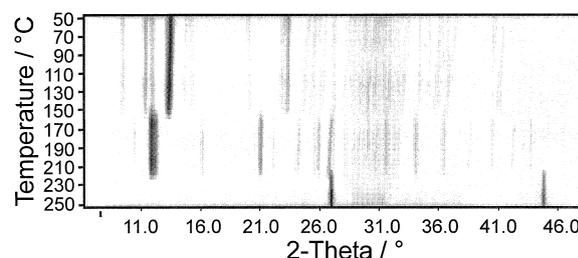


Fig. 8. Results of the temperature resolved X-ray powder diffraction experiments on catena[Cu<sub>3</sub>Br<sub>3</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')<sub>2</sub>] (I) (static air atmosphere; glass capillaries; powder patterns were measured every 5 °C; heating rate: 5 °C/min).

chloride three different coordination polymers can be obtained. The 1:1 compound poly[CuCl(μ<sub>2</sub>-2-ethylpyrazine-N,N')], the 3:2 compound catena[Cu<sub>3</sub>Cl<sub>3</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')<sub>2</sub>] and the poly[Cu<sub>2</sub>Cl<sub>2</sub>(μ<sub>2</sub>-2-ethylpyrazine-N,N')<sub>2</sub>] [22]. However, we made several experiments to prepare a 1:1 compound with CuBr using different temperatures and stoichiometries. All products obtained consisted either of the corresponding 3:2 compound or of mixtures of the 3:2 and the 2:1 compound or of the 2:1 compound with CuBr. These findings are in agreement with previous investigations [17 - 22], which showed that the stability of the 1:1 compounds increases from CuCl to CuI, whereas for the 2:1 compounds an opposite trend is observed. Therefore the 1:1 compound with CuBr and 2-ethylpyrazine

	1	2
Formula	C <sub>12</sub> H <sub>16</sub> N <sub>4</sub> Cu <sub>3</sub> Br <sub>3</sub>	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> Cu <sub>2</sub> Br <sub>2</sub>
MW / [g·mol <sup>-1</sup> ]	646.64	395.04
Crystal colour	deep orange	light orange
Crystal [size/mm]	0.08 × 0.09 × 0.11	0.08 × 0.08 × 0.11
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> / Å	7.562(1)	3.9525(2)
<i>b</i> / Å	9.203(1)	8.4106(7)
<i>c</i> / Å	13.002(2)	14.633(1)
$\alpha$ / °	92.78(2)	92.42(1)
$\beta$ / °	91.27(2)	90.73(1)
$\gamma$	90.87(2)	92.08(1)
<i>V</i> / Å <sup>3</sup>	903.5(2)	485.64(6)
Temperature / K	293	293
<i>Z</i>	2	2
<i>D</i> <sub>calc.</sub> [g·cm <sup>-3</sup> ]	2.377	2.702
<i>F</i> (000)	616	372
Diffractionmeter	STOE AED-II	STOE IPDS
2 $\theta$ -Range	3 - 54°	3 - 56°
<i>hkl</i> Ranges	-9/2, -11/11, -16/16	-5/5, -10/10, -18/19
Absorption corr.	numerical	numerical
$\mu$ (MoK $\alpha$ ) / mm <sup>-1</sup>	10.13	12.55
Max./min. transm.	0.2221/0.2610	0.1700/0.2299
Measured refl.	4957	3855
<i>R</i> <sub>int.</sub>	0.0445	0.0448
Independent refl.	3962	1666
Refl. with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	2560	1266
Refined parameters	208	110
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0374	0.0301
<i>wR</i> <sub>2</sub> [all data]	0.0980	0.0779
GoF	0.993	1.033
Min./max. res. / e·Å <sup>-3</sup>	1.08/-0.78	0.40/-0.52

Table 1. Crystal data and results of the structure refinement for catena[Cu<sub>3</sub>Br<sub>3</sub>( $\mu$ <sub>2</sub>-2-ethylpyrazine-N,N')<sub>2</sub>] (I) and poly-[Cu<sub>2</sub>Br<sub>2</sub>( $\mu$ <sub>2</sub>-2-ethylpyrazine-N,N')] (II).Table 2. Atomic coordinates [ $\cdot 10^4$ ] and equivalent isotropic displacement parameters [ $\text{Å}^2 \cdot 10^3$ ] for catena[Cu<sub>3</sub>Br<sub>3</sub>( $\mu$ <sub>2</sub>-2-ethylpyrazine-N,N')<sub>2</sub>] (I).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U <sub>eq</sub>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U <sub>eq</sub>
Cu(1)	7933(1)	7083(1)	6403(1)	73(1)	Cu(2)	7233(1)	7349(1)	8310(1)	75(1)
Cu(3)	7390(1)	10512(1)	7530(1)	53(1)	Br(1)	7809(1)	5044(1)	7429(1)	65(1)
Br(2)	9831(1)	9039(1)	8306(1)	61(1)	Br(3)	5264(1)	8623(1)	6670(1)	47(1)
N(1)	9319(6)	7625(5)	5223(3)	42(1)	C(1)	8703(7)	7519(6)	4246(4)	41(1)
C(2)	9702(7)	8030(6)	3462(4)	44(1)	N(2)	11319(6)	8635(5)	3629(3)	42(1)
C(3)	11929(7)	8733(6)	4600(4)	43(1)	C(4)	10932(8)	8241(6)	5390(4)	46(1)
C(5)	6937(9)	6779(8)	4024(5)	61(2)	C(6)	7069(12)	5157(9)	4052(7)	86(3)
N(3)	5843(7)	7741(5)	9574(4)	46(1)	C(11)	4188(9)	7287(7)	9706(4)	51(2)
C(12)	3298(8)	7744(6)	10584(4)	49(1)	N(4)	4017(6)	8627(5)	11329(4)	45(1)
C(13)	5700(7)	9020(6)	11193(4)	45(1)	C(14)	6605(8)	8596(7)	10327(4)	50(1)
C(15)	3362(11)	6275(9)	8892(6)	80(2)	C(16)	1885(17)	5332(12)	9248(9)	66(3)
C(16')	3040(40)	488(3)	900(2)	68(7)					

U<sub>eq</sub> is defined as a third of the trace of the orthogonalised U<sub>ij</sub> tensors.

Table 3. Atomic coordinates [ $\cdot 10^4$ ] and equivalent isotropic displacement parameters [ $\text{\AA}^2 \cdot 10^3$ ] for poly- $[\text{Cu}_2\text{Br}_2(\mu_2\text{-2-ethylpyrazine-N,N'})]$  (**II**).

Atom	x	y	z	$U_{\text{eq}}$
Cu(1)	6030(2)	3903(1)	7549(1)	47(1)
Cu(2)	10410(2)	1748(1)	8374(1)	48(1)
Br(1)	5402(1)	2835(1)	9187(1)	37(1)
Br(2)	10998(1)	2751(1)	6739(1)	36(1)
N(1)	7188(9)	6241(5)	7771(2)	34(1)
C(1)	6723(10)	7350(5)	7150(3)	32(1)
C(2)	7732(11)	8902(6)	7335(3)	37(1)
N(2)	9267(9)	9414(5)	8132(3)	37(1)
C(3)	9756(12)	8286(6)	8743(3)	40(1)
C(4)	8726(12)	6731(6)	8571(3)	39(1)
C(5)	5167(13)	6790(7)	6249(3)	46(1)
C(6)	4497(14)	8069(8)	5576(4)	57(2)

$U_{\text{eq}}$  is defined a third of the trace of the orthogonalised  $U_{ij}$  tensors.

is probably not thermodynamically stable at room temperature.

## Conclusion

In the present contribution we have demonstrated that the thermal decomposition of suitable CuX precursor compounds are an adequate alternative for the preparation of new coordination polymers. Dependent on the experimental conditions the compounds can be obtained as the phase pure compounds, which is favourable if these compounds cannot be prepared otherwise or if they are obtained only as mixtures from solutions. However, as we have shown in previous investigations, not all of the amine rich compounds decompose to give new amine poorer compounds and there is no simple correlation between the composition or the structure of the starting materials and their degradation.

## Experimental Section

*Synthesis - General procedures:* 2-Ethylpyrazine is commercially available. CuBr was freshly prepared as described in reference [24]. All reaction products were filtered off, washed with ethanol and diethylether and dried on air. The purity of all compounds was checked by elemental analysis and by comparing the experimental X-ray powder patterns with those calculated from single crystal data.

*Synthesis of catena* $[\text{Cu}_3\text{Br}_3(\mu_2\text{-2-ethylpyrazine-N,N'})_2]$  (**I**): 430.4 mg (3.0 mmol) CuBr and 216.3 mg (2.0 mmol) 2-ethylpyrazine were stirred in 4 ml of water

Table 4. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for catena $[\text{Cu}_3\text{Br}_3(\mu_2\text{-2-ethylpyrazine-N,N'})_2]$  (**I**) and poly- $[\text{Cu}_2\text{Br}_2(\mu_2\text{-2-ethylpyrazine-N,N'})]$  (**II**).

<i>catena</i> $[\text{Cu}_3\text{Br}_3(\mu_2\text{-2-ethylpyrazine-N,N'})_2]$ ( <b>I</b> )			
Cu(1)-N(1)	1.956(4)	Cu(1)-Br(1)	2.358(2)
Cu(1)-Br(3)	2.505(2)	Cu(1)-Cu(2)	2.549(2)
Cu(2)-N(3)	1.992(4)	Cu(2)-Br(1)	2.411(2)
Cu(2)-Br(2)	2.487(2)	Cu(2)-Br(3)	2.881(2)
Cu(3)-N(4A)	1.987(4)	Cu(3)-N(2A)	1.999(4)
Cu(3)-Br(2)	2.528(1)	Cu(3)-Br(3)	2.550(1)
N(1)-Cu(1)-Br(1)	134.9(2)	N(1)-Cu(1)-Br(3)	113.2(2)
Br(1)-Cu(1)-Br(3)	110.4(1)	N(3)-Cu(2)-Br(1)	128.6(2)
N(3)-Cu(2)-Br(2)	110.0(2)	Br(1)-Cu(2)-Br(2)	112.0(1)
N(3)-Cu(2)-Br(3)	105.6(2)	Br(1)-Cu(2)-Br(3)	97.6(1)
Br(2)-Cu(2)-Br(3)	96.7(1)	Cu(1)-Cu(2)-Br(3)	54.5(1)
N(4A)-Cu(3)-N(2A)	133.2(2)	N(4A)-Cu(3)-Br(2)	108.1(2)
N(2A)-Cu(3)-Br(2)	100.0(2)	N(4A)-Cu(3)-Br(3)	103.0(2)
N(2A)-Cu(3)-Br(3)	105.0(2)	Br(2)-Cu(3)-Br(3)	104.7(1)
<i>poly</i> $[\text{Cu}_2\text{Br}_2(\mu_2\text{-2-ethylpyrazine-N,N'})]$ ( <b>II</b> )			
Cu(1)-N(1)	2.015(4)	Cu(1)-Br(2A)	2.4502(7)
Cu(1)-Br(2)	2.5103(9)	Cu(1)-Br(1)	2.6063(8)
Cu(1)-Cu(2)	2.8455(9)	Cu(2)-N(2A)	2.014(4)
Cu(2)-Br(1B)	2.4208(7)	Cu(2)-Br(1)	2.5040(8)
Cu(2)-Br(2)	2.5810(8)	Br(1)-Cu(2A)	2.4208(7)
N(1)-Cu(1)-Br(2A)	126.2(1)	N(1)-Cu(1)-Br(2)	106.1(2)
Br(2A)-Cu(1)-Br(2)	105.6(1)	N(1)-Cu(1)-Br(1)	104.0(2)
Br(2A)-Cu(1)-Br(1)	103.1(1)	Br(2)-Cu(1)-Br(1)	111.7(1)
N(2A)-Cu(2)-Br(1A)	125.4(1)	N(2A)-Cu(2)-Br(1)	105.4(2)
Br(1A)-Cu(2)-Br(1)	106.7(1)	N(2A)-Cu(2)-Br(2)	102.0(2)
Br(1A)-Cu(2)-Br(2)	104.6(1)	Br(1)-Cu(2)-Br(2)	112.7(1)

at room temperature. After 3 d the deep orange precipitate was filtered off. Yield: 92.0 %. Elemental analysis for **I** (646.64) calcd. C 22.29, N 8.66, H 2.49; found C 21.96, N 8.46, H 2.42. Preparation of single crystals: 71.7 mg (0.5 mmol) CuBr and 54.1 mg (0.5 mmol) 2-ethylpyrazine were reacted in 4 ml of water in a glass container which was embedded in a teflon-lined steel autoclaves at 120 °C for 7 d under hydrothermal conditions. The product consisted of deep orange crystals of compound **I** and a microcrystalline powder of compound **II**.

*Synthesis of poly* $[\text{Cu}_2\text{Br}_2(\mu_2\text{-2-ethylpyrazine-N,N'})]$  (**II**): 143.5 mg (1.0 mmol) CuBr and 54.1 mg (0.5 mmol) 2-ethylpyrazine were reacted in 1.5 ml of acetonitrile in a sealed glass ampoule at 100 °C for 7 d. The precipitate consisted of light orange crystals and a microcrystalline powder. Yield: 91.0 %. Elemental analysis for **II** (395.04): calcd. C 18.24, N 7.09, H 2.04; found C 18.29, N 7.14, H 1.96.

*Crystal structure determination:* All structure solutions were performed with direct methods using SHELXS-97 [25]. The structure refinements were performed against  $F^2$  using SHELXL-97 [26]. For both compounds a numerical absorption correction was applied using X-Red [27] and X-Shape [28]. All non-hydrogen

atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealised geometry and refined with fixed isotropic displacement parameters using a riding model. In compound **I** the carbon atom C16 is disordered in two positions and was refined using a split model and site occupation factors of 70:30. All crystals of compound **II** were non-merohedrally twinned. The reflection of both individuals were indexed using Recipe [29] and integrated separately using Twin [29].

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 191292 (**I**), (CCDC 191293 (**II**)). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1E2, UK (fax: int.Code +(44)01223/3 36-033, e-mail: deposit@chemcryst.cam.ac.uk).

*X-ray powder diffraction experiments:* X-Ray powder diffraction experiments were performed using a STOE STADI P transmission powder diffractometer with an 4° PSD (position sensitive detector) using Cu-K $\alpha$ -radiation ( $\lambda = 1.540598 \text{ \AA}$ ). For temperature or time dependent X-ray powder diffraction the diffractometer was equipped with a graphite oven and a position sensitive detector (scan range: 5° - 50°) from STOE & CIE. All temperature resolved X-ray powder experiments were performed in glass capillaries under a static air atmosphere.

*Differential thermal analysis, thermogravimetry and mass spectroscopy:* TG measurements were performed in Al<sub>2</sub>O<sub>3</sub> crucibles using a STA-429 thermobalance from Netzsch. Several measurements under a nitrogen atmosphere (purity 5.0) with different heating rates with and without capes were performed. DTA-TG-MS measurements were performed simultaneously 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 a dynamic helium atmosphere (purity: 4.6) using heating rates of 1, 4 and 8 °C/min. All measurements were performed with a flow rate of 75 ml/min. and were corrected for buoyancy and current effects.

*Elemental analysis:* C, H, N analysis was performed using a CHN-O-RAPID combustion analyser from Heraeus. Elemental analysis (%) of the residues obtained during the thermal decomposition of **I**, calculated for (**II**): C 18.24, N 7.09, H 2.04; found C 17.96, N 6.97, H 1.92.

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