



Synthesis, crystal structures and thermal properties of new copper(I)halide 2-ethylpyrazine coordination polymers: the influence of solid-state kinetics on product formation

Christian Näther* and Inke Jeß

Institut für Anorganische Chemie, Universität zu Kiel, Olshausenstr. 40 (Otto-Hahn-Platz 6-7), D-24098-Kiel, Germany

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Abstract

Three new copper(I) coordination polymers were prepared by the reaction of copper(I) chloride with 2-ethylpyrazine in water at room temperature or under solvothermal conditions. In poly[CuCl(μ_2 -2-ethylpyrazine-*N,N'*)] (**I**), “zig-zag”-like CuCl chains are present, which are connected by the 2-ethylpyrazine ligand to a three-dimensional network. In comparison in catena[Cu₃Cl₃(μ_2 -2-ethylpyrazine-*N,N'*)₂] (**II**) six-membered Cu₃Cl₃ rings occur, which are connected to chains by the organic ligands. In poly[Cu₂Cl₂(μ_2 -2-ethylpyrazine-*N,N'*)] (**III**), CuCl double chains are found, which are linked by the ligands to form sheets. The thermal behaviour of the different compounds was investigated using simultaneous thermogravimetry, differential thermoanalysis and mass spectroscopy as well as temperature-dependent X-ray powder diffraction. Two mass steps are found upon heating compound **I** in a thermobalance with 1°C/min, where the first corresponds to the transformation into compound **III**, and the second to the loss of the remaining ligands under formation of CuCl. If the heating rate is increased to 16°C/min, compound **II** is formed as an intermediate in a consecutive reaction. Therefore, the product formation depends on the actual heating rate, which shows that the solid-state kinetics plays an important role in such thermal reactions.

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Keywords: Coordination polymers; Synthesis; Crystal structure; Thermal analysis; Solid-state kinetics

1. Introduction

The rational design of extended arrays based on multidimensional coordination polymers is of great current interest [1–10]. An important goal in this area is the preparation of compounds with useful physical properties [11–17]. However, for good characterization, the preparation of pure and large amounts of a material is required. For coordination polymers this is sometimes difficult to achieve because the synthesis is usually performed in solution using “normal” or solvothermal conditions. This often leads to mixtures of different compounds, or in some cases compounds are overlooked or cannot be prepared in solution. This is often the case for this class of compounds [18–22]. An alternative preparation method is the controlled thermal

decomposition of suitable precursor compounds. This possibility was demonstrated by us for several coordination polymers based on copper(I) halides or pseudohalides and aromatic amine ligands [18–22]. A part of our interest in these compounds lies in their luminescence and thermoluminescence properties, which are found in several of these coordination polymers. These compounds consist of typical Cu_xX substructures (X = Cl, Br, I, CN, SCN) that are connected by organic ligands forming multidimensional coordination polymers [18–35]. For one definite copper(I)halide or pseudohalide and one definite ligand often several compounds are found that differ in the ratio between the inorganic and organic part. We have demonstrated that most amine-rich compounds transform into pure copper halides or pseudohalides upon heating via amine-poor compounds as intermediates, whereas others transform directly to the copper(I) halides or pseudohalides [18–22]. In some cases more than one intermediate phase is observed.

*Corresponding author. Fax: +49-431-880-1520.

E-mail address: cnaether@ac.uni-kiel.de (C. Näther).

Starting from these results, we have systematically investigated the thermal properties of these coordination polymers. During our investigations on the copper(I) chloride 2-ethylpyrazine compounds, we found that product formation depends on the heating rate in the thermogravimetry measurements. This demonstrates that solid-state kinetics may play an important role in these thermal reactions. Here, we report on our investigations.

2. Experimental section

2.1. Synthesis

General procedures: All educts were commercially purchased. All reaction products were filtered off, washed with ethanol and diethylether and dried in air. The purity of all compounds was checked by elemental analysis and by comparing experimental X-ray powder patterns with those calculated from single-crystal data.

Synthesis of I: An amount of 99.0 mg (1.0 mmol) CuCl and 108.1 mg (1.0 mmol) 2-ethylpyrazine were stirred in

5 mL of water at room temperature. After 2 days the red-coloured precipitate was filtered off. Yield: 84.3%. Elemental analysis (%) theoretical: C: 34.79, N: 13.52, H: 3.89; measured: C: 34.192, N: 13.584, H: 3.433. Preparation of single crystals: 99.0 mg (1 mmol) CuCl and 216.2 mg (2.0 mmol) 2-ethylpyrazine were reacted in 3 mL acetonitrile at room temperature without stirring. After 3 days red-coloured crystals formed.

Synthesis of II: An amount of 148.5 mg (1.5 mmol) CuCl and 108.1 mg (1 mmol) 2-ethylpyrazine were stirred in 3 mL of water at room temperature. After 4 days the red-coloured precipitate was filtered off. Yield: 88.0%. Elemental analysis (%) theoretical for (II): C: 28.08, N: 10.92, H: 3.14; measured: C: 28.21, N: 11.13, H: 3.10. Preparation of single crystals: 148.5 mg (1.5 mmol) CuCl and 108.1 mg (1.0 mmol) 2-ethylpyrazine were reacted in 5 mL water at 115°C using hydrothermal conditions. After 5 days red-coloured crystals of II, as well as yellow-coloured crystals of III formed.

Synthesis of III: An amount of 49.5 mg (0.5 mmol) CuCl and 54.05 mg (0.5 mmol) 2-ethylpyrazine were reacted in 3 mL water at 125°C using hydrothermal conditions. After 5 days yellow–orange coloured crystals

Table 1

Crystal data and results of the structure refinement for poly[CuCl(μ_2 -2-ethylpyrazine-*N,N'*)] (I), catena[Cu₃Cl₃(μ_2 -2-ethylpyrazine-*N,N'*)₂] (II) and poly[Cu₂Cl₂(μ_2 -2-ethylpyrazine-*N,N'*)] (III)

Compound	I	II	III
Formula	C ₆ H ₈ N ₂ CuCl	C ₁₂ H ₁₆ N ₄ Cu ₃ Cl ₃	C ₆ H ₈ N ₂ Cu ₂ Cl ₂
MW (g mol ⁻¹)	207.14	513.28	306.15
Crystal colour	Red	Red	Yellow–orange
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	6.7771(4)	7.363(2)	3.8103(3)
<i>b</i> (Å)	9.3452(6)	9.024(2)	8.2770(4)
<i>c</i> (Å)	12.1533(9)	12.963(2)	28.666(2)
α (deg)	—	87.08(2)	—
β (deg)	—	104.452 (7)	91.01
γ (deg)	—	88.40(2)	—
<i>V</i> (Å ³)	769.7(1)	859.8 (3)	903.9(1)
Temperature (K)	293	293	293
<i>Z</i>	4	2	2
<i>D</i> _{calc.} (g cm ⁻³)	1.787	1.983	2.249
<i>F</i> (000)	416	508	600
Diffractometer	STOE IPDS	Nonius CAD4	STOE IPDS
2 θ -range	3–60°	3–54°	3–50°
<i>hkl</i> ranges	–8/8, –12/12, –16/16	0/8, –10/10, –15/15	–4/4, –9/9, –33/34
Absorption corr.	None	Numerical	Numerical
μ (MoK α) (mm ⁻¹)	3.10	4.14	5.23
Max./min. transm.	—	0.5144/0.5883	0.3811/0.5737
Measured refl.	7517	3912	6303
<i>R</i> _{int}	0.0509	0.0231	0.0447
Independent refl.	1813	3630	1513
Refl. with <i>I</i> > 2 σ (<i>I</i>)	1661	2058	1329
Refined parameters	92	199	110
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0311	0.0427	0.0459
w <i>R</i> ₂ [all data]	0.0813	0.1240	0.1335
GoF	1.050	1.008	1.245
Min./max. res. (e Å ⁻³)	0.51/–0.56	1.12/–0.86	0.99/–0.87

Table 2

Atomic coordinates [104] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for poly[CuCl(μ_2 -2-ethylpyrazine-*N,N'*)] (**I**)

	<i>X</i>	<i>Y</i>	<i>Z</i>	U_{eq}
Cu(1)	5944 (1)	6167 (1)	4980 (1)	31 (1)
Cl(1)	7487 (1)	8529 (1)	5186 (1)	32 (1)
N(1)	6949 (4)	5185 (3)	6352 (2)	28 (1)
N(2)	8297 (4)	4316 (3)	8407 (2)	32 (1)
C(1)	5970 (5)	4197 (3)	6937 (2)	30 (1)
C(2)	6661 (5)	3793 (4)	7969 (2)	34 (1)
C(3)	9329 (5)	5241 (4)	7794 (2)	33 (1)
C(4)	8644 (5)	5676 (4)	6780 (2)	33 (1)
C(5)	4196 (6)	3479 (4)	6459 (3)	44 (1)
C(6)	4757 (10)	2261 (6)	5707 (6)	88 (2)

 U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensor.

have formed which were suitable for X-ray structure analysis. Yield: 73.2%. Elemental analysis (%) theoretical for (**III**): C: 23.54, N: 9.15, H: 2.63; measured: C: 23.7, N: 8.98, H: 2.63.

2.2. Crystal structure investigation

Crystal structure determination: All structure solutions were performed using direct methods with SHELXS-97 [36]. The structure refinements were made against F^2 using SHELXL-97 [37]. For compounds **II** and **III**, a numerical absorption correction was applied using X-Red [38] and X-Shape [39]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding model. The absolute structure for compound **I** was determined and is in agreement with the selected setting Flack-*x*-Parameter: 0.03 [2]. In addition, inversion of the structure model leads to significantly poorer reliability factors after structure refinement ($R1$ for 1661 reflections with $I > 4\sigma(I) = 0.440$; $wR2$ for all 1813 reflections = 0.1201; Flack-*x*-parameter: 0.97 [3]). Selected crystal data, details of the structure refinement, as well as the atomic coordinates and isotropic displacement parameters are given in Tables 1–4.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 191302 (**I**), CCDC 191303 (**II**), CCDC 191304 (**III**)). 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).

2.3. 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)

Table 3

Atomic coordinates [104] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] catena[Cu₃Cl₃(μ_2 -2-ethylpyrazine-*N,N'*)₂] (**II**)

	<i>X</i>	<i>Y</i>	<i>Z</i>	U_{eq}
Cu(1)	7301 (1)	10471 (1)	7525 (1)	56 (1)
Cu(2)	7462 (1)	7332 (1)	6636 (1)	74 (1)
Cu(3)	7840 (1)	7084 (1)	8620 (1)	79 (1)
Cl(1)	7877 (3)	5184 (2)	7576 (1)	67 (1)
Cl(2)	9745 (2)	9098 (2)	6731 (1)	63 (1)
Cl(3)	5295 (2)	8637 (2)	8335 (1)	55 (1)
N(1)	9323 (6)	7620 (5)	9770 (3)	44 (1)
C(1)	8704 (7)	7509 (6)	10752 (4)	45 (1)
C(2)	9770 (7)	8014 (6)	11524 (4)	47 (1)
N(2)	11396 (6)	8626 (5)	11341 (3)	42 (1)
C(3)	11980 (7)	8728 (6)	10366 (4)	43 (1)
C(4)	10947 (7)	8232 (6)	9591 (4)	46 (1)
C(5)	6869 (8)	6812 (7)	11001 (5)	61 (2)
C(6)	7024 (12)	5148 (9)	10972 (7)	92 (3)
N(3)	6029 (6)	7780 (5)	5387 (3)	47 (1)
C(11)	4321 (8)	7328 (6)	5255 (4)	49 (1)
C(12)	3425 (8)	7764 (7)	4364 (4)	52 (2)
N(4)	4165 (6)	8643 (5)	3618 (3)	45 (1)
C(13)	5872 (7)	9070 (6)	3758 (4)	45 (1)
C(14)	6783 (8)	8642 (7)	4633 (4)	47 (1)
C(15)	3466 (11)	6318 (9)	6091 (5)	82 (2)
C(16)	1991 (14)	5391 (11)	5786 (7)	116 (4)

 U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensors.

Table 4

Atomic coordinates [104] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] poly[Cu₂Cl₂(μ_2 -2-ethylpyrazine-*N,N'*)] (**III**)

	<i>X</i>	<i>Y</i>	<i>Z</i>	U_{eq}
Cu(1)	4095 (3)	5948 (1)	1267 (1)	53 (1)
Cu(2)	−552 (3)	8253 (1)	771 (1)	51 (1)
Cl(1)	8983 (4)	7116 (2)	1600 (1)	37 (1)
Cl(2)	4634 (4)	7115 (2)	433 (1)	37 (1)
N(1)	2905 (15)	3649 (7)	1123 (2)	35 (1)
C(1)	3257 (16)	2454 (8)	1444 (2)	32 (1)
C(2)	2210 (18)	904 (8)	1327 (2)	35 (2)
N(2)	712 (14)	522 (7)	915 (2)	33 (1)
C(3)	412 (19)	1730 (8)	602 (2)	38 (2)
C(4)	1510 (20)	3261 (8)	708 (2)	40 (2)
C(5)	4723 (19)	2897 (9)	1910 (3)	42(2)
C(6)	5480 (20)	1522 (12)	2242 (3)	56(2)

 U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensors.

using CuK α -radiation ($\lambda = 1.540598 \text{\AA}$). The diffractometer is equipped with a graphite furnace and a position sensitive detector (scan range: 5–50°) from STOE & CIE) for temperature or time-dependent X-ray powder diffraction. All temperature-dependent X-ray powder experiments were performed in glass capillaries in air.

2.4. Differential thermal analysis (DTA), thermogravimetry (TG) and mass spectroscopy (MS)

DTA-TG measurements were performed in Al₂O₃ crucibles simultaneously using an STA-429 and

STA-409CD balance from Netzsch. Several measurements were made under an argon, nitrogen and air atmosphere with heating rates of 1 and 4°C/min. DTA-TG-MS measurements were performed simultaneously using the STA-409CD with Skimmer coupling from Netzsch that 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 Al₂O₃ crucibles under a flowing helium atmosphere (purity: 4.6) using heating rates of 1, 4 and 8°C/min. For the heating-rate-dependent measurements, the instrument is equipped with a Pt–Rh furnace. All measurements were performed with a flow rate of 75 mL/min, and were corrected for buoyancy and current effects.

2.5. Elemental analysis

C, H and N analysis were performed using a CHN-O-RAPID combustion analyser from Heraeus. Elemental

analysis (%) of the residues obtained during the thermal decomposition of **I**: theoretical for (**II**): C: 28.08, N: 10.92, H: 3.14; measured: C: 27.81, N: 10.71, H: 3.03 (obtained with 16°C/min); theoretical for (**III**): C: 23.54, N: 9.15, H: 2.63; measured: C: 23.72, N: 9.33, H: 2.74 (obtained with 0.5°C/min).

3. Results and discussion

3.1. Crystal structures

The 1:1 compound poly[CuCl(μ_2 -2-ethylpyrazine-*N,N'*)] (**I**) crystallizes in the orthorhombic chiral space group $P2_12_12_1$ with four formula units in the unit cell and all atoms are located in general positions. The copper atoms are surrounded by two symmetry-related chloride atoms and two symmetry-related 2-ethylpyrazine ligands in a distorted tetrahedron (Fig. 1 and

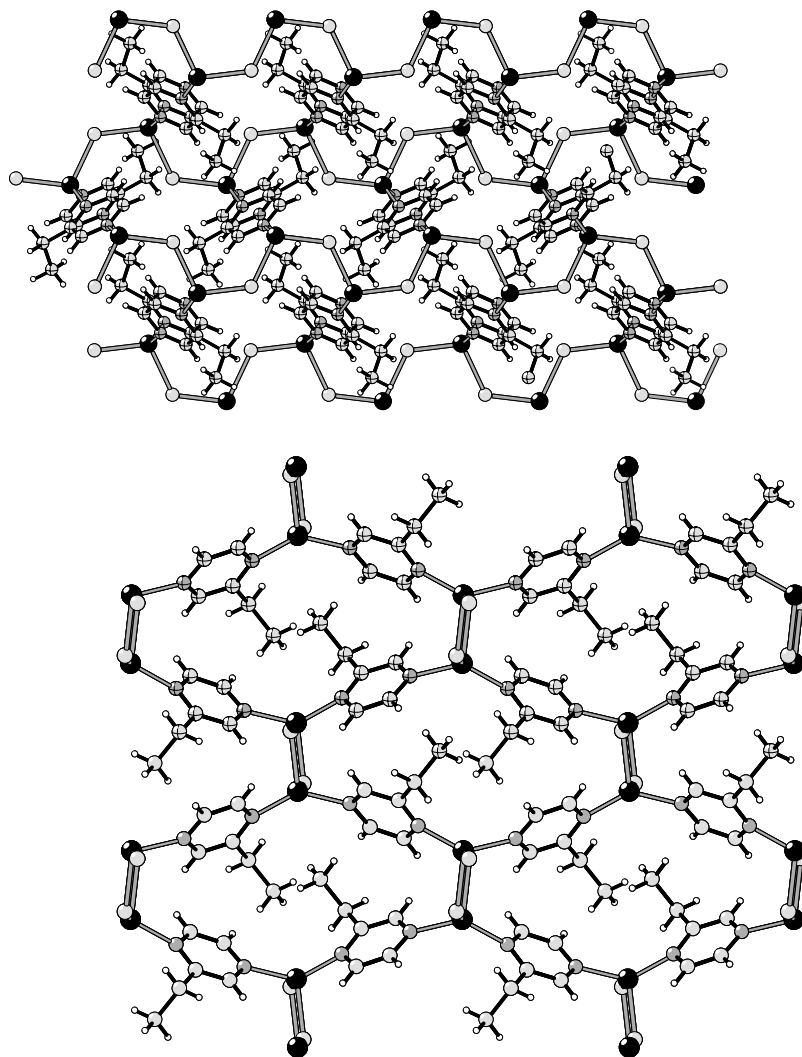


Fig. 1. Crystal structure of poly[CuCl(μ_2 -2-ethylpyrazine-*N,N'*)] (**I**) projected on (001) showing the zig-zag-like CuCl chains (top) and projected on (010) (bottom).

Table 5

Selected bond lengths (Å) and angles (deg) for poly[CuCl(μ_2 -2-ethylpyrazine- N,N')] (**I**), catena[Cu₃Cl₃(μ_2 -2-ethylpyrazine- N,N')₂] (**II**) and poly[Cu₂Cl₂(μ_2 -2-ethylpyrazine- N,N')] (**III**).

<i>Poly[CuCl(μ_2-2-ethylpyrazine-N,N')] (I)</i>			
Cu(1)–N(1)	2.021 (2)	Cu(1)–N(2)	2.031 (2)
Cu(1)–Cl(1)	2.369 (1)	Cu(1)–Cl(1)	2.456 (1)
N(1)–C(1)	1.340 (4)	N(1)–C(4)	1.341 (4)
N(2)–C(2)	1.323 (4)	N(2)–C(3)	1.338 (4)
N(1)–Cu(1)–N(2)	126.2 (1)	N(1)–Cu(1)–Cl(1)	117.3 (1)
N(2)–Cu(1)–Cl(1)	101.4 (1)	N(1)–Cu(1)–Cl(1)	100.4 (1)
N(2)–Cu(1)–Cl(1)	100.8 (1)	Cl(1)–Cu(1)–Cl(1)	108.8 (1)
<i>Catena[Cu₃Cl₃(μ_2-2-ethylpyrazine-N,N')₂] (II)</i>			
Cu(1)–N(2A)	1.988 (4)	Cu(1)–N(4)	1.990 (4)
Cu(1)–Cl(3)	2.404 (2)	Cu(1)–Cl(2)	2.417 (2)
Cu(2)–N(3)	1.981 (4)	Cu(2)–Cl(1)	2.260 (2)
Cu(2)–Cl(2)	2.330 (2)	Cu(2)–Cu(3)	2.593 (1)
Cu(3)–N(1)	1.953 (4)	Cu(3)–Cl(1)	2.237 (2)
Cu(3)–Cl(3)	2.362 (2)		
N(2)–Cu(1)–N(4)	132.0 (2)	N(2)–Cu(1)–Cl(3)	106.3 (2)
N(4)–Cu(1)–Cl(3)	103.1 (2)	N(2)–Cu(1)–Cl(2)	100.6 (2)
N(4)–Cu(1)–Cl(2)	106.8 (2)	Cl(3)–Cu(1)–Cl(2)	105.7 (1)
N(3)–Cu(2)–Cl(1)	131.0 (2)	N(3)–Cu(2)–Cl(2)	109.5 (2)
Cl(1)–Cu(2)–Cl(2)	115.8 (1)	N(3)–Cu(2)–Cu(3)	152.7 (2)
N(1)–Cu(3)–Cl(1)	133.9 (2)	N(1)–Cu(3)–Cl(3)	114.4 (2)
Cl(1)–Cu(3)–Cl(3)	111.5 (1)		
<i>Poly[Cu₂Cl₂(μ_2-2-ethylpyrazine-N,N')] (III)</i>			
Cu(1)–N(1)	1.998 (6)	Cu(1)–Cl(1)	2.292 (2)
Cu(1)–Cl(1A)	2.389 (2)	Cu(1)–Cl(2)	2.590 (2)
Cu(1)–Cu(2)	2.950 (2)	Cu(2)–N(2A)	1.980 (5)
Cu(2)–Cl(2A)	2.265 (2)	Cu(2)–Cl(2)	2.408 (2)
Cu(2)–Cl(1A)	2.565 (2)		
N(1)–Cu(1)–Cl(1)	131.9 (2)	N(1)–Cu(1)–Cl(1)	106.5 (2)
Cl(1)–Cu(1)–Cl(1)	109.0 (1)	N(1)–Cu(1)–Cl(2)	100.7 (2)
Cl(1)–Cu(1)–Cl(2)	98.7 (1)	Cl(1)–Cu(1)–Cl(2)	107.3 (1)
N(2)–Cu(2)–Cl(2)	132.5 (2)	N(2)–Cu(2)–Cl(2)	104.8 (2)
Cl(2)–Cu(2)–Cl(2)	109.2 (1)	N(2)–Cu(2)–Cl(1)	100.1 (2)
Cl(2)–Cu(2)–Cl(1)	100.1 (1)	Cl(2)–Cu(2)–Cl(1)	107.5 (1)

Table 5). Bond lengths and angles around the copper atoms fall in the range of those reported for similar coordination polymers [18–35]. The inorganic part of the structure consists of “ziz-zag”-like, coplanar CuCl chains which are parallel to the crystallographic c -axis. These chains are linked via μ - N,N' coordination by the organic ligands to form a three-dimensional network (Fig. 1).

The 3:2 compound catena[Cu₃Cl₃(μ_2 -2-ethylpyrazine- N,N')₂] (**II**) crystallizes in the triclinic space group P -1 with two formula units in the unit cell and all atoms are located in general positions. The Cu X substructure consists of six-membered Cu₃Cl₃ rings in an irregular conformation (Fig. 2). One of the three crystallographically independent copper atoms is connected to two crystallographically independent chloride atoms and two crystallographically independent 2-ethylpyrazine ligands. The other two copper atoms are only three coordinated by two crystallographically independent chloride atoms and one nitrogen ligand. The coordina-

tion sphere of the copper atoms is completed by one Cu–Cu contact of 2.593 Å. Therefore, d^{10} – d^{10} interactions may play an important role in the stabilization of the rings [40]. The CuCl bond lengths of the three-coordinated copper atoms are significantly shortened compared to those of the four-coordinated copper atom (Table 5). The Cu₃Cl₃ rings are connected by the organic ligands via μ - N,N' coordination forming double chains that are parallel to the crystallographic c -axis (Fig. 2).

The 2:1 compound poly[Cu₂Cl₂(μ_2 -2-ethylpyrazine- N,N')] (**III**) crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell and all atoms are located in general positions. Each copper atom is connected to three chloride atoms and one 2-ethylpyrazine ligand forming a distorted tetrahedron (Fig. 3 and Table 1). Bond lengths and angles around the copper atoms are similar to those in other Cu X coordination compounds [18–35]. The Cu X substructure consists of CuCl double chains that are connected by the 2-ethylpyrazine via μ - N,N coordination forming sheets parallel to (001). This structural motive is frequently found in Cu X coordination polymers of the general composition Cu₂X₂(base).

3.2. Thermoanalytical investigations

On heating the 1:1 compound **I** in the DTA-TG-MS experiment at 1°C/min, two endothermic events are observed at approximately 119°C and 172°C in the DTA curve and they are accompanied by two steps in the TG curve (Fig. 4). It is obvious from the DTG curve that both thermal reactions are well separated. The measured mass loss is in good agreement with that expected for the removal of one-half of the 2-ethylpyrazine ligands in each step (Δm_{calc} : $-\frac{1}{2}$ 2-ethylpyrazine = 26.1%). This proposal is further supported by mass spectroscopic investigations that show that only 2-ethylpyrazine ($m/z = 108$) is emitted (Fig. 4). Therefore, during the first reaction a 2:1 compound Cu₂Cl₂(2-ethylpyrazine) should have formed.

We undertook an additional TG experiment using a heating rate of 0.5°C/min to test this assumption. The measurement was stopped after the first mass loss at about 120°C and the residue was investigated using elemental analysis (see experimental part) and X-ray powder diffraction. The X-ray powder pattern of this residue is in good agreement with that calculated from single-crystal data for compound **III** (Fig. 5).

To get further insight into this thermal reaction heating rate dependent TG measurements were performed (Fig. 6). If the heating rate is increased to 16°C/min, the first mass loss decreases continuously to a value which is expected for the removal of $\frac{2}{3}$ of the organic ligands (Fig. 6). Therefore, a phase of composition Cu₃Cl₃(2-ethylpyrazine)₂ should have formed.

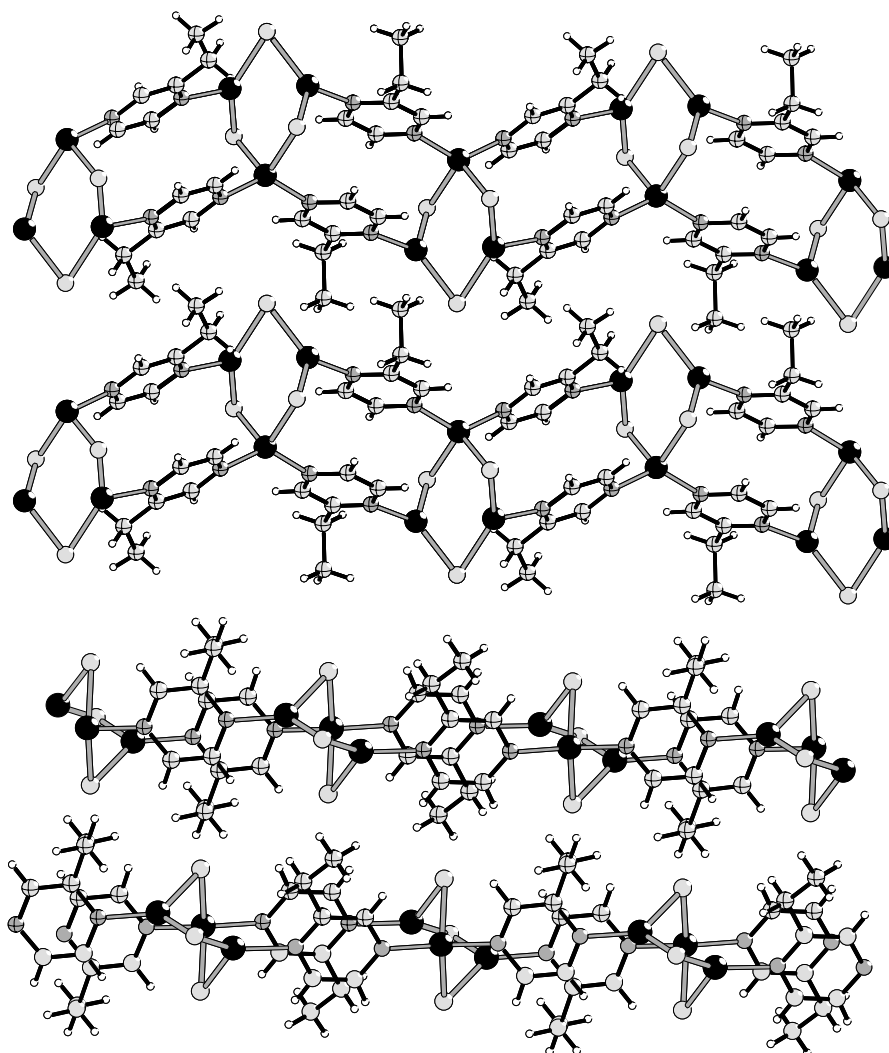


Fig. 2. Crystal structure of $\text{catena}[\text{Cu}_3\text{Cl}_3(\mu_2\text{-2-ethylpyrazine-}N,N')_2]$ (**II**) projected on (100) (top) and (010) (bottom).

If the thermal reaction is stopped after the first step using heating rates of $16^\circ\text{C}/\text{min}$, and the residue is characterized by elemental analysis (experimental section) and X-ray powder diffraction, one can show that the 3:2 compound **II** is formed (Fig. 7).

From TG measurements especially with $16^\circ\text{C}/\text{min}$, one can assume that the thermal reaction occurs in consecutive steps. However, to prove this and to exclude the possibility that parallel reactions are involved, we investigated pure **II** by thermogravimetric measurements and X-ray powder diffraction. The experimental mass loss during the thermal decomposition is in good agreement with that expected for the removal of $\frac{1}{4}$ of the organic ligands and the residue after the first TG step consists of pure **III** (Fig. 8). Therefore, compound **II** is an intermediate phase formed during the decomposition of **III** and a consecutive reaction exists. These measurements show that the kinetics play an important role in this reaction.

In some of the TG curves using faster heating rates additional reactions seem to occur that should correspond to the formation of a 4:1 or a 6:1 phase (Fig. 6). Therefore, we undertook additional TG experiments using heating rates of 1 and $16^\circ\text{C}/\text{min}$ starting with compounds **II** and **III** (Fig. 8). There was no hint for the occurrence of additional phases and the mass loss corresponded well with that expected. The thermal events in the TG curves with faster heating rates are not well resolved and a precise interpretation is difficult. However, in several additional TG experiments on all three compounds we isolated different residues at different temperatures where an 4:1 or 6:1 compound could exist. However, all diffraction patterns of these residues can be interpreted on the basis of mixtures of **II**, **III** and pure copper chloride. There is no hint of other phases.

To be sure that no intermediate was overlooked and to prove the sequence of the reaction, we performed

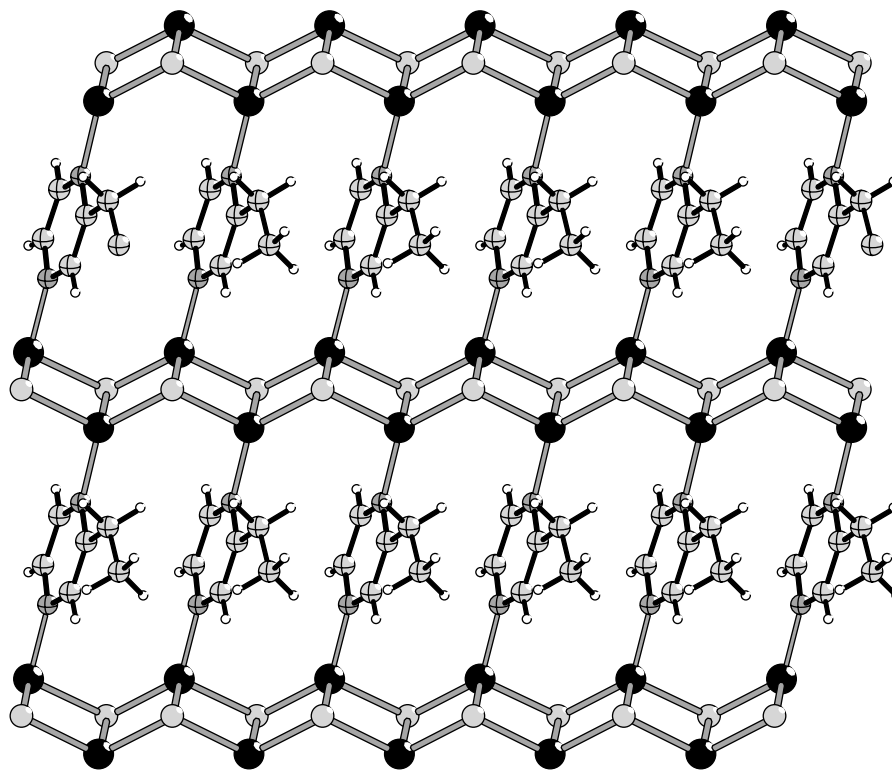


Fig. 3. Crystal structure of poly[Cu₂Cl₂(μ₂-2-ethylpyrazine-*N,N'*)] (**III**) projected on (001).

several measurements with temperature-dependent X-ray diffraction (Fig. 9). When compound **I** was investigated, a dramatic change in the diffraction pattern was observed leading to the formation of compound **II** starting at about 110°C. Compared to our TG investigations this phase is stable over a large temperature range and at about 180°C the transition into compound **III** is observed. Above about 190°C, the diffraction pattern gets lost because the compound was no longer in the X-ray beam. Several of such measurements showed that at this temperature the transition into copper(I) chloride occurs. We made several measurements using temperature-dependent X-ray powder diffraction on compounds **II** and **III** concerning the occurrence of a new 4:1 or a 6:1 phase. In agreement with the results presented above, we found no hints for intermediate compounds. The higher thermal stability of the phases observed in the temperature-dependent X-ray powder measurements and the fact that all transitions are shifted to higher temperatures may be due to different experimental conditions. In the X-ray measurements thin glass capillaries were used and static conditions were applied. Thus, the reaction took place in part in a self-produced atmosphere filled with the emitted amine, whereas in the TG measurements all gaseous products were rapidly transported out of the crucible. This proposal is supported by additional TG experiments in which for example crucibles with caps

were used. This affected the form of the TG curves and the stability range of all phases dramatically. It is well known that the experimental conditions like atmosphere, gas flow, the history of the sample and the kind of crucible have a large influence on thermal decomposition reactions, which makes these investigations difficult and complicated.

3.3. Synthetic aspects

The new 1:1 compound poly[CuCl(μ₂-2-ethylpyrazine-*N,N'*)] (**I**) can be prepared phase pure and in high yields by the reaction of CuCl and 2-ethylpyrazine at room temperature. The 2:1 compound poly[Cu₂Cl₂(μ₂-2-ethylpyrazine-*N,N'*)] (**III**) is in comparison always obtained as a phase mixture at room temperature. This compound can be obtained phase pure if the synthesis is performed using solvothermal conditions at about 125°C. That show that this phase, in agreement with our thermal investigations, should be more stable thermodynamically at higher temperatures. The second phase, which occurs during the room temperature synthesis of compound **II**, consists of the 3:2 compound catena-[Cu₃Cl₃(μ₂-2-ethylpyrazine-*N,N'*)₂] (**II**), which was first identified in our thermal measurements (see thermo-analytical investigations). Later, we showed that compound **II** can also be prepared at room temperature. These results are in agreement with our previous

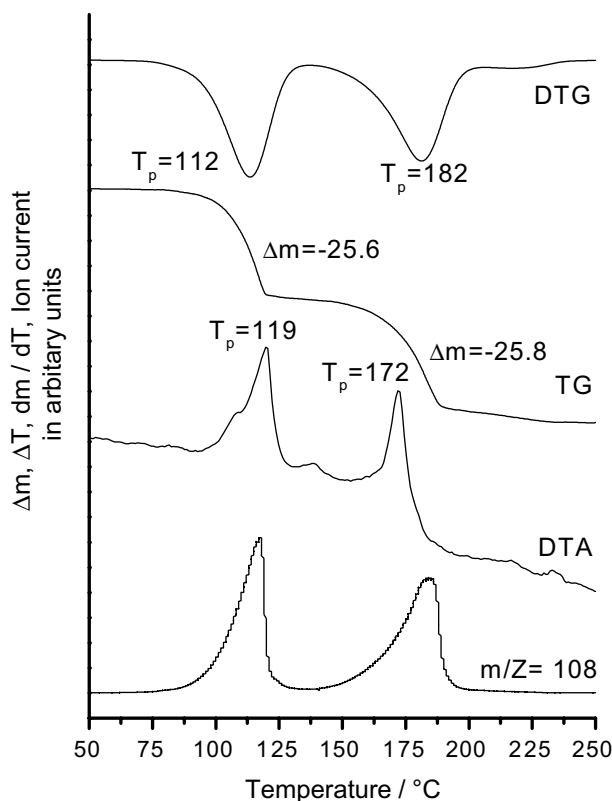


Fig. 4. DTA, TG, DTG and MS trend scan curve for poly[CuCl(μ_2 -2-ethylpyrazine-*N,N'*)] (I) (simultaneous measurement; powder; weight: 21.8 mg; heating rate: 1°C/min; dynamic helium atmosphere; flow rate: 75 mL/min; $m/z = 108$ (2-ethylpyrazine); Al₂O₃-crucible; The mass changes are given in percentage and the peak temperatures T_p in °C).

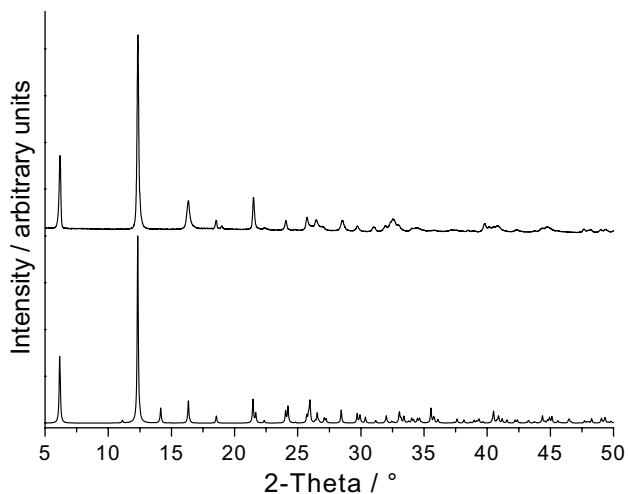


Fig. 5. X-ray powder pattern measured for the residue obtained at 120°C after the first transition in a TG experiment with 0.5°C/min from the thermal decomposition of poly[CuCl(μ_2 -2-ethylpyrazine-*N,N'*)] (I) (top) and calculated powder pattern for the 2:1 compound poly[Cu₂Cl₂(μ_2 -2-ethylpyrazine-*N,N'*)] (II) (bottom).

investigations, which show that the coordination polymers with CuCl are available more easily. Therefore, they should become more stable on going to amine-rich

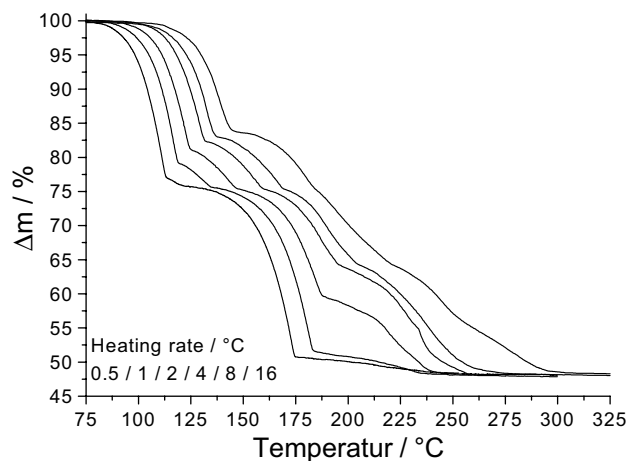


Fig. 6. Heating-rate-dependent TG curves for poly[CuCl(μ_2 -2-ethylpyrazine-*N,N'*)] (I) (Al₂O₃ crucibles without cap).

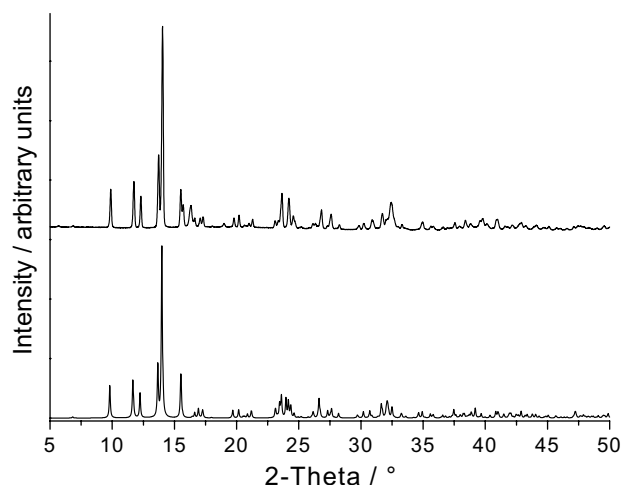


Fig. 7. X-ray powder pattern measured for the residue obtained at 148°C after the first transition in a TG experiment with 16°C/min from the thermal decomposition of poly[CuCl(μ_2 -2-ethylpyrazine-*N,N'*)] (I) (top) and calculated powder pattern for the 3:2 compound catena [Cu₃Cl₃(μ_2 -2-ethylpyrazine-*N,N'*)₂] (II) (bottom).

compounds, whereas for compounds with CuI an opposite trend is observed [18–22]. In practically all copper(I) halide coordination polymers, the ligands coordinated to the copper atoms are exchanged successively by halide atoms on going to the amine-poorer compounds. Because copper(I) cations are soft Lewis acids and the softness of the halide atoms increases from chlorine to iodine, the amine-poorer compounds with CuI should be more stable than those with CuCl. However, the observations made for the present CuCl compounds cannot be explained easily with this simple concept because in this case the amine-rich compounds are more easily available than the amine-poorer compounds. Because nitrogen ligands should be slightly harder than chloride atoms an opposite trend is expected. However, there are other

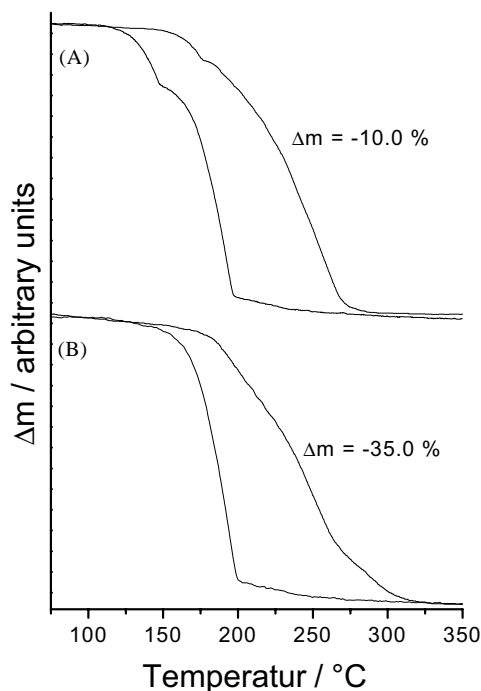


Fig. 8. TG curves for catena[Cu₃Cl₃(μ₂-2-ethylpyrazine-*N,N'*)₂] (**II**) (top) and poly[Cu₂Cl₂(μ₂-2-ethylpyrazine-*N,N'*)] (**III**) (bottom) using heating rates of 1 and 16°C/min (simultaneous measurement; powder; dynamic nitrogen atmosphere; flow rate: 75 mL/min; Al₂O₃-crucible; given are the mass changes (%)).

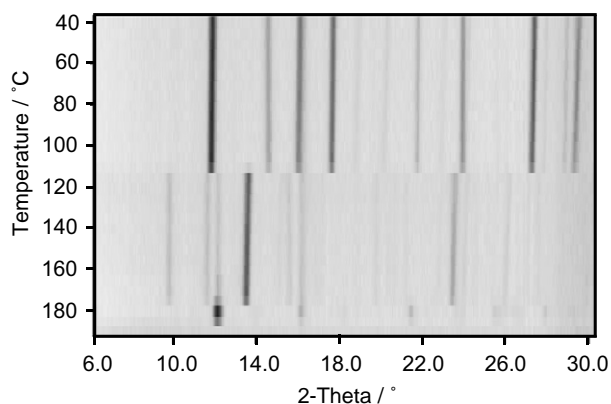


Fig. 9. Results of the temperature-resolved X-ray powder diffraction on poly[CuCl(μ₂-2-ethylpyrazine-*N,N'*)] (**I**) (shown are two comparable measurements; static air atmosphere; glass capillaries; powder patterns were measured every 5°C; heating rate: 5°C/min).

parameters which one should consider like for example the steric repulsion between the ligands.

4. Conclusions

In the present work, we have demonstrated that thermal decomposition reactions of suitable precursor compounds offer an alternative method for the preparation of new inorganic–organic coordination poly-

mers. This leads to a successive condensation of the inorganic substructures into the direction of the pure inorganic compounds. Even if in the present example the phases can be obtained also in solution there are several exceptions [18–22]. However, what is more important is the fact that we have demonstrated that the kinetics of all steps involved in the decomposition reactions play an important role and can determine the product formation. The kinetic properties can be investigated preferably by heating-rate-dependent TG measurements, which are normally not used in conventional TG experiments. With such investigations, data on the kinetics of these reactions can be acquired. Moreover, phases are accessible which easily could be overlooked if the preparation is performed at constant temperatures. In our present work, the first hints for the existence of compound **II** we see in our heating-rate-dependent measurements. Moreover, applying such measurements allows to influence the product formation in a more directed way and information on the intermediates of these reactions is obtained. From additional structural investigations of the intermediates, information on a molecular level is obtained, which can help to understand the mechanism of such reactions in more detail.

However, the preparation of coordination polymers by this route is not limited to copper(I) halide and pseudohalide compounds because it can easily be expanded to other coordination polymers which contain magnetically interesting transition metals. This will be the subject of a further contribution.

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