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Dimorphism of a New CuI Coordination Polymer:Synthesis, Crystal Structures and Properties of Catena[CuI(2-Iodopyrazine-N)] and Poly[CuI(μ_2-2-Iodopyrazine-N,N′)]

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Two modifications of the new copper(I) iodide coordination polymer CuI(2-iodopyrazine) were obtained by the reaction of CuI and 2-iodopyrazine in acetonitrile. During this reaction, intensely yellow crystals of form **I** appear first which transform within several minutes to intensely red crystals of form **II** which is the thermodynamically most stable form at room temperature. In catena[CuI(2-iodopyrazine-*N*)] (form **I**; $a = 4.1830$ (6) Å; $b = 10.814$ (1) Å; $c = 17.961$ (4) Å; $V = 812.5$ (2) Å^3; orthorhombic; $P2_12_12_1$; $Z = 4$), corrugated CuI double chains are found in which each copper atom is coordinated by one additional 2-iodopyrazine ligand. In poly[CuI(μ-2-iodopyrazine-*N*,*N*′)] (form **II**; $a = 4.2679$ (5) Å; $b = 13.942$ (2) Å; $c = 13.017$ (2) Å; $b = 92.64$ (1)°; $V = 773.76$ (2) Å^3; monoclinic; $P2_1/c$; $Z = 4$), CuI single chains occur which are connected via μ-*N*,*N*′ coordination by the 2-iodopyrazine ligands to layers parallel to (010). The thermal behavior of both forms was investigated using simultaneous differential thermoanalysis, thermogravimetry, and mass spectrometry as well as differential scanning calorimetry and temperature resolved X-ray powder diffraction. On heating, both forms decompose to copper(I) iodide, and the decomposition temperature of form **I** is significantly lower than that of form **II**. From all experiments, there is no indication of a phase transition of one form into the other or for the formation of a phase with lower amine content.

Introduction

The design of new coordination polymers based on transition metal atoms and organic ligands has become of increasing interest recently.[1−14] One major goal in this area is the development of synthetic strategies for a more directed design of the structures of these solids in order to influence their physical properties in a desired way.[1−14] One interesting class of coordination polymers is based on copper(I)halides or pseudo-halides and multidendate amino ligands. These compounds are mostly intense red to yellow with some of them showing luminescence and thermoluminescence. The crystal structures of these coordination polymers are based on inorganic CuX substructures (X = halide or pseudo halide) which are linked by the organic ligands to multidimensional coordination polymers. Dependent on the copper(I) halide or pseudo-halide and the nature of the organic ligand, different CuX substructures such as dimers, tetramers,

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and single, double, or helical single chains are observed.[15−36] The dimensionality of the coordination network can be influenced predominantly by the coordination properties of the organic ligands. For one definite copper(I) halide or pseudo-halide and one specific ligand, frequently several compounds are found, which differ in the ratio between the inorganic and organic parts. We have found that most of the amine rich compounds can be quantitatively transformed to amine poorer compounds via controlled thermal decomposition. In some cases, decomposition to the copper(I) halides or pseudo-halides is observed without the formation of an intermediate phase.[30−37] Nevertheless, this method is an attractive strategy for the preparation of new coordination polymers which cannot be synthesized directly, which are obtained as mixtures, or which are frequently overlooked if the reaction is performed in solution. The number of intermediate compounds that can be observed depends, for example, on the experimental conditions and the heating rate used in the experiments. That shows that the kinetics of all reactions involved may play an important role.[34] To understand such thermal reactions in more detail, we have started systematic investigations on the synthesis, preparation and the thermal behavior of these compounds. In order to obtain strategies for a more directed design of specific structures, to define structure property relationships, and to investigate thermodynamic and kinetic properties of such compounds, one has to be aware of the phenomena of polymorphism or isomerism. This is frequently found in organic or metal organic compounds.[3,29,38−40] These phenomena are of interest from several points of view. First of all, the structural aspects of polymorphism and isomerism provide information on intermolecular interactions in crystals and, therefore, can be used for a more rational crystal design. Moreover, investigations on the thermodynamic and kinetic aspects, e.g., of polymorphism provide important information about the stability of each modification and the transformation behavior.[41−43]

During our investigations on CuX coordination polymers, we have found two forms of CuI(2-iodopyrazine) which differ in the arrangement of the building blocks. Here we report on the synthesis, the crystal structures, and the thermal behavior of both forms. The structural and thermodynamic aspects as well as the properties of these modifications are discussed and compared with those obtained for related CuX coordination polymers.

Experimental Section

Synthesis of Catena[CuI(2-iodopyrazine-*N*)] (I). Copper(I) iodide (518.7 mg (5.24 mmol)) and 600 mg (5.24 mmol) of 2-iodopyrazine were stirred in 9 mL of acetonitrile at room temperature. Within a few minutes, yellow crystals of **I** appear which were filtered off before the transformation into the red form **II** started and were washed with ethanol and diethyl ether. In some of the isolated powders, extremely small single crystals have formed which were suitable for X-ray single crystal determination. Yield: 88.1%. Anal. (%) Calcd: C, 12.20; N, 6.99; H, 0.67. Found: C, 12.12; N, 7.07; H, 0.76. X-ray powder diffraction: phase pure.

Synthesis of Poly[CuI(μ-2-iodopyrazine-*N*,*N*′)] (II). If the reaction mixture described in the preceding paragraph were stirred for about 15 min, all yellow crystals of **I** would transform into the red crystals of **II**. Yield: 92.3%. Anal. (%) Calcd: C, 12.20; N, 6.99; H, 0.67. Found: C, 12.21; N, 7.00; H, 0.70. X-ray powder diffraction: phase pure.

Single Crystal Structure Determination. For both compounds, a face-indexed absorption using X-SHAPE[44] and XEMP[45] was applied. The structure solution was performed using SHELXS-97,[46] and structure refinement was done against F^2 using SHELXL-97.[47] All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined with isotropic displacement parameters using the riding model. For compound **I**, the absolute structure

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Table 1. Crystal Data and Results of the Structure Refinement for Catena[CuI(2-iodopyrazine-N)] (**I**) and Poly[CuI(μ-2-iodopyrazine-N,N′)] (**II**)

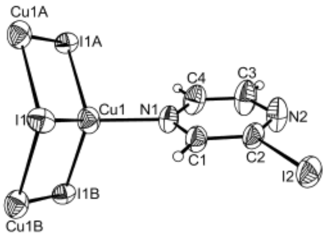
	I	**II**
chemical formula	$C_4H_3N_2CuI_2$	$C_4H_3N_2CuI2$
fw	396.42	396.42
space group	$P2_12_12_1$	$P2_1/c$
a	4.1830 (6) Å	4.2679 (5) Å
b	10.814 (1) Å	13.942 (2) Å
c	17.961 (4) Å	13.017 (2) Å
β		92.64 (1)°
V	812.5 (2) Å^3	773.76 (2) Å^3
T	20 °C	20 °C
Z	4	4
D_{calcd}	3.241 g·cm^{-3}	3.403 g·cm^{-3}
μ	10.20 mm^{-1}	10.71 mm^{-1}
λ	0.71073 Å	0.71073 Å
R1^a [$I > 2\sigma(I)$]	0.0214	0.0171
wR2^a [all data]	0.0477	0.0390

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Lengths and Angles for Catena[CuI(2-iodopyrazine-*N*)] (**I**) and Poly[CuI(μ-2-iodopyrazine-*N*,*N*′)] (**II**)[a]

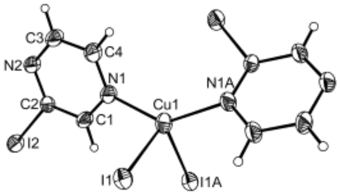
Form **I**

Cu(1)	- N(1)		2.068 (4)				
Cu(1)	- I(1)		2.627 (1)				
Cu(1)	- I(1A)		2.658 (1)				
Cu(1)	- I(1B)		2.638 (1)				
Cu(1)	- Cu(1A)		2.860 (1)				
N(1)	- Cu(1)	- I(1)	107.5 (1)				
N(1)	- Cu(1)	- I(1B)	109.5 (2)				
I(1)	- Cu(1)	- I(1B)	114.68 (3)				
N(1)	- Cu(1)	- I(1A)	106.4 (2)				
I(1)	- Cu(1)	- I(1A)	114.01 (3)				
I(1B)	- Cu(1)	- I(1A)	104.35 (2)				
Cu(1)	- I(1)	- Cu(1A)	64.08 (2)	Cu(1)	- I(1)	- Cu(1B)	63.97 (2)
Cu(1)	- I(1)	- Cu(1A)	65.80 (2)	Cu(1)	- I(1)	- Cu(1B)	65.51 (2)
C(4)	- N(1)	- Cu(1)	121.1 (4)	C(1)	- N(1)	- Cu(1)	121.2 (3)



Form **II**

Cu(1)	- N(1)		2.034 (2)				
Cu(1)	- N(2A)		2.047 (2)				
Cu(1)	- I(1A)		2.6883 (5)				
Cu(1)	- I(1)		2.6910 (5)				
N(1)	- Cu(1)	- N(2A)	137.92 (9)				
N(1)	- Cu(1)	- I(1A)	103.85 (7)				
N(2A)	- Cu(1)	- I(1A)	101.61 (7)				
N(1)	- Cu(1)	- I(1)	102.02 (7)				
N(2A)	- Cu(1)	- I(1)	103.02 (7)				
Cu(1)	- I(1)	- Cu(1A)	64.08 (2)	Cu(1)	- I(1)	- Cu(1B)	63.97 (2)
I(1A)	- Cu(1)	- I(1)	105.00 (2)	Cu(1A)	- I(1)	- Cu(1)	105.00 (2)
C(4)	- N(1)	- Cu(1)	124.9 (2)	C(1)	- N(1)	- Cu(1)	118.4 (2)
C(2)	- N(2) -	Cu(1)	125.8 (2)	C(3)	- N(2)	- Cu(1)	117.7 (2)



[a] Displacement ellipsoids are drawn at the 50% probability level.

was determined and is in agreement with the selected setting (Flack *x*-parameter: −0.003 (48)). In addition, inversion of the structure leads to significantly worse reliability factors (R1 for all reflections with $I > 2\sigma(I) = 0.0237$; wR2 for all data = 0.0544). Details of the structure determination and lists with selected bond lengths and angles are given in Tables 1 and 2.

X-ray Powder Diffraction. Powder diffraction experiments were performed using a STOE STADI P transmission powder and a Siemens D-5000 diffractometer in reflection geometry both with Cu Kα radiation ($\lambda = 1.540598$ Å). The temperature-dependent X-ray powder experiments were performed with a $\theta-\theta$-diffractometer from STOE and CIE in reflection geometry from Bühler-Otto GmbH with Cu Kα radiation which is equipped with a position sensitive detector and a high-temperature device HDK 2.41. The measurements were performed every 5 °C under a dynamic nitrogen atmosphere.

Differential Thermal Analysis, Thermogravimetry, and Mass Spectrometry. 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 analogue and trend scan mode, in Al_2O_3 crucibles under a dynamic helium (purity 4.6) or nitrogen (purity 5.0) atmosphere 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. The heating rate dependent TG measurements were performed under nitrogen atmosphere (purity 5.0) in Al_2O_3 crucibles using a STA-409CD thermobalance from Netzsch. Several measurements with different heating rates of 0.5, 1, 2, 4, 8, and 16 °C/min were performed.

Differential Scanning Calorimetry. DSC experiments were performed with the DSC 204/1/F from Netzsch in Al_2O_3 crucibles. For all compounds, several measurements were performed using heating rates between 1 and 10 °C/min. The calorimeter was calibrated using standard reference substances. All characteristic temperatures as well as all enthalpies were estimated from different measurements at 2 °C/min.

Optical Microscopy. Microscopy was performed using a hot stage from Linkam and a microscope BM60 from Olympus equipped with a video recorder and a video camera.

Elemental Analysis. C, H, N analysis was performed using a CHN-O-RAPID combustion analyzer from Heraeus, and energy dispersive analysis of X-rays (EDAX) was performed using a Philips XL30 environmental scanning electron microscope (ESEM) with an EDAX system from Philips.

Results

Crystal Structures. Catena[CuI(2-iodoopyrazine-*N*)] (**I**) crystallizes in the orthorhombic, chiral space group $P2_12_12_1$ with four formula units in the unit cell and all atoms in general positions (Table 1). In the crystal structure, the copper atoms are coordinated by one nitrogen atom of one 2-iodopyrazine ligand and three iodine atoms which are related by symmetry within a strongly distorted tetrahedron (Figure 1 and Table 2). Corrugated CuI double chains are found as the CuX substructure which are oriented in the direction of the crystallographic *a*-axis (Figure 1, top). The 2-iodopyrazine ligand does not act as a bridging ligand and is coordinated only with that nitrogen atom to the copper atom which is not neighbored to the iodine atom. This leads to the formation of a chain structure. Bond lengths and angles around the copper atoms are in the range of those found in other CuI coordination polymers containing CuI double chains. In the crystal, the chains are closely packed in a way that each chain is surrounded by six symmetry related chains (Figure 1, bottom).

Poly[CuI(μ-2-iodopyrazine-*N*,*N*′)] (**II**) crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell and all atoms in general positions (Table 1). Each copper atom is surrounded by two nitrogen atoms of two symmetry related 2-iodopyrazine ligands and two symmetry related iodine atoms within a distorted tetrahedron (Figure 2 and Table 2). Bond lengths and angles around the copper atoms are in the range of those found in other CuI coordination polymers containing a topologically similar coordination network. The copper atoms are connected via the iodine atoms to form CuI single chains as the CuX substructure. These chains are oriented in the direction of

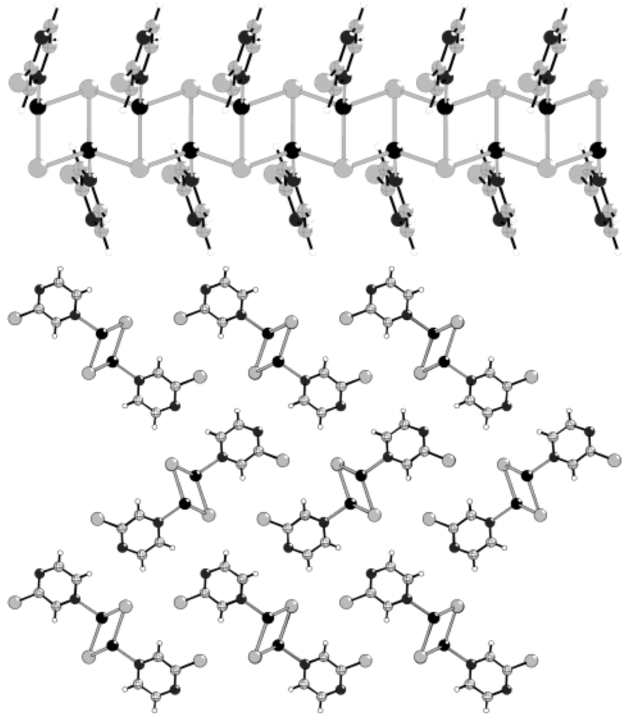


Figure 1. Crystal structure of catena[CuI(2-iodopyrazine-*N*)] (**I**) with view along the crystallographic *b*-axis (top) and *a*-axis (bottom).

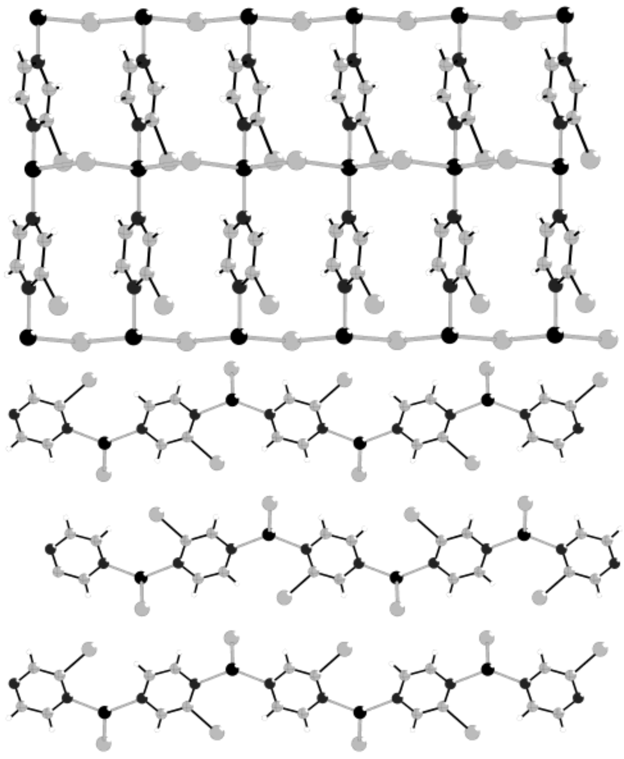


Figure 2. Crystal structure of poly[CuI(μ-2-iodopyrazine-*N*,*N′*)] (**II**) with view along the crystallographic *b*-axis (top) and *a*-axis (bottom).

the crystallographic *a*-axis. They are connected via μ-*N*,*N′* coordination by the 2-iodopyrazine ligands to layers parallel to (010).

Thermoanalytical Investigations. On heating compound **I** in a simultaneous DTA−TG−MS experiment, an endothermic event is observed at a peak temperature of 170 °C which is accompanied with a mass loss in the TG curve of 50.9% (Figure 3). This experimental mass loss is in good agreement with that calculated for the complete removal of the 2-iodo-pyrazine ligands (Δm_{theo}: −2-iodopyrazine = 52.0%). This is proved by mass spectrometry which shows that only 2-iodopyrazine (m/z = 206) is emitted. From the DTG curve, it is obvious that the reaction occurred in only one step and that no amine poorer intermediate phase has formed. The final product of this reaction is CuI as shown by X-ray powder diffraction.

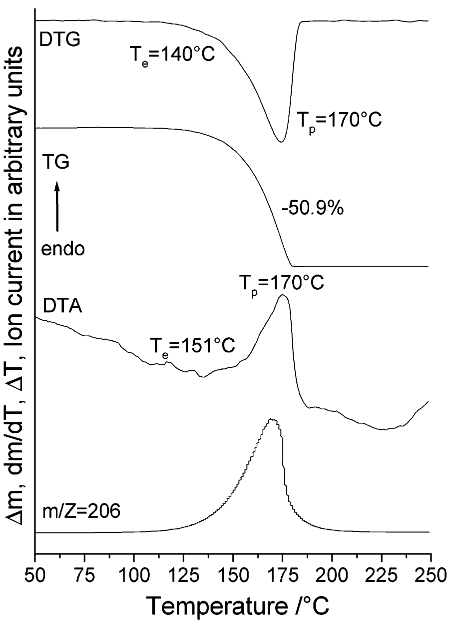


Figure 3. DTA, TG, DTG, and MS trend scan curves for catena[CuI(2-iodopyrazine-N)] (**I**) [simultaneous measurement, crystalline powder, weight = 22.4 mg, heating rate = 4 °C/min, dynamic helium atmosphere (flow rate = 75 mL/min); Al_2O_3 crucible; T_p = peak temperature; T_e = extrapolated onset temperature; m/z (206) = 2-iodopyrazine].

If form **II** is heated in a thermobalance, a similar behavior is found (Figure 4). The decomposition temperature is shifted to 182 °C, and the experimental mass loss of 51.0% is in good agreement with that calculated for the complete removal of the 2-iodopyrazine ligands (Δm_{theo}: −2-iodopyrazine = 52.0%). These investigations demonstrate that in contrast to the thermal behavior of most of the 1:1 CuX coordination polymers no amine poorer phase is obtained. Because the product formation in such thermal decomposition reactions can depend on the kinetics of all reactions involved,[34] measurements were performed at different heating rates. However, these investigations gave no evidence for any additional intermediate compounds.

From the DTA curves presented in Figures 3 and 4, there is no hint for a phase transition of one form into the other. To control this and to obtain information on the energy difference between both forms, investigations using differential scanning calorimetry were performed. On heating, decomposition is observed at peak temperatures of 210 °C for **I** and of 214 °C for **II** (Figure 5).

The difference between the decomposition energies that corresponds to the energy difference between both forms is about 21 kJ/mol. From these measurements, there is no

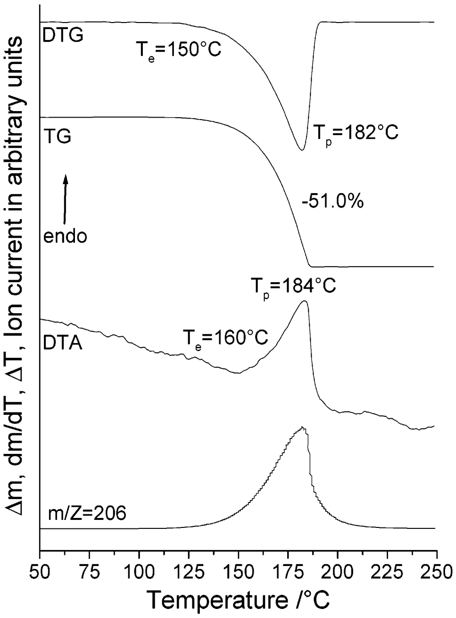


Figure 4. DTA, TG, DTG, and MS trend scan curves for poly[CuI(μ-2-iodopyrazine-*N*,*N′*)] (**II**) [simultaneous measurement, crystalline powder, weight = 24.5 mg, heating rate = 4 °C/min, dynamic helium atmosphere (flow rate = 75 mL/min), Al_2O_3 crucible, T_p = peak temperature, T_e = extrapolated onset temperature, *m*/*z* (206) = 2-iodopyrazine].

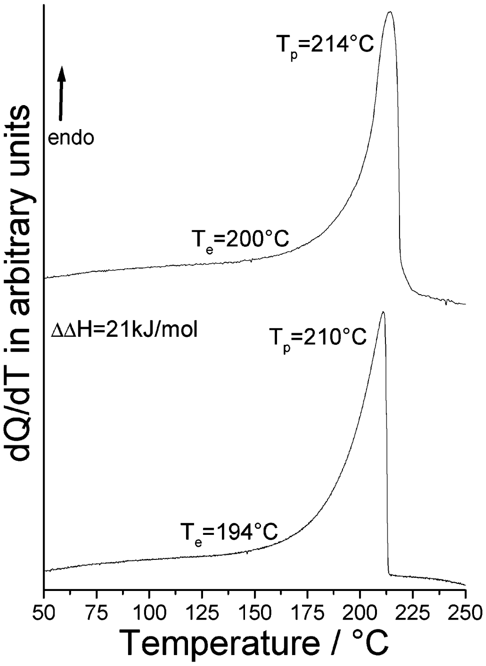


Figure 5. DSC curves for catena[CuI(2-iodopyrazine-*N*)] (**I**) (top) and poly[CuI(μ-2-iodopyrazine-*N*,*N′*)] (**II**) (bottom) (crystalline powder, heating rate = 2 °C/min, Al pans, T_p = peak temperature, T_e = extrapolated onset temperature, given is the difference between the enthalpies for the complete removal of the 2-iodopyrazine ligand).

evidence for a transformation between both forms or the occurrence of additional phases. The decomposition temperatures in the DSC measurements are shifted to higher values compared to those obtained from DTA−TG−MS investigations because in this case the gaseous reaction products are not transported out of the crucibles by a continuous gas flow and, therefore, the reaction takes place in part under a self-produced atmosphere.

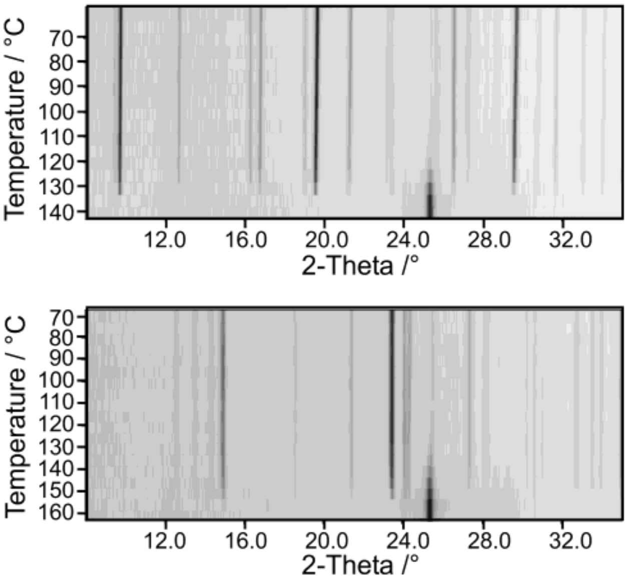


Figure 6. Results of the temperature resolved X-ray powder diffraction experiments on catena[CuI(2-iodopyrazine-*N*)] (**I**) (top) and poly[CuI(μ-2-iodopyrazine-*N*,*N′*)] (**II**) (bottom) measured in reflection geometry (Cu Kα radiation, crystalline powder, dynamic nitrogen atmosphere, powder patterns were measured every 5 °C).

The thermal behavior was additionally investigated by temperature dependent X-ray powder diffraction (Figure 6). On heating a crystalline powder sample of **I** under a nitrogen atmosphere, a dramatic change of the diffraction pattern is observed at about 135 °C, which corresponds to the decomposition of the material (Figure 6). The experimental powder diffraction pattern after this transformation is identical with that calculated for CuI from single crystal data. Similar observations were made for **II**, but the decomposition temperature is shifted to about 155 °C (Figure 6). From the temperature resolved X-ray powder diffraction experiments, there is no evidence for a transformation of one compound into the other or for the occurrence of a new amine poorer phase in agreement with the thermoanalytic results already described.

Crystallization Experiments. When equimolar amounts of CuI and 2-iodopyrazine were reacted in acetonitrile, yellow crystals of compound **I** appeared first. After a few minutes, red crystals of **II** started to precipitate and grew on the cost of the yellow crystals. After about 15 min, the transformation had finished and the crystals of compound **I** had completely disappeared. The same is observed if crystals of pure **I** were reacted in acetonitrile. These experiments clearly prove that compound **II** is the thermodynamically most stable form at room temperature. To investigate the range in which **II** is the thermodynamic most stable form, temperature dependent crystallization experiments were performed in different solvents between −40 and 150 °C for both modifications. In these experiments, a saturated solution with an excess of crystal powder of each of the pure modifications was stirred at different temperatures for about 1 day. Because both modifications are different colors, a possible transformation could easily be observed. In addition, all residues obtained at different temperatures were investigated by X-ray powder diffraction. If solvents were used

Table 3. Selected Crystal Data for Some 1:1 CuX Coordination Polymers[a]

	CuI(2-chloro-pyrazine)	CuI (2-iodo-pyrazine)	CuCl (2-chloro-pyrazine	CuBr (2-chloro-pyrazine	CuCl (2-methyl-pyrazine)	CuBr (2-methyl-pyrazine)	CuI (2-iodo-pyrazine)
a/Å	4.1128 (6)	4.1830 (6)	3.7752(4)	3.9068 (3)	3.862 (1)	4.023 (1)	4.2679 (5)
b/Å	10.482 (2)	10.814 (1)	12.859 (1)	13.159 (2)	12.887 (3)	12.940 (4)	13.942 (2)
c/Å	17.9852 (4)	17.961 (4)	12.709 (2)	12.765 (2)	12.585 (3)	12.801 (4)	13.017 (2)
β/deg			90.72 (2)	90.53 (1)	95.59 (2)	96.83 (2)	92.64 (1)
V/Å^3	775.4 (2)	812.5 (2)	614.1 (1)	656.3 (1)	623.2 (2)	661.6 (3)	773.76 (2)
space group	orthorhombic $P2_12_12_1$	orthorhombic $P2_12_12_1$	monoclinic $P2_1/c$	monoclinic $P2_1/c$	monoclinic $P2_1/c$	monoclinic $P2_1/c$	monoclinic $P2_1/c$
CuX structure	double chains	double chains	single chains	single chains	single chains	single chains	single chains
dimensionality	1-D structure	1-D structure	2-D structure	2-D structure	2-D structure	2-D structure	2-D structure
2:1 on heating	yes	no	no	no	yes	yes	no
color	yellow	yellow	red	red	red	orange-red	red
ref	32	this work	32	32	31	31	this work

[a] The phrase "2:1 on heating" means that the 1:1 compound transform into a amine poorer 2:1 compound on heating.

which evaporate below 150 °C, the reaction was performed in glass ampules. These experiments were performed for both modifications separately. If form **I** was stirred at −40 °C, this compound was stable over several hours before the transformation into the red form **II** was observed, whereas this transformation proceeded faster at elevated temperatures. However, at all temperatures tested between −40 and 150 °C, form **I** always transformed into form **II**, and therefore, form **II** is the thermodynamically most stable form in this temperature range. In agreement with this observations, if form **II** is investigated in this temperature range, no phase transformation is observed.

Discussion

Concerning the correct nomenclature in the case of coordination polymers, no consistent trend can be found in the literature.[48] Following the nomenclature of Champness et al., both compounds can be labeled as structural isomers[29] whereas according to the notation of Zaworotko et al., they should correspond to supramolecular isomers.[3] There are arguments for both opinions which predominantly depend on the point of view. The fact that in the solid no transformation of one form into the other is observed is also found for polymorphic systems.[49] However, for the present compounds a transformation is observed in solution. In both compounds, the coordination sphere and the arrangement of the building blocks differ which would justify the term "isomerism". However, as in the case of polymorphism, this behavior is coupled to the solid state. In solution, this arrangement probably does not exist. Therefore, we have used the older and more general notation "polymorphism", which is defined as the ability of a compound to exist in more than one modification. This should also include the phenomena of structural and supramolecular isomerism in the case of coordination polymers.

Concerning the thermodynamic aspects of the dimorphism, the results of the room temperature synthesis show clearly that form **II** is the thermodynamically most stable form at room temperature. Because the density of **II** is significantly higher compared to that of **I**, form **II** should also be more stable at 0 °C.[41] However, our thermoanalytical investigations and temperature dependent crystallization experiments gave no evidence for a polymorphic phase transition up to the decomposition point of both forms. In addition, our DSC experiments show clearly that form **II** is more stable than form **I**. Therefore, it can be assumed that form **II** is the thermodynamic most stable form over the whole temperature range, whereas form **I** is metastable and both modifications behave monotropically.[41] In addition, none of these modifications form amine poorer phases on heating.

Concerning the structural aspects of the dimorphism, it is difficult to decide why form **II** is more stable than form **I**. The crystal structure of form **I** represents one rare example in which double CuI chains occur in a 1:1 CuX compound containing organic ligands, which exhibit two possible coordination sites. It is unlikely that this is due to some steric crowding of the bulky iodo substituent, because the same structure is also found if 2-chloropyrazine is used as ligand[32] (see later). However, such double chains are mostly found in 2:1 compounds in which the chains are connected by the ligands to layers. The corresponding 1:1 compounds usually exhibit CuX single chains which are connected to layers as in form **II**. In the structure of form **I** compared to that of form **II**, the ligands do not bridge different CuX double chains and only a one-dimensional structure is formed. Therefore, the connection of the CuX single chains to layers in form **II** seems to be responsible for the higher thermodynamic stability.

In this context, it is interesting to compare the structures and properties of the related CuX coordination polymers with 2-methylpyrazine[31] and 2-chloropyrazine[32] (Table 3). All structures can be divided into two different groups (Table 3). The first group contains structures in which CuX double chains are found and in which the organic part does not act as the bridging ligand as in **I**. Therefore, only one-dimensional structures are found. The second group contains 1:1 CuX compounds in which CuX single chains are found that are connected by the organic ligands to form two-dimensional structures as in **II**. All of them are based on a similar coordination network (Table 3).

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(48) This problem was extensively discussed with Stuart Batten, Neil Champness, and Mike Zaworotko. Thanks for their help.

(49) Bock, H.; Schödel, H.; Näther, C.; Butenschön, F. *Helv. Chim. Acta.* **1997**, *80*, 593−605.

The compounds with CuCl and CuBr as well as 2-chloropyrazine are isotypic to the thermodynamically most stable form **II** with 2-iodopyrazine. For these copper(I) halides, only these modifications can be prepared, and therefore, they should represent the most stable forms at room temperature. The same applies to the 2-methylpyrazine compounds.[31] They are not exactly isotypic to the 2-chloro- and 2-iodopyrazine compounds but contain topologically identical coordination networks.

If CuI is reacted with 2-chloropyrazine, crystals of the 1:1 compound are obtained which are isotypic with the thermodynamically metastable form **I** of CuI(2-iodopyrazine). In contrast to form **I**, the compound with 2-chloropyrazine represents the only and therefore thermodynamically most stable form at room temperature. Unfortunately, no 1:1 CuX compound with CuI and 2-methylpyrazine can be prepared. However, from these results it is obvious that no simple correlation between the structure and the thermodynamic stability can be found.

The same is true for the thermal reactivity of the compounds already discussed. The thermodynamically most stable form **II** of CuI(2-iodopyrazine) as well as the isotypic compounds CuX(2-chloropyrazine) ($X = Cl, Br$) does not form an amine poorer phase on heating and decompose directly to CuX. In contrast, the two compounds CuX(2-methylpyrazine) ($X = Cl, Br$), which are nearly isotypic and contain an identical coordination network, transform into amine poorer 2:1 compounds on heating. This is also found for the thermodynamically most stable 1:1 compound CuI(2-chloropyrazine), which transforms into the new 2:1 phase Cu_2I_2(2-chloropyrazine) on heating.[32] In contrast, the metastable modification **I** of CuI(2-iodopyrazine) which is isotypic to the former compound does not form an amine poorer phase. This shows that in these compounds no simple property relationships can be found.

Conclusions

In the present contribution, we have shown that polymorphism or isomerism plays an important role in the structural chemistry of coordination polymers and it allows us to compare structural, thermodynamic, and physical properties of compounds exhibiting the same chemical composition but a different arrangement of their building blocks. This is very important in the area of crystal engineering, in which compounds with defined structures and desired physical properties are constructed. However, it also shows how difficult structure prediction is on the basis of simple consideration of the coordination properties of all building blocks involved. Therefore, it is justified to label the phenomenon of polymorphism as the “nemesis” of crystal design.

However, the results of our present work raise some interesting questions regarding whether it is possible to influence the structures, the thermodynamic stability, and the thermal reactivity of these compounds by preparation of mixed crystals. Investigations in the 2-methylpyrazine/2-chloropyrazine system reveal that such crystals can be prepared and that they exhibit a different thermal reactivity. However, this will be the subject of a further contribution.

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Supporting Information Available: Lists with details of the structure determination, atomic coordinates, isotropic and anisotropic displacement parameters, as well as CIF files and drawings of the two structures. These materials are available free of charge via the Internet at http://pubs.acs.org.

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