Synthesis, Crystal Structure and Thermal Reactivity of New Copper(I) Halide Pyrimidine-Containing Coordination Polymers

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Reaction of copper(I) chloride with pyrimidine in acetonitrile leads to the formation of the ligand-rich 1:1 compound poly[CuCl(μ_2-pyrimidine-N,N')] (**1**). "Zig-zag"-like CuCl chains are found in the crystal structure that are connected by the pyrimidine ligands to form layers. This compound loses half of its ligands upon heating and transforms into the new l2:1 coordination polymer poly[$(CuCl)_2$(μ_2-pyrimidine-N,N')] (**2**). In this structure, ladder-like CuCl double chains occur which are connected by the pyrimidine ligands to form layers. If copper(I) iodide is used in the synthesis, the new 1:1 coordination polymer poly[CuI(μ_2-pyrimidine-N,N')] (**3**) forms. In contrast to compound **1**, CuI single chains and $(CuI)_2$ dimers are found as the CuX substructure, and these are connected by the ligands to form sheets. On heating this compound a similar behaviour as for compound **1** is observed, and a transformation into the new 2:1 compound poly[$(CuI)_2$(μ_2-pyrimidine-N,N')] (**4**) occurs. This compound is not isotypic to **2** even though the topology of the coordination network is identical (CuI double chains are connected into layers by the pyrimidine ligands). The thermal behaviour of the known compounds poly[CuBr(μ_2-pyrimidine-N,N')] (**5**) and poly[$(CuBr)_2$(μ_2-pyrimidine-N,N')] (**6**) was also investigated. A transformation of the ligand-rich 1:1 compound **5** into the 2:1 compound **6** is also observed in the thermal decomposition reaction.

Introduction

Inorganic-organic coordination polymers based on copper(I) halides or pseudohalides and aromatic nitrogen-donor ligands are well-known and several of them have been synthesised and structurally characterised in the past.[1−38] These compounds consist of CuX substructures such as four- or six-membered rings, "zig-zag"-like or helical single chains, or "ladder-like" double chains, which are connected by the nitrogen-donor ligands to give one-, two- or three-dimensional coordination polymers. For each combination of copper(I) halide or pseudohalide and nitrogen-donor ligand several different compounds are frequently found, each of which has a different ratio — 1:1, 1:2, 2:1, 3:2 or 4:1 — between the copper(I) halide or pseudohalide and the organic ligand. We have found that most ligand-rich copper(I) halide or pseudohalide compounds can be transformed into ligand-poorer compounds by thermal decomposition, whereas others loses all their ligands in one step forming the pure copper(I) halides or pseudohalides.[26−38] This method is therefore an alternative route for the preparation of new CuX (X = Cl, Br, I, SCN, CN) coordination polymers that cannot be prepared in solution or that are always obtained as mixtures. We have found, for example, no simple relationship between the structure of the starting compound and its thermal reactivity or the structure of the decomposition product.[26−38] However, our investigations do show that the product formation depends on the kinetics of all the reactions involved.[31] In some cases several ligand-poorer intermediates (2:1 or 4:1) or different polymorphic modifications can be isolated.[32−34] In order to investigate the influence of the coordination behaviour of the organic ligands on the structure and the thermal reactivity of these coordination polymers we have prepared and structurally characterised several of them. In most cases we have used small six-membered nitrogen heterocycles (e.g. pyrazine or its derivatives). 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)][9] the 2:1 compound [$(CuBr)_2$(pyrimidine)][37] and the 2:1 compound [$(CuCN)_2$(pyrimidine)][18,24] have been structurally characterized. The amine-poorer compounds [$(CuX)_2$pyrimidine] (X = Cl, Br, I) were also prepared and characterised by elemental analysis and thermogravimetric measurements.[25] It was shown that these compounds lose all of the pyrimidine ligands in one step forming the pure copper(I)-halides. Here we report on the synthesis, the crystal structure and the thermal reactivity of CuX and $(CuX)_2$ pyrimidine-containing coordination polymers.

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Results and Discussion

Crystal Structures

The 1:1 compound poly[CuCl(μ_2-pyrimidine-*N*,*N′*)] (**1**) crystallizes in the orthorhombic space group *Pma*2 with two formula units in the unit cell. The compound is not isotypic with the 1:1 coordination polymer poly[CuBr(μ_2-pyrimidine-*N*,*N′*)] (**5**), and the topology of the coordination network is also different.[9] The asymmetric unit consists of one copper and one chlorine atom as well as one pyrimidine ligand, all of which are located in special positions. Each copper(I) atom is coordinated by two chlorine atoms and two nitrogen atoms of pyrimidine ligands within a distorted tetrahedron (Figure 1, top).

The bond lengths and angles are similar to those of related compounds (Table 1). The copper atoms are connected through the chlorine atoms forming "zig-zag" CuCl chains in the direction of the crystallographic *b*-axis (Figure 1, bottom). These chains are connected by the pyrimidine ligands to form layers that are parallel to (001) (Figure 1, bottom).

The ligand-poorer 2:1 compound poly[(CuCl)$_2$(μ_2-pyrimidine-*N*,*N′*)] (**2**) crystallizes in the orthorhombic space group *Pnma* with four formula units in the unit cell. The asymmetric unit consists of one crystallographically independent Cu and Cl atom in general positions and one pyrimidine ligand which is located in a special position (Figure 2, top). The compound is not isotypic with the previously reported compound poly[(CuBr)$_2$(μ_2-pyrimidine-*N*,*N′*)] (**6**)[37] but contains an identical topology of the coordination network. The copper atoms are coordinated by three chlorine atoms and one nitrogen atom of the pyrimidine ligand within strongly distorted tetrahedra (Table 1). The Cu−N bond length is significantly shorter than that observed in compound **1**, whereas the Cu−Cl bond lengths are longer.

The CuX substructure consists of CuCl double chains which are connected by the pyrimidine ligands to form layers which are parallel to the *bc* plane (Figure 2, bottom). This topology of the coordination network is frequently found in such ligand-poorer 2:1 compounds.

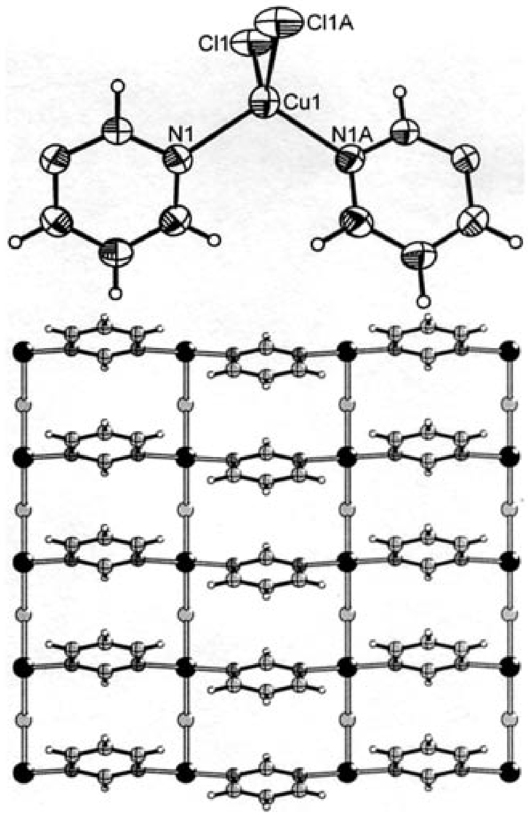

Figure 1. Crystal structure of poly[CuCl(μ_2-pyrimidine-*N*,*N′*] (**1**) showing the coordination sphere of the copper atoms with labelling and displacement ellipsoids drawn at the 50% probability level (top); view of the coordination network along the crystallographic *c*-axis (bottom)

The 1:1 compound poly[CuI(μ_2-pyrimidine-*N*,*N′*)] (**3**) crystallizes in the monoclinic space group $P2_1/c$ with eight formula units in the unit cell. The asymmetric unit consists

Table 1. Selected bond lengths (Å) and angles (°) for poly[CuCl(μ_2-pyrimidine-*N*,*N′*] (**1**) and poly[(CuCl)$_2$(μ_2-pyrimidine-*N*,*N′*] (**2**)

poly[CuCl(μ_2-pyrimidine-*N*,*N′*] (**1**)			
Cu(1)−N(1A)	2.060(2)	Cu(1)−N(1)	2.060(2)
Cu(1)−Cl(1)	2.337(1)	Cu(1)−Cl(1A)	2.337(1)
N(1A)−Cu(1)−N(1)	112.91(9)	N(1A)−Cu(1)−Cl(1)	111.40(4)
N(1)−Cu(1)−Cl(1)	106.18(5)	N(1A)−Cu(1)−Cl(1A)	106.18(5)
N(1)−Cu(1)−Cl(1A)	111.40(4)	Cl(1)−Cu(1)−Cl(1A)	108.79(3)
Cu(1)−Cl(1)−Cu(1A)	108.79(3)		
poly[(CuCl)$_2$(μ_2-pyrimidine-*N*,*N′*] (**2**)			
Cu(1)−N(1)	2.011(2)	Cu(1)−Cl(1A)	2.293(1)
Cu(1)−Cl(1B)	2.447(1)	Cu(1)−Cl(1)	2.476(1)
Cu(1)−Cu(1A)	2.887(1)		
N(1)−Cu(1)−Cl(1A)	126.02(8)	N(1)−Cu(1)−Cl(1A)	104.67(8)
Cl(1A)−Cu(1)−Cl(1B)	105.61(4)	N(1)−Cu(1)−Cl(1)	104.95(8)
Cl(1A)−Cu(1)−Cl(1)	109.26(3)	Cl(1A)−Cu(1)−Cl(1)	104.42(3)
Cu(1A)−Cl(1)−Cu(1B)	105.61(4)	Cu(1A)−Cl(1)−Cu(1)	74.39(3)
Cu(1B)−Cl(1)−Cu(1)	71.81(3)		

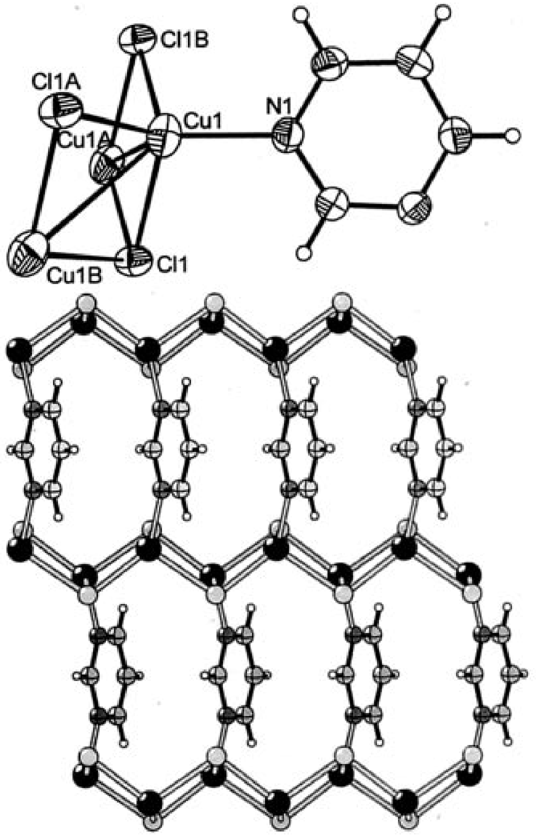

Figure 2. Crystal structure of poly[$(CuCl)_2$(μ_2-pyrimidine-*N*,*N′*] (**2**) showing the coordination sphere of the copper atoms with labelling and displacement ellipsoids drawn at the 50% probability level (top); view of the coordination network along the crystallographic *a*-axis (bottom)

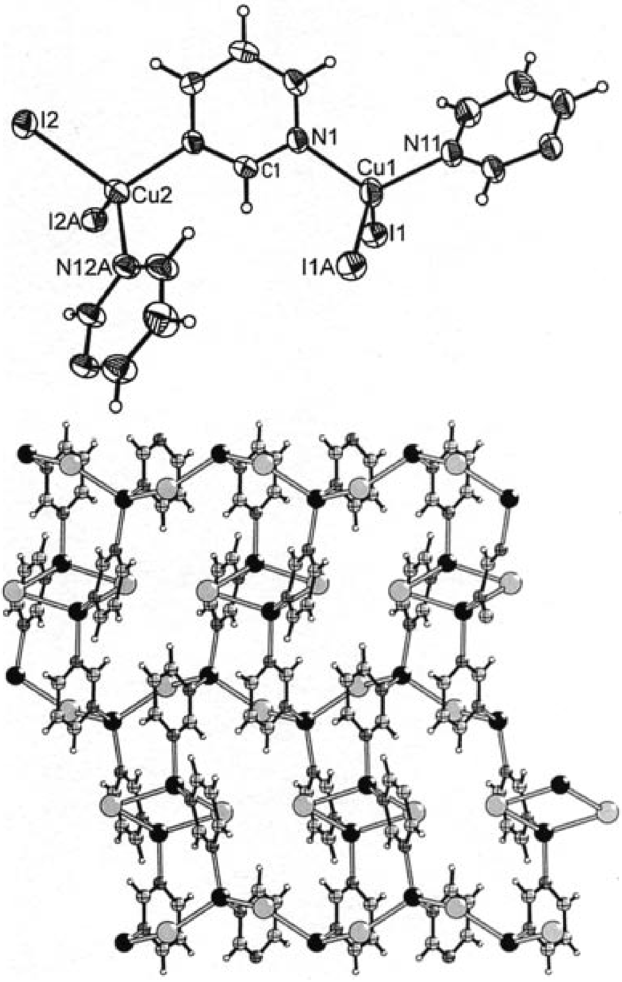

Figure 3. Crystal structure of poly[CuI(μ_2-pyrimidine-*N*,*N′*] (**3**) showing the coordination sphere of the copper atoms with labelling and displacement ellipsoids drawn at the 50% probability level (top); view of the coordination network along the crystallographic *a*-axis (bottom)

of two crystallographically independent Cu atoms and one I atom as well as two pyrimidine ligands located in general positions (Figure 3, top). This compound is isotypic to the 1:1 coordination polymer poly[CuBr(μ_2-pyrimidine-*N*,*N′*)] (**1**).[9] Each of the two crystallographically independent copper atoms is coordinated by two iodine atoms and two organic ligands within a distorted tetrahedra (Table 2 and Figure 3, top). In contrast to compound **1**, two different building units are found as the CuX substructure. Cu1 and I1 form coplanar $(CuI)_2$ dimers which are located on centres of inversion, whereas Cu2 and I2 are connected to "zig-zag"-like CuI single chains which propagate in the direction of the crystallographic *c*-axis (Figure 3, bottom). The dimers and single chains are connected by the pyrimidine ligands into corrugated layers in the *bc* plane.

The ligand poorer 2:1 compound poly[$(CuI)_2$(μ_2-pyrimidine-*N*,*N′*)] (**4**) crystallizes in the monoclinic space group $P2_1/m$ with two formula units in the unit cell (Table 3). The asymmetric unit contains one copper atom and one iodine in general positions as well as one pyrimidine ligand which is located in the crystallographic mirror plane. The compound is isotypic with the previously reported coordination polymer poly[$(CuBr)_2$(μ_2-pyrimidine-*N*,*N′*)] (**6**).[37] The copper atoms are surrounded by three iodine atoms and one nitrogen atom of the pyrimidine ligand within a distorted tetrahedron (Figure 4, top). The bond lengths and angles are similar to those observed in other ligand-poorer 2:1 CuX compounds. As in the CuCl compound **1** and the CuI compound **4**, CuX double chains are found as the CuX substructure, and these are connected to form layers by the pyrimidine ligands. Therefore, the topology of the coordination network is identical in all ligand-poorer 2:1 compounds.

If the crystal structures of the present pyrimidine compounds are compared with those of the previously reported pyrazine and pyridazine compounds some interesting features become obvious. The ligand-rich 1:2 coordination polymers with pyrazine have an identical topology of the coordination network to the present pyrimidine compounds. CuX single chains (X = Cl,[39] Br[15]) are observed as the CuX substructure, and these are connected into layers by the pyrazine ligands. If the N-donor atoms are located in the 1- and 2-positions, like in pyridazine, the topology of the coordination network in the 1:1 compounds is completely different.[9,34] Due to steric restrictions no layered structures can be formed and typical one-dimensional

Table 2. Selected bond lengths (Å) and angles (°) for poly[CuI(μ_2-pyrimidine-*N*,*N'*] (**3**) and poly[(CuI)$_2$(μ_2-pyrimidine-*N*,*N'*] (**4**)

poly[CuI(μ_2-pyrimidine-*N*,*N'*] (**3**)			
Cu(1)−N(11)	2.047(4)	Cu(1)−N(1)	2.078(4)
Cu(1)−I(1)	2.653(1)	Cu(1)−I(1A)	2.668(1)
Cu(2)−N(2)	2.059(4)	Cu(2)−N(12A)	2.063(4)
Cu(2)−I(2A)	2.601(1)	Cu(2)−I(2)	2.614(1)
N(11)−Cu(1)−N(1)	117.9(2)	N(11)−Cu(1)−I(1)	105.1(2)
N(1)−Cu(1)−I(1)	106.3(2)	N(11)−Cu(1)−I(1A)	107.5(2)
N(1)−Cu(1)−I(1A)	100.9(2)	I(1)−Cu(1)−I(1A)	120.0(1)
N(2)−Cu(2)−N(12A)	107.4(2)	N(2)−Cu(2)−I(2A)	114.3(2)
N(12A)−Cu(2)−I(2A)	112.1(2)	N(2)−Cu(2)−I(2)	106.8(2)
N(12A)−Cu(2)−I(2)	110.7(2)	I(2A)−Cu(2)−I(2)	105.5(1)
poly[(CuI)$_2$(μ_2-pyrimidine-*N*,*N'*] (**4**)			
Cu(1)−N(1)	2.058(6)	Cu(1)−I(1)	2.620(2)
Cu(1)−I(1A)	2.634(2)	Cu(1)−I(1B)	2.691(2)
Cu(1)−Cu(1A)	2.722(2)	Cu(1)−Cu(1B)	2.776(2)
N(1)−Cu(1)−I(1)	107.7(2)	N(1)−Cu(1)−I(1A)	110.0(2)
I(1)−Cu(1)−I(1A)	117.6(1)	N(1)−Cu(1)−I(1B)	100.6(2)
I(1)−Cu(1)−I(1B)	117.0(1)	I(1A)−Cu(1)−I(1B)	102.6(1)
Cu(1)−I(1)−Cu(1A)	62.4(1)	Cu(1)−I(1)−Cu(1B)	63.0(1)
Cu(1A)−I(1)−Cu(1B)	102.6(1)		

Table 3. Selected crystal data and results of the structure refinements for compounds **1**−**4**

Compound	**1**	**2**	**3**	**4**
Formula	$C_4H_4N_2CuCl$	$C_4H_4N_2Cu_2Cl_2$	$C_4H_4N_2CuI$	$C_4H_4N_2Cu_2I_2$
Mol. mass (g·mol^{-1})	179.08	278.08	270.53	460.97
Crystal colour	orange	yellow	yellow	yellow
Crystal size (mm^{-1})	0.07 × 0.10 × 0.13	0.05 × 0.09 × 0.12	0.07 × 0.10 × 0.13	0.07 × 0.10 × 0.13
Diffractometer	STOE AED-II	STOE IPDS	STOE AED-II	STOE AED-II
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	*Pma*2	*Pnma*	$P2_1/c$	$P2_1/m$
a (Å)	11.610 (1)	14.737 (1)	9.564 (2)	4.1554 (7)
b (Å)	3.8000 (6)	13.379 (1)	17.689 (3)	15.159 (2)
c (Å)	6.4900 (8)	3.7772 (2)	8.073 (1)	7.049 (1)
α (°)	−	−	−	−
β (°)	−	−	108.47 (1)	96.81 (2)
γ (°)	−	−	−	−
V (Å^3)	283.33 (6)	744.72 (8)	1295.4 (4)	440.9 (1)
Temperature (K)	room temp.	room temp.	room temp.	room temp.
Z	2	4	8	2
$D_{calcd.}$ (g·cm^{-3})	2.077	2.480	2.774	3.472
F(000)	176	536	992	412
2θ range (°)	3-60	3−56	3-56	3−54
h/k/l ranges	−16/16 −5/5 −9/9	−19/19 −17/17 −4/4	−12/11 −15/23 −0/10	−2/5 −19/5 −8/8
μ(Mo-K_α) (mm^{-1})	4.15	6.34	8.03	11.75
Absorption corr.	numerical	−	numerical	numerical
Min./max. transm.	0.4858/0.5930	−	0.2671/0.3970	0.1503/0.2451
Measured refl.	3360	6535	6133	2098
$R_{int.}$	0.0529	0.0342	0.0376	0.0481
Independent refl.	884	914	3143	996
Refl. with $I > 2\sigma(I)$	755	742	2065	733
Parameters	42	50	146	50
R_1 [$I > 2\sigma(I)$]	0.0189	0.0332	0.0274	0.0310
wR_2 [all data]	0.0499	0.0955	0.0674	0.0771
Goof	1.058	1.067	0.971	1.088
Res. elec. den. (e·Å^{-3})	0.24 / −0.17	0.62 / −0.66	0.78 / −0.86	1.23 / −0.97

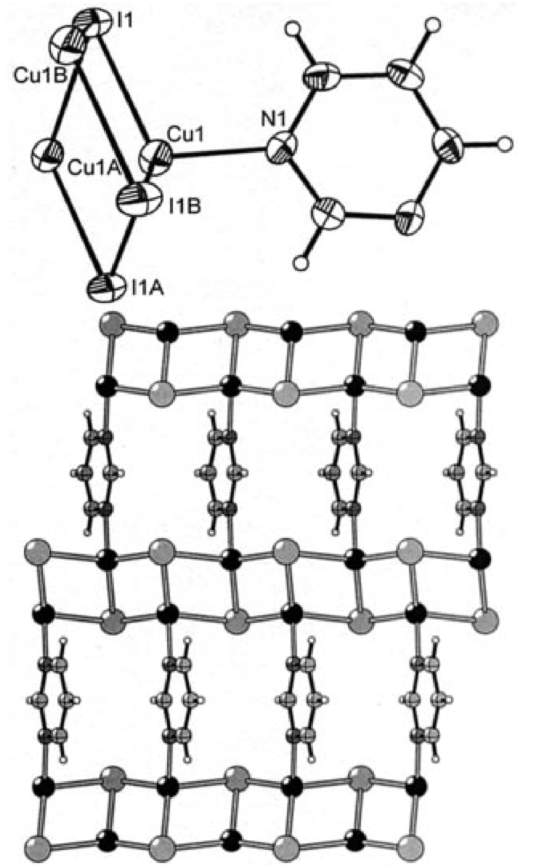

Figure 4. Crystal structure of poly[$(CuI)_2$(μ_2-pyrimidine-*N*,*N*′] (**4**) showing the coordination sphere of the copper atoms with labelling and displacement ellipsoids drawn at the 50% probability level (top); view of the coordination network along the crystallographic *a*-axis (bottom)

structures result. A similar observation is made for the ligand-poorer 2:1 compounds. The topology of the structures with pyrazine is identical to that of the structures with pyrimidine. CuX double chains (X = Cl,[40] Br[11]) are observed that are connected to form layers. This arrangement cannot be formed with pyridazine as ligand and therefore completely different CuX substructures (X = Cl, Br,[34] I[9]) and a completely different coordination network result.

Thermal Properties

The thermal properties of compounds **1**−**5** were investigated by simultaneous differential thermoanalysis, thermogravimetry and mass spectrometry, as well as temperature-dependent X-ray powder diffraction.

On heating poly[CuCl(μ_2-pyrimidine-*N*,*N*′] (**1**) in a thermobalance two mass steps are observed, which are accompanied by two endothermic events in the DTA curve at peak temperatures of 132 and 219 °C (Figure 5).

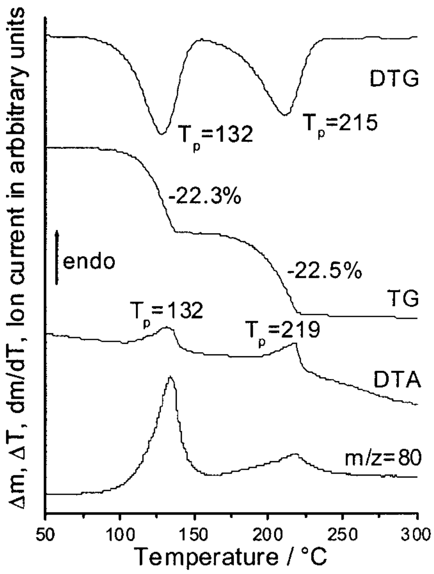

Figure 5. DTA, TG, DTG and MS trend scan curves for poly[CuCl(μ_2-pyrimidine-*N*,*N*′] (**1**) (weight: 19.98 mg; heating rate: 4 °C/min.; MS: m/z = 80 (pyrimidine); T_p = peak temperature)

The experimental mass-loss of 22.3 and 22.5% in both steps is in good agreement with that calculated for the removal of half of the pyrimidine ligands in each step [Δm_{theo} = 22.3%]. The DTG curve shows that both steps are well resolved and that only pyrimidine (m/z = 80) is emitted. The final product of this reaction was identified as $Cu^{I}Cl$ by X-ray powder diffraction. These results suggest that in the first step the ligand-poorer 2:1 compound poly[$(CuCl)_2$(μ_2-pyrimidine-*N*,*N*′] (**2**) is formed, which on further heating loses its remaining pyrimidine ligands. The results found for the decomposition of the amine-poorer 2:1 compound are in agreement with those found by Mayer et al.[25]

To identify the intermediate after the first TG step a second TG experiment was performed which was stopped after the first TG step. The residue isolated was investigated by elemental analysis and X-ray powder diffraction. When this experimental powder pattern was compared with that calculated for the 2:1 compound **2** from single crystal data, it was confirmed that the ligand poorer coordination polymer **2** had formed (Figure 6).

On heating the 1:1 compound poly[CuI(μ_2-pyrimidine-*N*,*N*′] (**3**) a similar behaviour as for compound **1** was found. Two endothermic events were observed at peak temperatures of 110 and 215 °C which are accompanied by two well-resolved mass steps in the TG curve (Figure 7). The MS spectra show that in both steps only pyrimidine ligands are emitted and the experimental mass loss is in good agreement with that calculated for the emission of half of the pyrimidine ligands in each step (Δm_{theo} = 14.8%). Therefore, the first TG step should lead to the formation of the ligand-poorer compound **4**. The residue after the second TG step was identified as CuI by X-ray powder diffraction, which is in agreement with previous investigations.[25]

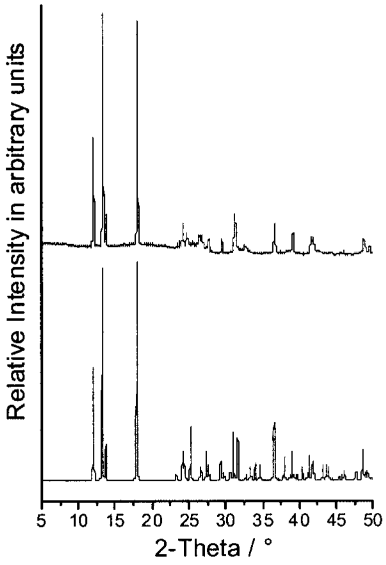

Figure 6. Powder pattern of the residue isolated after the first TG step during the thermal decomposition of poly[CuCl(μ_2-pyrimidine-*N*,*N'*] (**1**) (top), and calculated pattern for the ligand-poorer 2:1 compound poly[$(CuCl)_2$(μ_2-pyrimidine-*N*,*N'*] (**2**) (bottom)

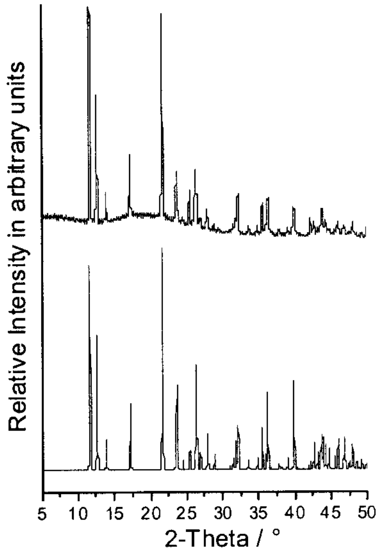

Figure 8. Powder pattern of the residue isolated after the first TG step during the thermal decomposition of poly[CuI(μ_2-pyrimidine-*N*,*N'*] (**3**) (top), and calculated pattern for the ligand-poorer 2:1 compound poly[$(CuI)_2$(μ_2-pyrimidine-*N*,*N'*] (**4**) (bottom).

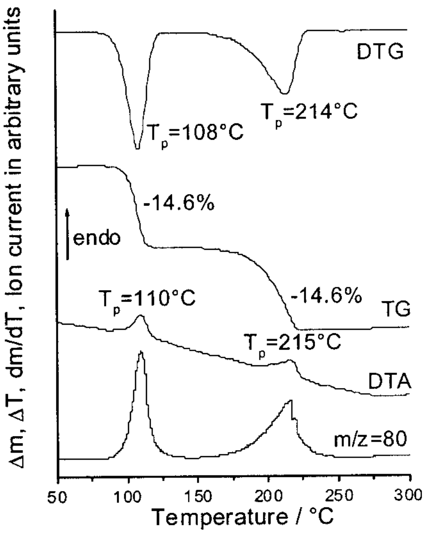

Figure 7. DTA, TG, DTG and MS trend scan curves for poly[CuI(μ_2-pyrimidine-*N*,*N'*] (**3**) (weight: 19.98 mg; heating rate: 4 °C/min.; MS: *m*/*z* = 80 (pyrimidine); T_p = peak temperature)

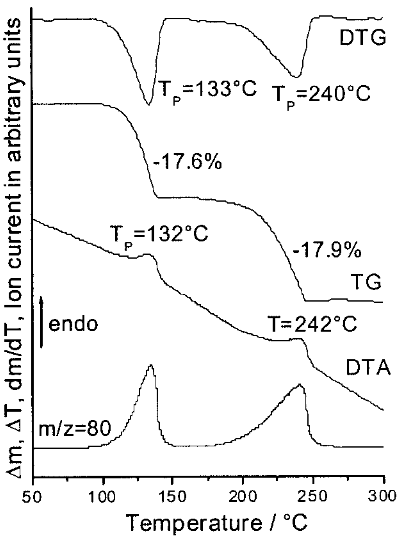

Figure 9. DTA, TG, DTG and MS trend scan curves for poly[CuBr(μ_2-pyrimidine-*N*,*N'*] (**5**) (weight: 19.98 mg; heating rate: 4 °C/min.; MS: *m*/*z* = 80 (pyrimidine); T_p = peak temperature)

In a second TG run the experiment was stopped after the first TG step and the intermediate was investigated by X-ray powder diffraction and elemental analysis. The CHN content is in agreement with that calculated for a ligand-poorer 2:1 compound and the experimental powder pattern is identical with that calculated for compound **4** (Figure 8).

If the known 1:1 compound poly[CuBr(μ_2-pyrimidine-*N*,*N'*)] (**5**) is heated in a thermobalance two well-resolved mass steps occur which are accompanied by two endothermic events in the DTA curve (Figure 9). The MS curve shows that only the N-donor ligands are removed and the experimental mass loss of 17.6 and 17.9% in both steps is in good agreement with that calculated for the removal of half of the pyrimidine ligands in each step (Δm_{theo} = 17.9%). The residue formed after the first TG step was identified as the ligand-poorer 2:1 compound poly[$(CuBr)_2$(μ_2-pyrimidine-*N*,*N'*)] (**6**; Figure 10).

Because in previous investigations we have shown that the product formation sometimes depends on the kinetics of all the reactions involved[31] heating-rate-dependent studies were performed for all compounds at rates of between 0.5 and 16 °C/min. However, these experiments showed no changes in the TG curves and gave no hints for the presence of additional intermediates during the thermal reactions.

To investigate if the reaction is more complex and, for example, different polymorphic modifications occur, temperature-dependent X-ray powder measurements were performed[33−35] (Figure 11).

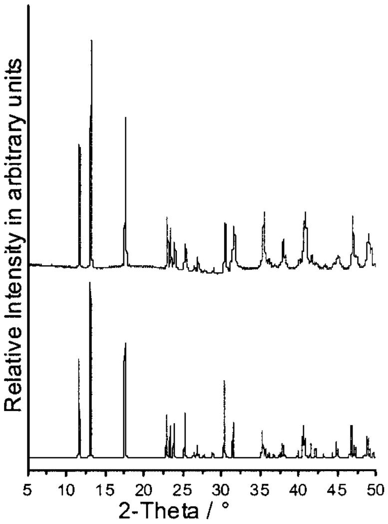

Figure 10. Powder pattern of the residue isolated after the first TG step during the thermal decomposition of poly[CuBr(μ_2-pyrimidine-*N*,*N*′] (**5**) (top), and calculated pattern for the ligand-poorer 2:1 compound poly[(CuBr)$_2$(μ_2-pyrimidine-*N*,*N*′] (**6**) (bottom)

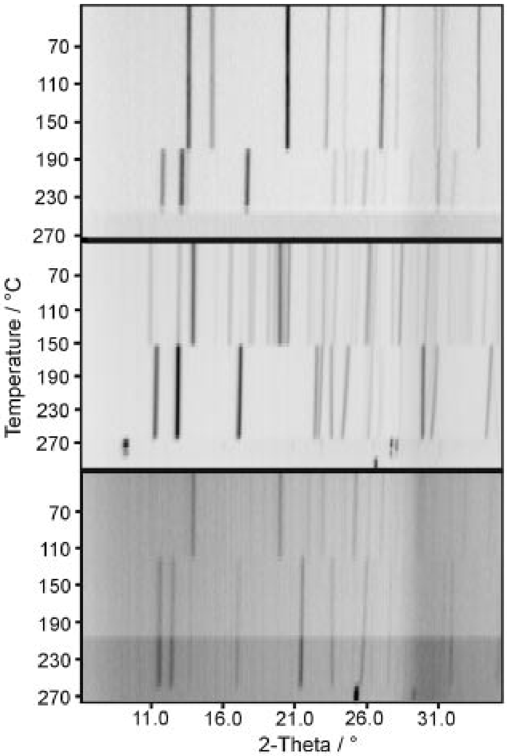

Figure 11. Temperature-resolved X-ray powder pattern for poly[CuCl(μ_2-pyrimidine-*N*,*N*′] (**1**) (top), poly[CuBr(μ_2-pyrimidine-*N*,*N*′] (**5**) (middle) and poly[CuI(μ_2-pyrimidine-*N*,*N*′] (**3**) (bottom); heating rate: 5 °C/min; the diffraction pattern was measured every 5 °C

It must be noted that the decomposition temperatures cannot be compared with those from the DTA-TG-MS measurements because different conditions, for example static or flowing atmosphere, are used. On heating the CuCl compound **1** the formation of the 2:1 compound is observed at about 180 °C, which is obvious from the dramatic change of the diffraction pattern (Figure 11, top). The 2:1 compound **2** is stable up to about 250 °C and then formation of CuCl is observed. The formation of CuCl is not visible in the presented pattern because in this experiment the gaseous product blows out the powder from the X-ray beam. However, this was proven in additional experiments. When poly[CuBr(μ_2-pyrimidine-*N*,*N*′] (**5**) was heated similar observations were made. The 1:1 compound is stable up to about 150 °C before the transformation into the 2:1 compound occurs. On further heating the ligand-poorer compound **6** decomposes at about 260 °C. Decomposition of the iodine compound **3** starts at about 120 °C (Figure 11, bottom). The 2:1 phase **4** is stable up to 260 °C and then the formation of CuI is observed. From these experiments there is no hint of additional intermediates or the occurrence of different polymorphic modifications. However, it should be noted that the stability range of the ligand-poorer 2:1 compounds increases from CuCl to CuI, whereas for the 1:1 compounds an opposite trend is observed. This is in agreement with previous results which shows that the stability of the ligand-poorer coordination polymers increases from CuCl to CuI.

Conclusion

In the present work we have prepared several new coordination polymers based on copper(I) halides and pyrimidine as the N-donor ligand. Comparison of these structures with those of the previously reported compounds with pyrazine and pyridazine as the organic ligands shows that the structure of these coordination polymers can be understand to some extent by taking into account the coordination behaviour of the N-donor ligands. However, the influence of the ligands on the actual CuX substructure is difficult to predict.

For all of these compounds ligand-poorer 2:1 compounds are observed during the thermal decomposition, which, on further heating, decompose to the pure copper(I) halides. The results observed for the amine-poorer 2:1 compounds are in agreement with those of previous investigations.[25] However, our investigations shows that this is a general phenomena and that there is no simple relationship between the structure of the ligand-rich phases and their thermal reactivity. Because the topology of the coordination network in the ligand-poorer coordination polymers is identical, whereas that of the ligand-rich coordination polymers is different, there is also no obvious relationship between the structures of the starting compounds and those formed by the thermal decomposition reaction. However, our investigation shows that new ligand-poorer coordination polymers can be prepared by thermal decomposition of suitable ligand-rich precursor compounds.

Experimental Section

Synthesis of poly[CuCl(μ_2-pyrimidine-*N*,*N*′)] (1): CuCl (49.5 mg, 0.5 mmol), pyrimidine (160 μL, 2 mmol) and 2 mL of acetonitrile were placed into a glass ampoule which was sealed and heated for 1 week at 100 °C. The reaction mixture was cooled to room temp. and the orange-red residue was filtered off and washed with ethanol and diethyl ether. Yield: 79.3% based on CuCl. $C_4H_4ClCuN_2$ (179.08): calcd. C 26.8, H 2.2, N 15.6; found C 26.5, H 2.2, N 15.5.

Synthesis of poly[$(CuCl)_2(\mu_2$-pyrimidine-*N,N'*)] (2): Single crystals were prepared by the reaction of CuCl (98.9 mg, 1.0 mmol), pyrimidine (40 µL, 0.5 mmol) and 2 mL acetonitrile in a glass ampoule which was sealed and heated for 4 days at 100 °C. The reaction mixture was cooled to room temp. and the yellow residue was filtered off and washed with ethanol and diethyl ether. Under these conditions the precipitate consists of a mixture of the 1:1 compound **1** and the 2:1 compound **2**. If an excess of CuCl is used the product is contaminated with a small amount of unchanged copper(I) chloride. However, this compound can be prepared in large amounts and very pure by thermal decomposition of **1**.

Synthesis of poly[CuI(μ_2-pyrimidine-*N,N'*)] (3): CuI (95.2 mg, 0.5 mmol), pyrimidine (160 µL, 2 mmol) and 2 mL of acetonitrile were stirred together at room temp. for 3 days. The yellow residue was filtered off and washed with ethanol and diethyl ether. Yield: 84.3% based on CuI. $C_4H_4CuIN_2$ (270.53): calcd. C 17.8, H 1.5, N 10.4; found C 17.7, H 1.4, N 10.3. Single crystals were prepared by the reaction of CuI (47.6 mg, 0.25 mmol) and pyrimidine (80 µL, 1 mmol) in 2 mL of acetonitrile. After 5 days yellow single crystals were grown.

Synthesis of poly[$(CuI)_2(\mu_2$-pyrimidine-*N,N'*)] (4): CuI (190.5 mg, 1.0 mmol), pyrimidine (40 µL, 0.5 mmol) and 3 mL of acetonitrile were placed into a glass ampoule which was sealed and heated for 3 days at 110 °C. The reaction mixture was cooled to room temp. and the yellow residue was filtered off and washed with ethanol and diethyl ether. The product consists of yellow needles and a yellow microcrystalline powder. Yield: 84.5%. $C_4H_4Cu_2I_2N_2$ (460.97): calcd. C 10.4, H 0.9, N 6.1; found C 10.4, H 0.8, N 6.2.

Synthesis of poly[CuBr(μ_2-pyrimidine-*N,N'*)] (5): CuBr (71.7 mg, 0.5 mmol), pyrimidine (160 µL, 2 mmol) and 3 mL of acetonitrile were placed into a glass ampoule which was sealed and heated for 4 days at 100 °C. The reaction mixture was cooled to room temp. and the orange residue was filtered off and washed with ethanol and diethyl ether. Yield: 86.8%. $C_4H_4BrCuN_2$ (223.54): calcd. C 21.5, H 1.8, N 12.5; found C 20.4, H 1.8, N 12.4.

Single-Crystal Structure Analysis: All structure solutions were performed with direct methods using SHELXS-97.[41] Further details are given in Table 3. Structure refinement was done against F^2 using SHELXL-97.[42] All non-hydrogen atoms were refined with anisotropic displacement parameters. The C−H hydrogen atoms were positioned with idealised geometry and were refined with isotropic displacement parameters using the riding model. For compounds **1**, **3** and **4** a numerical absorption correction was performed using X-RED and X-SHAPE.[43] The absolute structure for compound **1** was determined and is in agreement with the selected setting [Flack x parameter = −0.047(15)]. In addition, refinement of the inverted structure leads to significant poorer reliability factors [$R1$ for 755 $F_o > 4\sigma(F_o)$ = 0.0440, $wR2$ for all 884 reflections = 0.1525, Flack x parameter = 1.026 (0.042)].

CCDC-226928 (for **1**), -226929 (for **2**), -226926 (for **3**) and -226927 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

X-ray Powder Diffraction: X-ray powder diffraction experiments were performed using a STOE STADI P transmission powder diffractometer equipped with a 4° PSD (position sensitive detector) using Cu-K_α radiation (λ = 1.540598 Å). For the temperature-dependent X-ray powder measurements a 45° PSD and a graphite furnace from STOE & CIE were used. These measurements were carried out in glass capillaries under a static air atmosphere.

Differential Thermal Analysis, Thermogravimetry and Mass Spectrometry: DTA-TG-MS measurements were performed using an STA-409CD with Skimmer coupling from Netzsch, 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_2O_3 crucibles under helium atmosphere (purity: 4.6) at heating rates of 4 °C/min. The heating-rate-dependent measurements were performed with the same instrument in a Pt-Rh furnace in flowing nitrogen (purity: 5.0). 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.

Elemental Analysis: C, H and N analysis was performed using a CHN-O-RAPID combustion analyser from Heraeus and EDAX was performed using a Philips XL30 Environmental Scanning Electron Microscope (ESEM) equipped with an EDAX system from Philips.

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