Investigations on the Thermal Decomposition of Coordination Polymers Based on Copper(I) Halides and 2-Methylpyrazine

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The thermal behaviour of the three coordination polymers \( \frac{1}{2}\text{poly}[\text{CuX}(\mu-2\text{-methylpyrazine-N,N'})] (X = \text{Cl} \ (I), \text{Br} \ (II)), \) and \( \frac{1}{2}\text{poly}[\text{CuI}(\mu-\text{pyrazine-N,N'})] \cdot \text{2-methylpyrazine} \) (III) was investigated using differential thermal analysis and thermogravimetry (DTA-TG) measurements as well as temperature resolved X-ray powder diffraction in argon and in air. On heating all compounds decompose in two steps. In the first step compound I and II loose one and compound III looses two of the 2-methylpyrazine ligands to form the corresponding 2:1 compounds \( \text{Cu}_2\text{Cl}_2(2\text{-methylpyrazine}) \) (IV) and \( \frac{1}{2}\text{poly}[\text{Cu}_2\text{X}_2(\mu-2\text{-methylpyrazine-N,N'})] \) (X = Br (V), I (VI)). From the experiments there is no evidence for the formation of a 1:1 compound of Cul and 2-methylpyrazine as an intermediate phase during the thermal decomposition. On further heating the 2:1 compounds IV, V and VI transform directly to the corresponding copper(I) halides.

Introduction

The synthesis and structural characterisation of new coordination polymers based on copper(I) halides or pseudo halides and multidentate organic ligands such as aromatic amines has recently become of increasing interest. Depending on the copper(I) halide and the nature of the organic ligands used in the synthesis interesting inorganic substructures like CuX dimers, “zig-zag” single or staircase-like double chains are observed which are connected by the organic spacer molecules to one- or multi-dimensional inorganic-organic coordination polymers [1 - 18]. Therefore, such compounds may have interesting physical properties suitable for applications such as nonlinear optics, catalysis or molecular sieving. However, for any further investigation it is necessary that each compound can be prepared very pure and in high yields [11]. How­ever, we have shown that the 1:1 adduct with CuCl transforms quantitatively to the 2:1 adduct on heating [16] which means that large amounts of this compound can be prepared by controlled thermal decomposition. In a different study we have shown that the 1:1 adducts \( \frac{1}{2}\text{poly}[\text{CuX}(\mu-4,4’\text{-bipyridine-N,N'})] \) (X = Cl, Br, I) can also be transformed to the corresponding 2:1 adducts on heating [17]. Because the structures of the 1:1 compounds of pyrazine and 4,4’-bipyridine are completely different this might be a general reaction pathway for this class of compounds. Similar results for different CuX coordination polymers were published recently [18].

Cu-X coordination polymers consisting of 2-methylpyrazine were also reported [3]. The structures of the 1:1 adducts \( \frac{1}{2}\text{poly}[\text{CuX}(\mu-2\text{-methylpyrazine-N,N'})] \) (X = Cl (I), Br (II)) are very similar to those of \( \frac{1}{2}\text{poly}[\text{CuX}(\mu-\text{pyrazine-N,N'})] \) (X = Cl [11], Br [18]). In the crystal structure “zig-
zag” CuX single chains are found which are connected by the 2-methylpyrazine ligands to sheets (Fig. 1: A) [3]. The composition and structure of the 2-methylpyrazine rich compound $\zeta_2$ poly[[Cu$_2$X$_2$(mu-2-methylpyrazine-N,N')]$_2$·2-methylpyrazine] (III) (B) is completely different from those of I and II. In its crystal structure (CuI)$_2$ dimers are found which are connected by the 2-methylpyrazine ligands to sheets (Fig. 1: B). The sheets are stacked parallel to (010) to form channels parallel to the crystallographic b-axis (Fig. 1: B). Within the channels additional 2-methylpyrazine molecules are located which can be removed in vacuum leading to a compound of the formal composition CuI(2-methylpyrazine) [3]. The structures of the 2:1 adducts of 2-methylpyrazine $\zeta_2$ poly[[Cu$_2$X$_2$(mu-2-methylpyrazine-N,N')] (X = Br (V), I (VI)) [3] are only slightly different from those of the pyrazine compounds. Staircase-like CuX double chains are found which are connected by the methylpyrazine ligands to sheets (Fig. 1: C) [3]. In contrast to the pyrazine compounds, in the 2-methylpyrazine compounds the relative orientation between the 2-methylpyrazine ligands and the double chains alternates leading to a doubling of one crystallographic axis in $\zeta_2$ poly[[Cu$_2$X$_2$(mu-2-methylpyrazine-N,N')] (X = Br (V), I (VI)) compared to $\zeta_2$ poly[[Cu$_2$X$_2$(mu-pyrazine-N,N')] (X = Br [9], I [8]).

Because of the structural similarities we are interested in the thermal behaviour of the 2-methylpyrazine compounds compared to that of the pyrazine compounds. The compounds were investigated using differential thermal analysis and thermogravimetry (DTA-TG) as well as temperature resolved X-ray diffraction. Additionally we will report on some synthetic aspects concerning the preparation of the unknown adduct Cu$_2$Cl$_2$(2-methylpyrazine).

Results and Discussion
Thermoanalytical investigations

On heating the compounds I, II and III in a dynamic air atmosphere decompose in several steps (Fig. 2: A-C). For X = Cl a loss in mass of about 22.0% and for X = Br of about 18.3% is observed in the first TG step which corresponds roughly to that calculated for the removal of half of the 2-methylpyrazine ligands (theo: X = Cl: -24.4%; X = Br: -19.8%). On further heating a second loss in mass is observed for both compounds which can be regarded as loss of the remaining ligands. These results suggest that I and II transform in the first TG step to the 2:1 adducts which finally form the corresponding copper(I) halides in the second TG step. For compound III decomposition starts at significantly lower temperatures. The loss in mass of about 26.9% is in good agreement with that calculated for the removal of two 2-methylpyrazine molecules (theo: X = Cl: -24.4%; X = Br: -19.8%). On further heating a second loss in mass is observed for both compounds which can be regarded as loss of the remaining ligands. These results suggest that I and II transform in the first TG step to the 2:1 adducts which finally form the corresponding copper(I) halides in the second TG step. For compound III decomposition starts at significantly lower temperatures. The loss in mass of about 26.9% is in good agreement with that calculated for the removal of two 2-methylpyrazine molecules (theo: -28.4%) which would lead to a compound of the formal composition Cu$_2$I$_2$·2-methylpyrazine. On further heating a second TG step of about -13.4% is observed which corresponds to the loss of the remaining 2-methylpyrazine molecules. The final products of all compounds were identified as CuO [19] by X-ray powder diffraction. If the reaction is stopped after the second step of each reaction the residues can be identified as the corresponding copper(I) halides [20 - 24] by X-ray powder diffraction. The CuCl phase is contaminated
Temperature / °C

Fig. 2. DTA-TG-curves for \(^{2}\)poly\([\text{CuCl}(\mu-2\text{-methylpyrazine-N,N'})]\) (I) (A), \(^{2}\)poly\([\text{CuBr}(\mu-2\text{-methylpyrazine-N,N'})]\) (II) (B), and \(^{2}\)poly\([\text{Cu}_{2}L_{2}(\mu-\text{pyrazine-N,N'})_{2} \cdot 2\text{-methylpyrazine}]\) (III) (C) (simultaneous measurement; powdered single crystals; heating rate: 1 °C/min.; dynamic air atmosphere (flow rate: 100 ml/min.); Al\(_{2}\)O\(_{3}\)-crucible; given are the peak temperatures in °C and the mass change in %).

Fig. 3. DTA-TG-curves for \(^{2}\)poly\([\text{CuCl}(\mu-2\text{-methylpyrazine-N,N'})]\) (I) (A), \(^{2}\)poly\([\text{CuBr}(\mu-2\text{-methylpyrazine-N,N'})]\) (II) (B), and \(^{2}\)poly\([\text{Cu}_{2}L_{2}(\mu-\text{pyrazine-N,N'})_{2} \cdot 2\text{-methylpyrazine}]\) (III) (C) (simultaneous measurement; powdered single crystals; heating rate: 1 °C/min.; dynamic argon atmosphere (flow rate: 100 ml/min.); Al\(_{2}\)O\(_{3}\)-crucible; given are the peak temperatures in °C and the mass change in %).

with small amounts of CuO. The continuous raise of the TG curve of I starting after the second step is presumably due to a partial oxidation of the CuCl formed as an intermediate phase to CuO and the copper oxychloride Cu\(_{2}\)Cl\(_{2}\)O (Fig. 2: A).

In order to investigate the thermal behaviour using different gas atmospheres additional DTA-TG experiments were performed in an argon atmosphere (Fig. 3: A-C). Our recent investigations on the pyrazine and the 4,4'-bipyridine compounds have shown that the thermal decomposition pathway of such compounds as well as the purity of the observed intermediate phases depend strongly on the atmosphere used in the experiments [16 - 17]. For compound I in argon the agreement between the observed and calculated loss in mass for the stepwise removal of the organic ligands is much better. The raise in the TG curve after the second step does not occur and the isolated CuCl phase does not contain any contaminations with oxygen. The last TG step observed for all compounds is due to the vapourization of the copper halides. The reason for the discrepancy between the experimental and the calculated loss in mass in the first TG step of the iodine compound III can be ascribed to a partial decomposition of the starting material during the generation of the argon atmosphere in the thermobalance for which several cycles of evacuation are needed. As described in previous work this compound decomposes very quickly in vacuum by partial loss of the ligand [3].

To identify the intermediate products and to prove the sequence of the thermal reactions additional DTA-TG experiments were performed in which the
samples were cooled down immediately after the first TG step and the isolated residues were investigated by X-ray powder diffraction and elemental analysis. As can be seen in Fig. 4 the experimental pattern for the residues obtained from the decomposition of compound II and III are in good agreement with those calculated for the corresponding 2:1 compounds V and VI from single crystal data (Fig. 4). In addition the results of an elemental analysis of these residues are in good agreement with calculated data. Because the 2:1 compound with CuCl is unknown no authentical powder pattern is available. However the elemental analysis as well as the results of the DTA-TG investigations suggest strongly that this compound has formed during the first reaction and therefore the diffraction pattern shown in Fig. 4 should belong to this compound.

To be sure that no additional phases occur during the thermal decomposition additional investigations using temperature resolved X-ray powder diffraction were performed (Fig. 5). On heating the compounds in glass capillaries a dramatic change of the diffraction pattern occurs starting at about 220 °C for I, 250 °C for II and 240 °C for III. The powder patterns obtained after the first transformation of the bromine and the iodine compounds II and III are identical with those calculated for the corresponding 2:1 compounds V and VI. The pattern of the residue of the chlorine compound I is identical with that shown in Fig. 4 for the corresponding 2:1 phase IV. There are only minor differences in the intensity of some reflections which suggest that one of the patterns shows a strong texture. The crystallinity of this compound generated by the thermal decomposition is very poor.

The experiments show that for all compounds investigated both phases are stable simultaneously over a small temperature range which is in agreement with a reconstructive and heterogeneous phase transition. On further heating the samples transform to the corresponding copper(I) halides. There are no hints for the occurrence of additional phases. Therefore the decomposition of \( \frac{1}{2} \text{poly}[\{\text{Cu}_2\text{Br}_2(\mu-\text{pyrazine})_2\} \cdot 2\text{-methylpyrazine}] \) (II) proceeds directly to the 2:1 compound and a possible 1:1 compound as an intermediate phase obviously does not occur. The
reason that during the composition of compound I no reflections of Cu₂Cl₂O are observed can be ascribed to the special experimental conditions. Under static conditions in thin capillaries the reaction can take place under a “self-produced” atmosphere filled with the emitted amine. This is also the reason that the decomposition temperatures observed in the temperature resolved X-ray powder diffraction are shifted to higher temperatures compared to those measured in the DTA-TG experiments. However, if the reaction is stopped at about 380 °C during a DTA-TG experiment in air the copper oxychloride Cu₂Cl₂O [25] can be easily identified by X-ray powder diffraction.

**Synthetic aspects**

Our investigations have shown that a 2:1 compound Cu₂Cl₂(2-methylpyrazine) exists and that this compound occurs at higher temperatures as an intermediate phase during the thermal decomposition of the 1:1 compound I. Therefore we have tried to prepare this compound by mixing stoichiometric amounts of CuCl and 2-methylpyrazine in water and acetonitrile. From recent investigations we know that in solution an equilibrium between the 1:1 and the 2:1 compounds exists which strongly depends on the composition. For some other bases we observed that after mixing both components the 1:1 compound is formed first and transforms dependent on the amine within a few seconds or days into the corresponding 2:1 compound [16, 17, 26]. The transformation of the 2:1 to the 1:1 compounds has also been observed. However, for CuCl and 2-methylpyrazine independent of the experimental conditions and the stoichiometry the 2:1 phase does not occur in solution. Directly at the beginning of the reaction the red coloured 2₂poly[CuCl(μ-2-methylpyrazine-N,N')] (I) starts to precipitate and does not transform into the 2:1 compound even after several days. It can be concluded that at room-temperature compound I is thermodynamically more stable than compound IV. There is also no evidence for the occurrence of a 1:1 compound of 2-methylpyrazine and CuI in solution. Only the 2-methylpyrazine rich phase III can be prepared. These results are in agreement with those obtained for the coordination polymers with pyrazine [16, 27]. In this system on going from CuCl to CuI the 2:1 adducts become more stable. Thus the 1:1 compound with CuI cannot be prepared and the 2:1 compound with CuCl can only be prepared in low yields and as a phase mixture with the 1:1 compound as the major phase. The reason for this behaviour is not clear but a qualitative explanation can be given on the basis of the HSAB principle. As the 1:1 adducts are transformed to the 2:1 adducts one nitrogen atom of the pyrazine or the 2-methylpyrazine ligand is replaced by a halide ligand in the coordination sphere of each copper cation. Because copper(I) cations are soft acids and the softness of the halide anions increases from chloride to iodide the 2:1 adducts are more stable for the CuI compounds than for the CuCl compounds.

**Conclusion**

The present contribution demonstrates that the preparation of copper(I)halide CuX coordination polymers by controlled thermal decomposition of suitable precursor compounds can be an adequate alternative to conventional preparation in solution. For preparing large amounts of phase pure Cu₂Cl₂(2-methylpyrazine) (VI) this seems to be the only method. Our investigations on the thermal behaviour of the compounds with pyrazine, 4,4'-bipyridine and 2-methylpyrazine have shown that independent of the structure of the starting amine rich phase always a transformation into an amine poor phase occurs before decomposition to the corresponding copper(I) halides is observed. If this is a general phenomenon will be the subject of further investigations.

**Experimental Section**

*Synthesis of ₂poly[CuCl(μ-2-methylpyrazine-N,N')] (I):* 98.9 mg (1 mmol) of CuCl (freshly prepared according to [27]) and 188.2 mg (2.0 mmol) of 2-methylpyrazine (ACROS) in 5 ml of deionized water were stirred for 2 d. The product was filtered off and washed with deionized water, ethanol and diethylether. Red coloured microcrystalline powder, yield: 90.3% based on CuCl. If stoichiometric quantities of CuCl and 2-methylpyrazine are used the product is always contaminated with small amounts of the corresponding 2:1 compound.

*Synthesis of ₂[CuBr(μ-2-methylpyrazine-N,N')] (II):* 191.8 mg (1.33 mmol) of CuBr (freshly prepared according to [27]) and 125.8 mg (1.33 mmol) of 2-methylpyrazine (ACROS) in 5 ml of deionized water were stirred for 3 d. The product was filtered off and washed with deionized water, ethanol and diethylether. Orange-red microcrystalline powder, yield: 91.3% based on CuBr.
Poly(Cu$_2$h(ß-pyrazine-N,N')$_2$) • 2-methylpyrazine (III): 69.0 mg (2.80 mmol) of Cul (freshly prepared according to [27]) and 395.3 mg (4.20 mmol) of 2-methylpyrazine (ACROS) were mixed together and allowed to stand at room temperature for 1 day. The product was filtered off and washed with diethylether. Orange crystals, yield: 88.3% based on Cul. This compound decomposes on air within several days.

The homogeneity of all samples was checked by X-ray powder diffractometry.

X-ray powder diffraction: Powder diffraction experiments were performed using a STOE STADI P transmission powder diffractometer with Cu-K$_\alpha$-radiation ($\lambda = 154.0598$ pm) and a Siemens D-5000 diffractometer with Cu-K$_\alpha$-radiation ($\lambda = 154.0598$ pm). For temperature and time resolved X-ray powder diffraction the STOE diffractometer is equipped with a graphite oven and a position sensitive detector (scan range: $5^\circ \leq 2\theta \leq 50^\circ$) from STOE & CIE. All experiments were performed in glass capillaries under a static air atmosphere.

Differential thermal analysis and thermogravimetry: DTA-TG measurements were performed simultaneously using a STA-429 balance from Netzsch. All investigations were performed using heating rates of 1, 2 and 3 °C/min., in Al$_2$O$_3$ crucibles under a dynamic argon or air atmosphere (flow-rate: 100 ml/min).

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

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