

# Preparation of a Copper(I) Halide Coordination Polymer by Thermal Decomposition of a Precursor with Predefined Stoichiometry

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The ligand-rich precursor compound tetra- $\mu$ -chloro-bis( $\mu_2$ -2,3-dimethylpyrazine)-tetrakis-(acetonitrile-N)tetra-copper(I) (**1**) was prepared by the reaction of CuCl with 2,3-dimethylpyrazine in acetonitrile. On heating this compound decomposes quantitatively in a single step directly to the ligand-deficient coordination polymer di- $\mu_3$ -chloro-( $\mu_2$ -2,3-dimethylpyrazine-N,N')copper(I).

**Key words:** Copper(I) Halide Coordination Polymers, Crystal Structures, Thermal Decomposition

## Introduction

A major goal in the area of coordination polymers, inorganic-organic hybrid compounds and metal organic frameworks is the development of new strategies for a rational design of their structures, in order to prepare new materials with desired physical properties [1–12]. For any new application, large quantities of a desired compound must be prepared in pure form, and this is sometimes difficult to achieve if the synthesis is performed in solution. In some cases coordination polymers can be prepared by thermal decomposition of suitable precursor compounds, constituting an alternative tool for the discovery of compounds which cannot be routinely synthesized, are obtained only as mixtures, or may be overlooked if the preparations are performed in solution. We have exemplarily demonstrated this method for the synthesis of novel coordination polymers based on copper(I) halides or *pseudo* halides and N-donor ligands [13–21]. For a given copper(I) halide or *pseudo* halide and a specific N-donor ligand, several compounds which differ in the ratio between the inorganic and organic parts are frequently

found. On heating, most of the ligand-rich compounds lose some of the N-donor ligands and are transformed quantitatively into ligand-deficient compounds, before decomposing to the pure copper(I) halides or *pseudo* halides as the ultimate residues [22–29]. The ligand-deficient intermediates are obtained not only in very pure form but also in quantitative yield. However, one disadvantage of this method is that part of the ligands used in the synthesis gets irreversibly lost during decomposition. This disadvantage can be overcome by designing alternative ligand-rich precursors containing additional volatile sacrificial donors which can be removed first, such that the desired amine ligands are retained, as shown in this work.

## Experimental Section

### Synthesis

A polycrystalline powder of **1** was prepared by stirring a suspension of 1 mmol (98.9 mg) CuCl with 0.5 mmol (54.1 mg) of 2,3-dimethylpyrazine in 2 mL of acetonitrile at r. t. for 3 d. For the preparation of single crystals the same amounts of reactants and solvent were transferred into a glass ampoule, which was sealed and heated to 140 °C. Afterwards the ampoule was cooled to r. t. over 5 d.

Analytical data for **1**: (C<sub>20</sub>H<sub>28</sub>Cl<sub>4</sub>Cu<sub>4</sub>N<sub>8</sub>): calcd. C 30.74, H 3.63, N 14.23; found C 30.56, H 3.75, N 13.98. – EDX-analysis: Cu : Cl = 1 : 1. Analytical data of the residue obtained after the first TG step in the thermal decomposition of **1**: (C<sub>6</sub>H<sub>8</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>2</sub>): calcd. C 23.54, H 2.63, N 9.15; found C 23.42, H 2.75, N 9.23.

### Single crystal structure analysis

An Imaging Plate Diffraction System (IPDS1) from STOE & CIE (MoK $\alpha$  radiation) was used for data collection. The structure was solved with Direct Methods using SHELXS-97 [30]. The structure refinement was performed with SHELXL-97 [30]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were positioned with idealised geometry and refined isotropically using a riding model. Selected crystal data and results of the structure refinement are shown in Table 1.

CCDC 600156 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### DTA-TG-MS Measurements

DTA-TG-MS measurements were performed in Al<sub>2</sub>O<sub>3</sub> crucibles using a STA-409CD thermobalance from Netzsch,

Table 1. Crystal data and results of the structure refinement for compound **1**.

Empirical formula	C <sub>20</sub> H <sub>28</sub> Cl <sub>4</sub> Cu <sub>4</sub> N <sub>8</sub>
MW, g mol <sup>-1</sup>	776.46
Crystal colour	colourless
Crystal size, mm <sup>-1</sup>	0.2 × 0.2 × 0.1
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> , Å	7.2561(6)
<i>b</i> , Å	8.4445(7)
<i>c</i> , Å	12.3986(10)
$\alpha$ , deg	105.463(10)
$\beta$ , deg	93.692(10)
$\gamma$ , deg	102.424(10)
<i>V</i> , Å <sup>3</sup>	709.06(10)
Temperature, K	170
<i>Z</i>	1
<i>D</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.818
2 $\theta$ -Range, deg	5–56
<i>hkl</i> ranges	–9/9, –11/11, –16/16
$\mu$ (MoK $\alpha$ ), mm <sup>-1</sup>	3.362
Measured reflections	7278
<i>R</i> <sub>int</sub>	0.0301
Independent refl.	3280
Refl. with <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )	2667
Parameters	168
<i>R</i> <sub>1</sub> ( <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> ))	0.0291
<i>wR</i> <sub>2</sub> (all data)	0.0717
Goof	0.970
Residual electron density, e Å <sup>-3</sup>	0.58 / –0.47

which is equipped with a quadrupole mass spectrometer from Balzers. The MS measurements were performed in analog and trend scan mode crucibles under a helium atmosphere with a heating rate of 4 °C/min.

#### X-Ray powder diffraction experiments

X-Ray powder diffraction was performed using a STOE STADI P transmission powder diffractometer with a fixed 45° PSD (position sensitive detector) using CuK $\alpha$  radiation ( $\lambda$  = 1.540598 Å) and a graphite monochromator.

#### Results and Discussion

The reaction of copper(I) chloride with 2,3-dimethylpyrazine in acetonitrile results in the formation of the new coordination compound tetra- $\mu$ -chloro-bis( $\mu_2$ -2,3-dimethylpyrazine)-tetrakis-acetonitrile-N)tetra copper(I) (**1**) in which the ratio between copper(I) chloride and the 2,3-dimethylpyrazine ligand is exactly 2 : 1. The compound crystallizes in the triclinic space group *P* $\bar{1}$  with half a formula entity in the asymmetric unit (Table 1 and Fig. 1). (CuCl)<sub>2</sub> dimers are found in which the copper atoms are linked by two  $\mu_2$ -bridging chlorine atoms (Fig. 1). All four Cu–Cl bond lengths

Table 2. Selected bond lengths (Å) and angles (°) for compound **1**.

Cu(1)–N(3)	1.946(2)	Cu(2)–N(4)	1.947(2)
Cu(1)–N(1)	2.0542(19)	Cu(2)–N(2A)	2.0427(19)
Cu(1)–Cl(1)	2.3680(7)	Cu(2)–Cl(2)	2.3951(7)
Cu(1)–Cl(2)	2.4555(7)	Cu(2)–Cl(1)	2.4356(7)
Cu(1)–Cu(2)	3.0173(5)		
N(3)–Cu(1)–Cl(2)	102.83(6)	N(4)–Cu(2)–N(2A)	120.64(9)
N(1)–Cu(1)–Cl(2)	106.04(6)	N(4)–Cu(2)–Cl(2)	116.81(7)
Cl(1)–Cu(1)–Cl(2)	98.57(2)	N(2A)–Cu(2)–Cl(2)	104.63(6)
N(3)–Cu(1)–Cu(2)	140.97(7)	N(4)–Cu(2)–Cl(1)	107.66(6)
N(1)–Cu(1)–Cu(2)	96.01(6)	N(2A)–Cu(2)–Cl(1)	105.99(5)
Cl(1)–Cu(1)–Cu(2)	52.093(17)	Cl(2)–Cu(2)–Cl(1)	98.39(2)
Cl(2)–Cu(1)–Cu(2)	50.642(18)	N(4)–Cu(2)–Cu(1)	141.66(7)
Cu(1)–Cl(1)–Cu(2)	77.81(2)	N(2A)–Cu(2)–Cu(1)	97.08(6)
N(3)–Cu(1)–N(1)	120.97(9)	Cl(2)–Cu(2)–Cu(1)	52.438(18)
N(3)–Cu(1)–Cl(1)	121.82(7)	Cl(1)–Cu(2)–Cu(1)	50.095(17)
N(1)–Cu(1)–Cl(1)	103.26(6)	Cu(2)–Cl(2)–Cu(1)	76.92(2)

Symmetry transformations used to generate equivalent atoms:  
A:  $-x + 1, -y + 1, -z + 1$ .

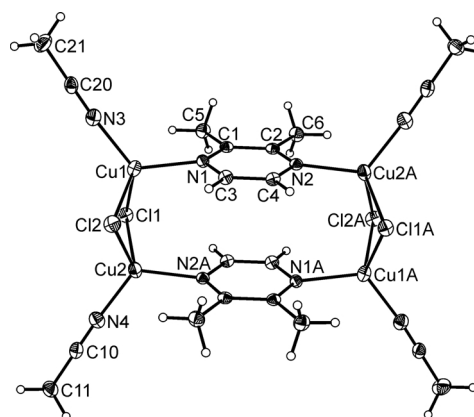


Fig. 1. Crystal structure of compound **1** with labelling and displacement ellipsoids drawn at the 50 % probability level (symmetry code: A =  $-x + 1, -y + 1, -z + 1$ ).

in the dimers are slightly different but correspond to values found in comparable coordination compounds of CuCl (Table 2). The atoms in the (CuCl)<sub>2</sub> unit are not coplanar but exhibit a butterfly-like conformation. Each copper atom is coordinated by two chlorine atoms, one acetonitrile ligand and one nitrogen atom of a 2,3-dimethylpyrazine ligand in a distorted tetrahedral geometry. Two symmetry related dimers are connected by two 2,3-dimethylpyrazine ligands *via*  $\mu$ -N,N'-coordination into discrete complexes which are located on centres of inversion (Fig. 1).

Based on the structural results it can be postulated that this compound will decompose in different steps on heating, and that in the first step only the more volatile acetonitrile ligands will be emitted. In

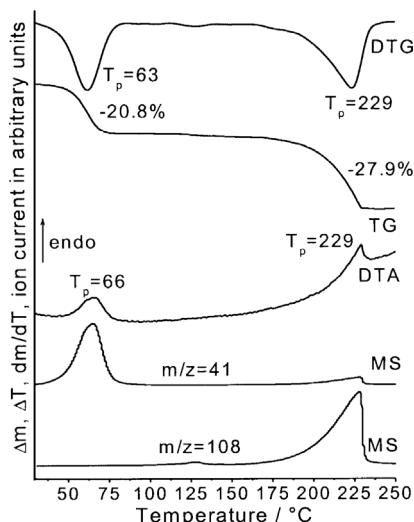


Fig. 2. DTA, TG, DTG and MS trend scan curve for compound **1** ( $m/z = 41$ : acetonitrile;  $m/z = 108$ : 2,3-dimethylpyrazine;  $T_p$  = peak temperatures in  $^{\circ}\text{C}$ ).

this case a compound can be isolated at this stage, in which the ratio between copper(I) chloride and the 2,3-dimethylpyrazine ligand is retained, corresponding to the ligand-deficient coordination polymer di- $\mu_3$ -chloro- $\mu_2$ -2,3-dimethylpyrazine- $N,N'$ -dicopper(I) reported previously by our group [29].

In order to verify the above postulate, measurements using simultaneous differential thermoanalysis and thermogravimetry coupled to mass spectroscopy were performed. On heating compound **1** to  $250^{\circ}\text{C}$  two mass steps are observed in the TG curve which are accompanied by two endothermic events in the DTA curve (Fig. 2). In the DTG curve both mass steps are well resolved, and from the MS trend scan curve it is evident that in the first step only the more volatile acetonitrile is emitted as predicted, whereas in the second step only 2,3-dimethylpyrazine is removed (Fig. 2). The experimental mass loss in the first step of 20.8 % is in good agreement with that calculated for the removal of only acetonitrile (21.1 %) and therefore, indicates the formation of a ligand-deficient 2 : 1 compound. The experimental mass loss in the second TG step of 27.9 % is in good agreement with the emission of all the 2,3-dimethylpyrazine ligands (27.9 %). The final product of this thermal decomposition reaction was confirmed to be CuCl by X-ray powder diffraction.

To conclusively prove the formation of the 2 : 1 compound a second TG measurement was performed on **1** in which the residue formed after the first TG step was isolated and investigated by X-ray powder diffraction. The experimental powder pattern of this residue is in good agreement with that calculated for the 2 : 1 compound from single crystal data. In addition, the result of an elemental analysis of this residue is in very good agreement with that calculated (see Experimental Section), showing that the coordination polymer di- $\mu_3$ -chloro- $\mu_2$ -2,3-dimethylpyrazine- $N,N'$ -dicopper(I) was obtained in very pure form.

It is to be noted that this compound can also be prepared by thermal decomposition of several different 2,3-dimethylpyrazine-rich compounds, but in this case the TG steps are not well resolved and hence it is difficult to obtain the 2 : 1 compound [29]. In contrast, if the new ligand-rich precursor compound **1** is thermally decomposed the ligand-deficient compound can easily be isolated as a pure compound. In addition, in this procedure the 2,3-dimethylpyrazine ligand is conserved and only the acetonitrile used as solvent in the synthesis is sacrificed. The ligand-deficient compound di- $\mu_3$ -chloro- $\mu_2$ -2,3-dimethylpyrazine- $N,N'$ -dicopper(I) can also be prepared in solution, but not in quantitative yield. In the present reaction it is formed quantitatively. Concerning the mechanistic aspects of the thermal transformation no clear reaction pathway can be proposed. It is interesting to note that compound **1** consists of  $(\text{CuCl})_2$  dimers as discrete building units, while the ligand-deficient 2 : 1 compound contains CuCl double chains connected into layers by the 2,3-dimethylpyrazine ligands, indicating that this reaction is accompanied by large rearrangements of the coordination network.

Thus our present results clearly show that coordination polymers can be prepared selectively, if ligand-rich precursors are designed with predefined stoichiometry, and that dependent on the type and choice of the ligands in the precursor, the desired ligands can be retained without any loss, during thermal decomposition.

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