Synthesis, Crystal Structure and Thermal Decomposition Reaction of the New Copper(I) Cyanide Coordination Polymer Poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethyl-pyrazine-N,N)]tricopper(I)

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

The new copper(I) coordination polymer poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethyl-pyrazine-N,N)] tricopper(I) (**I**) was prepared by the reaction of copper(I) cyanide with 2,3-dimethylpyrazine in acetonitrile. In the crystal structure of **I** a novel CuCN substructure is found which is connected by the dimethylpyrazine ligands into a three-dimensional coordination network. The thermal properties of **I** were investigated using simultaneous differential thermoanalysis (DTA), thermogravimetry (TG) and mass spectrometry (MS) as well as temperature resolved X-ray powder diffraction. On heating, compound **I** looses a part of the dimethylpyrazine ligands in an endothermic reaction to form the known ligand poor compound (CuCN)$_2$-(2,3-dimethylpyrazine) **II** as an intermediate which decomposes to CuCN on further heating.

Key words: Copper(I) Pseudohalide, Dimethylpyrazine, Coordination Polymers, Crystal Structure, Thermal Decomposition

Introduction

Currently we are interested in the synthesis, the structure and reactivity of inorganic-organic coordination polymers based on copper(I) halides and N-donor ligands. The structures of these compounds are composed of typical CuX-substructures (X = Cl, Br, I) that are connected by multidentate N-donor ligands into one-, two- or three-dimensional coordination networks [1 – 29] The dimensionality of these networks can be influenced predominantly by the coordination properties of the organic ligands. For a specific copper(I) halide and a specific N-donor ligand a variety of compounds are known which differ in the mole stoichiometry between the copper(I) halide and the organic ligands [18 – 29]. These can be classified as ligand rich and ligand poor compounds depending on the ratio of Cu(I)halide and N-donor ligand. These compounds are in an equilibrium in solution and therefore, sometimes mixtures of different compounds are obtained. Recently, we have demonstrated that most of the ligand rich compounds can loose a part of their ligands and form ligand poor intermediate compounds on

heating while in certain cases they transform directly to the copper(I)halides [18 – 29]. Thus new CuX coordination polymers can be prepared by the thermal decomposition of suitable CuX precursor compounds. Our previous results show that there is no simple correlation between the structures of the products and that of the starting compounds and their thermal reactivity. However, we have observed that the kinetics of all reactions involved play an important role in product formation [23]. In certain cases, different polymorphic modifications are also obtained [25 – 27].

In contrast to the copper(I) halide coordination polymers, compounds based on copper(I) pseudo halides like cyanide or thiocyanate are rare and some examples have appeared in recent literature [30 – 36]. Most of the compounds were only structurally characterized and a few of them were investigated for their thermal properties. The reported thermal reactivity of CuCN(4,4'bipyridine)-(4,4'-bipyridine)$_2$ [35] is very similar to that of some of the compounds with copper(I) halides. In view of this we have initiated systematic investigations on the thermal properties of the copper(I) pseudohalide coordination poly-

Table 1. Selected bond lengths [Å] and angles [°] for poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethylpyrazine-N,N)] tricopper(I) (**I**).

Cu(1)-N(5A)	1.976(3)	Cu(1)-C(22)	1.981(3)
Cu(1)-C(23A)	2.011(3)	Cu(1)-N(4A)	2.187(2)
N(5A)-Cu(1)-C(22)	117.7(2)	N(5A)-Cu(1)-C(23A)	108.1(2)
C(22)-Cu(1)-C(23A)	119.4(2)	N(5A)-Cu(1)-N(4A)	109.3(2)
C(22)-Cu(1)-N(4A)	101.0(2)	C(23A)-Cu(1)-N(4A)	98.9(2)
Cu(2)-N(6)	1.938(3)	Cu(2)-N(7)	1.939(3)
Cu(2)-N(2A)	2.158(3)	Cu(2)-N(3)	2.220(3)
N(6)-Cu(2)-N(7)	134.2(2)	N(6)-Cu(2)-N(2A)	109.3(2)
N(7)-Cu(2)-N(2A)	97.3(2)	N(6)-Cu(2)-N(3)	99.3(2)
N(7)-Cu(2)-N(3)	101.9(2)	N(2A)-Cu(2)-N(3)	115.5(2)
Cu(3)-C(21)	1.903(3)	Cu(3)-N(1)	2.083(2)
Cu(3)-C(22)	2.264(3)	Cu(3)-C(23A)	2.309(3)
C(21)-Cu(3)-N(1)	127.8(2)	C(21)-Cu(3)-C(22)	112.8(2)
N(1)-Cu(3)-C(22)	97.9(2)	C(21)-Cu(3)-C(23A)	114.9(2)
N(1)-Cu(3)-C(23A)	100.6(2)	C(22)-Cu(3)-C(23A)	97.8(2)

mers in order to isolate additional novel compounds by thermal decomposition. During these investigations we have prepared the new copper(I) pseudohalide coordination polymer poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethylpyrazine-N,N)] tri-copper(I) (**I**). On heating, this compound transforms into the known ligand poor 2:1 compound $(CuCN)_2$-(2,3-dimethylpyrazine) (**II**) [36]. Here we report on these investigations.

Results and Discussion

Crystal structure

The 3:2 compound poly[tri-μ2-cyano-C,N)-bis(μ2-2,3-dimethyl-pyrazine-N,N)] tricopper(I) (**I**) crystallises in the orthorhombic, chiral space group $P2_12_12_1$ with $Z = 4$ formula units in the unit cell. The asymmetric unit contains three copper cations, three cyanide anions and two 2,3-dimethylpyrazine ligands all of them located in general positions. Cu1 is coordinated by two carbon atoms and one nitrogen atom of three symmetry related cyanide anions and one nitrogen atom of the 2,3-dimethylpyrazine ligand (Fig. 1 and Table 1). The Cu-N and Cu-C bond lengths to the cyanide anions are comparable and the Cu-N distance to the N-donor ligand is significantly elongated. The angles around the copper atom are between 98.9 and 117.7° and the coordination polyhedron can be described as a strongly distorted tetrahedron (Table 1).

Cu2 is coordinated by two nitrogen atoms of two symmetry related cyanide anions and two nitrogen atoms of the two crystallographically independent organic ligands within a strongly distorted tetrahedron (Fig. 1 and Table 1). The Cu-N distances to the negatively charged cyanide anions are slightly shorter than
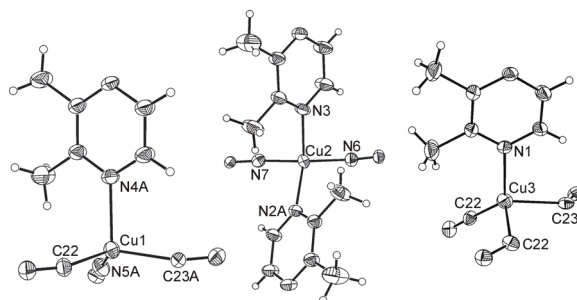

Fig. 1. Crystal structure of poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethylpyrazine-N,N)] tricopper(I) (**I**) with labelling and view of the copper coordination spheres (Displacement ellipsoids are drawn at the 50% probability level).
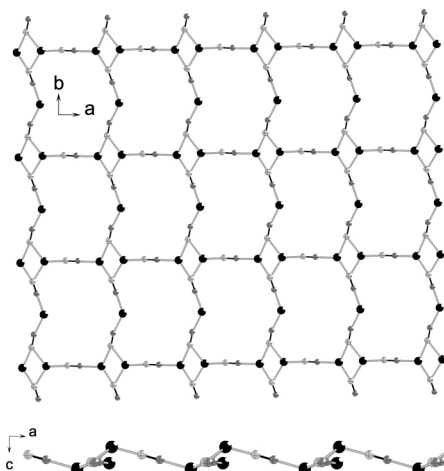

Fig. 2. Crystal structure of poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethylpyrazine-N,N)] tricopper(I) (**I**) with view of the CuCN substructure along the c-axis (top) and and along the b-axis (bottom).

those to Cu1 and the Cu-N distances to the nitrogen atoms of the 2,3-dimethylpyrazine ligands are elongated (Table 1). The coordination polyhedron around this copper atom is more distorted than that around Cu1 (angles around Cu: 97.3 – 134.2°).

Cu3 is coordinated by three carbon atoms of the three crystallographically independent cyanide anions and one nitrogen atom of the dimethylpyrazine ligand within distorted tetrahedra (angles around Cu: 97.9 – 127.8°) (Fig. 1 and Table 1). Two of the three Cu-C distances are elongated by about 0.3 Å. This might be due to an additional extremely short Cu-Cu distance of 2.491 Å between Cu3 and Cu1. Comparable short Cu-Cu distances are found *e. g.* in tris(μ3-7-diphenylphosphino-2,4-dimethyl1,8-naphthyridine)-acetonitrilo-tri-copper(I)
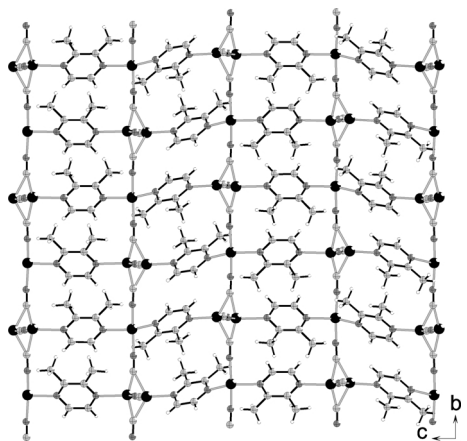
Fig. 3. Crystal structure of poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethylpyrazine-N,N)] tricopper(I) (**I**) with view along the *a*-axis.

Fig. 4. DTA, TG, DTG and MS trend scan curves for poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethylpyrazine-N,N)] tricopper(I) (**I**) (weight: 24.1 mg; heating rate: 4 °C/min.; $m/z = 108$: 2,3-dimethylpyrazine; given are the mass changes in % and the peak temperatures T_p in °C).

triperchlorate aceto-nitrile solvate (2.449 Å) [37] and in (μ2-1,4,7,10,13,16,21,24-octa-azabicyclo(8.8.8.)-hexacosa-4,6,13,15,21,23-hexaene)-copper(II)-copper (I) diperchlorate (2.448 Å) [38] and in bis(nona-aqua-tetrakis(μ3-sulfido)-tri-molybdenum-copper) octakis(p-toluenesulfonate) icosahydrate (2.426 Å) [39].

From the connection of the different copper atoms a CuCN substructure results that consists of Cu_2C_2 rings built up of Cu1 and Cu3 which are connected by the cyanide anions into chains parallel to the *a*-axis (Fig. 2). These chains are connected *via* C-N-Cu-N-C units into corrugated layers which are parallel to (001) (Fig. 2). From this arrangement 18-membered $Cu_6(CN)_6$ rings result.

The CuCN layers are linked by the 2,3-dimethylpyrazine ligands *via* μ-N,N'-coordination forming a three dimensional coordination network (Fig. 3). In this network the 2,3-dimethylpyrazine ligands are stacked into the direction of the *a*-axis (Fig. 3).

Thermoanalytical investigations

If compound **I** is heated a mass loss of 44.3% is observed in the TG curve which is accompanied with two endothermic signals at peak temperatures of about 154 and 189 °C in the DTA curve (Fig. 4). The experimental mass loss in this step of 44.3% is in good agreement with that calculated for the removal of all 2,3-dimethylpyrazine ligands (Δm$_{calcd.}$(-2 2,3-dimethylpyrazine)= 44.5%). Additional experiments using mass spectroscopy show clearly that in this

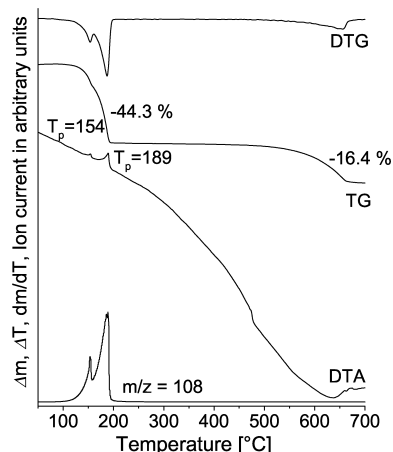step only the 2,3-dimethylpyrazine ligands are emitted ($m/z = 108$) and from the DTG curve it is obvious that the reaction occurs in two different steps which cannot be resolved successfully using these conditions (Fig. 4). The investigations of the residue formed after the first step by elemental analysis and X-ray powder diffraction conclusively prove the formation of CuCN (see Experimental Section).

From the DTG curve it is obvious that the reaction is more complicated and that the first TG step consists of two different steps. In earlier work we have shown that the kinetics of all reactions involved play an important role in the decomposition reactions of the copper(I) halides [23]. In view of this the title compound was investigated at different heating rates to resolve the TG steps more successfully. As it is obvious from Fig. 5 both thermal events can be much better resolved if the heating rate is increased. In this case it can be assumed that the intermediate product is much faster accumulated than it decomposes to CuCN. If the TG curves were analysed assuming two different steps a mass loss of about 11% is calculated for the first reaction. This value is in good agreement with that calculated for the removal of $^1/_4$ of the organic ligands (Δm$_{calcd.}$ ($-^1/_4$ (2,3-dimethylpyrazine)$_2$) = 11.1%) leading to a compound of the formal composition (CuCN)$_2$-(2,3-dimethylpyrazine).

In a second TG run compound **I** was heated using 16 °C/min and the reaction was stopped after the first TG step at about 162 °C and the residue
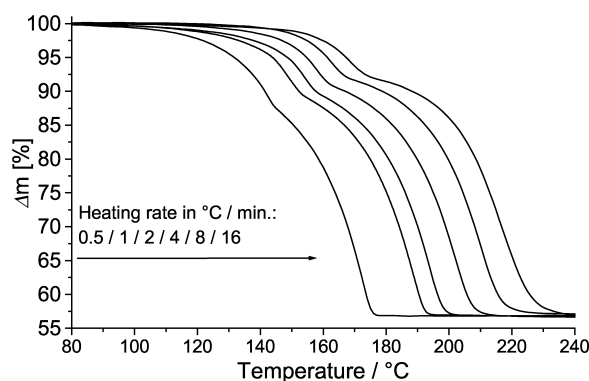
Fig. 5. Heating rate dependent TG measurements for and poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethylpyrazine-N,N)] tri-copper(I) (**I**).
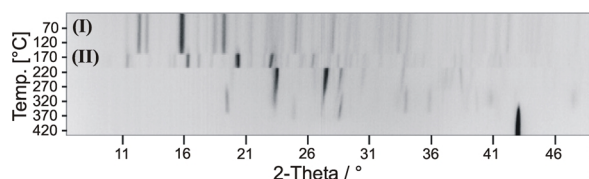

Fig. 6. Temperature dependent X-ray powder pattern for poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethylpyrazine-N,N)] tricopper(I) (**I**) measured in transmission geometry (Cu-K$_\alpha$-radiation, powdered single crystals; static air atmosphere; heating rate 2 °C/min.; powder patterns were measured every 5 °C in glass-capillaries).

was investigated using elemental analysis (see Experimental Section). The composition determined is in good agreement with that calculated for (CuCN)$_2$-(2,3-dimethylpyrazine). If this residue is investigated using X-ray powder diffraction it can be shown that a new compound has formed and that there are no reflections of the starting compound (**I**) or CuCN. A search in the Cambridge Structural Database for a structure of this composition shows that this phase is a known compound that was prepared in a hydrothermal reaction at 170 °C in 40% yield and structurally characterised by Chesnut *et al.* in 2001 [36]. If the experimental powder pattern of the residue is compared with the pattern calculated based on the single crystal data of Chesnut *et al.* it is proven that the ligand poorer coordination polymer (CuCN)$_2$-(2,3-dimethylpyrazine) has formed.

In order to ensure that no additional phases like *e. g.* polymorphic modifications occur during the thermal decomposition of compound **I** additional investigations using temperature resolved X-ray powder diffraction were performed (Fig. 6). On heating compound **I** transforms into compound **II** at about 170° (Fig. 6). Under these reaction conditions compound **II** is sta-
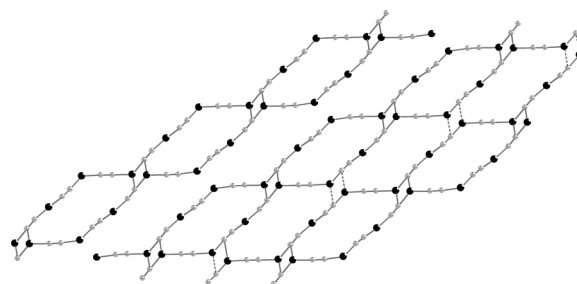

Fig. 7. CuCN-substructure of the known compound **II** according to ref. [36] (The long Cu-C/N distances are shown as dotted lines).

ble over a large temperature range and decomposes at about 190° to CuCN. These investigations clearly indicate that no additional intermediate phases are formed during the thermal decomposition.

The crystal structures of the ligand rich compound **I** and the ligand poor compound **II** exhibit similarities in the CuCN substructure (compare Fig. 2 and 7). It must be noted that in compound **I** all cyanide anions are fully ordered whereas in compound **II** all of the cyanide anions are statistically disordered in a way that each C or N position is only half occupied. As in compound **I** the copper atoms are connected into chains by the cyanide anions. Each two parallel chains are connected *via* (CuC/N)$_2$ rings into large 18-membered Cu$_6$(CN)$_6$ rings. The Cu-Cu distance within these rings of 2.747 Å is much longer than that in compound **I**. Between two neighboured double chains longer Cu-C/N distances of 2.811 Å occur (dotted in Fig. 7). If these distances are taken into account ribbons are formed which consist of each of the two double chains and three neighboured 18-membered rings. Both structural motifs, the double chains and the ribbons are also found in compound **I**. If these ribbons would be connected by additional cyanide anions which are absent in compound **II** the layered CuCN substructure of compound **I** would be formed. Therefore, the topology of the coordination network in compound **I** and **II** is very similar.

Conclusion

The reaction of the ligand rich compound **I** which transforms into the known compound **II** presented in this work clearly indicates that novel coordination polymers based on copper(I) pseudohalides can be prepared *via* thermal decomposition of ligand rich precursor compounds. The isolation of a phase pure product

Table 2. Selected crystal data and results of the structure refinements for poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethyl-pyrazine-N,N)] tricopper(I) (**I**).

Compound	I
Formula	$C_{15}N_7H_{16}Cu_3$
MW [g·mol^{-1}]	484.98
Crystal colour	orange
Crystal system	orthorombic
Space group	$P2_12_12_1$
a [Å]	6.9494 (3)
b [Å]	9.1996 (4)
c [Å]	28.299 (2)
V [Å^3]	1809.3 (2)
Temperature [K]	293
Z	4
$D_{calcd.}$ [g·cm^{-3}]	1.780
$F(000)$	968
2θ-Range	$3-54°$
$h/k/l$ ranges	$-8/8, -11/11, -36/35$
Absorption corr.	numerical
μ(Mo-K$_\alpha$) [mm^{-1}]	3.51
Min./max. transm.	0.5475/0.6842
Measured refl.	14994
$R_{int.}$	0.0643
Independent refl.	3894
Refl. with $I > 2\sigma(I)$	3564
Refined parameters	230
$R_1[I > 2\sigma(I)]$	0.0301
wR_2 [all data]	0.0763
GoF	1.026
Min./max. res. [e·Å^{-3}]	$0.55/-0.69$

Table 3. Atomic coordinates [·10^4] and isotropic displacement parameters [Å^2 · 10^3] for poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethylpyrazine-N,N)] tricopper(I) (**I**).

Atom	x	y	z	U_{eq}
Cu(1)	2442(1)	4597(1)	3667(1)	25(1)
Cu(2)	5264(1)	9579(1)	3785(1)	31(1)
Cu(3)	5478(1)	4487(1)	4134(1)	32(1)
N(1)	4286(4)	4599(3)	4809(1)	28(1)
C(1)	4933(4)	5495(4)	5149(1)	28(1)
C(2)	3891(5)	5688(3)	5571(1)	26(1)
N(2)	2237(4)	4997(3)	5643(1)	26(1)
C(3)	1633(5)	4090(4)	5304(1)	33(1)
C(4)	2609(5)	3896(4)	4893(1)	32(1)
C(5)	6791(7)	6299(6)	5061(2)	57(1)
C(6)	4590(6)	6684(5)	5948(1)	44(1)
N(3)	6559(4)	9555(4)	3068(1)	30(1)
C(11)	7852(5)	10465(4)	2887(1)	30(1)
C(12)	8270(5)	10462(4)	2398(1)	30(1)
N(4)	7370(4)	9554(3)	2104(1)	28(1)
C(13)	6075(6)	8633(5)	2294(1)	39(1)
C(14)	5687(6)	8629(5)	2770(1)	40(1)
C(15)	8820(8)	11495(6)	3220(1)	56(1)
C(16)	9738(8)	11461(6)	2189(2)	65(2)
N(5)	9710(4)	4514(3)	3859(1)	32(1)
C(21)	8131(4)	4443(4)	3968(1)	27(1)
N(6)	4401(4)	7579(3)	3820(1)	29(1)
C(22)	3894(5)	6396(3)	3813(1)	26(1)
N(7)	3970(4)	11446(3)	3792(1)	31(1)
C(23)	3641(5)	12654(3)	3807(1)	25(1)

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

indicates also that the thermal decomposition is a useful alternative method for the preparation of phase pure novel copper(I) halide and pseudohalide coordination polymers in quantitative yields.

As compound **II** was earlier isolated using hydrothermal synthesis at 170 °C [36] and it is also formed by thermal decomposition at about 170 °C, it is expected that compound **II** is more stable than compound **I** at elevated temperatures.

A comparison of the structures of the ligand rich compound **I** and the ligand poor compound **II** shows that both structures are related. To form the ribbons observed in compound **I** only small translational changes are needed. For the connection of the ribbons into layers present in compound **I** additional cyanide anions are required. Because all cyanide anions are fully ordered in compound **I** whereas they are fully disordered in compound **II** which was prepared at elevated temperatures the question raises if this disordering is also present in compound **II** which is prepared by thermal decomposition. As mentioned above most of the fragments of the CuCN substructure observed in **I** are also present in **II** or can be formed by only minor transla-

tional changes. However, this topic will be the subject of further investigations.

Experimental Section

*Synthesis of poly[tri-μ_2-cyano-C,N)-bis(μ_2-2,3-dimethyl-pyrazine-N,N)] tricopper(I) (**I**)*

179.1 mg (2 mmol) copper(I) cyanide (Fluka) and 250 mg (2.3 mmol) 2,3-dimethylpyrazine were stirred in 6 ml acetonitrile at room-temperature. After 3 d the yellow precipitate was filtered off and was washed with ethanol and diethylether. Yield: 85.3% (based on CuCN). Elemental analysis: $C_{15}N_7H_{16}Cu_3$ (484.98): calcd. C 37.2, N 20.3, H 3.3; found: C 37.0, N 20.1, H 3.3. X-ray powder diffraction: phase pure. Single crystals of this compound were prepared by the reaction of 53.72 mg (0.6 mmol) CuCN and 60 mg (1 mmol) of 2,3-dimethylpyrazine in 4 ml acetonitrile without stirring. After 7 d orange crystals were obtained.

Single crystal structure investigation

The data collection was performed using an Imaging Plate Diffraction System (IPDS-I) from STOE & CIE. The intensities were corrected for absorption effects using X-RED [40] and X-Shape [41]. The structure solutions was performed

using SHELXS-97 [42] and the structure refinements were done against F^2 using SHELXL-97 [43]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealised geometry and refined with fixed isotropic displacement parameters using a riding model. The absolute structure was determined and is in agreement with the selected setting (Flack-x-Parameter: 0.02 (2)). Selected crystal data, details of the structure determination as well as lists with atomic coordinates and equivalent isotropic displacement parameters are given in Table 2 and 3.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 251538). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1E2, UK (fax: int.Code +(44)01223/3 36-033, e-mail: deposit@chemcrys.cam.ac.uk).

X-ray powder diffraction experiments

X-Ray powder diffraction experiments were performed using a STOE STADI P transmission powder diffractometer and a Siemens D-5000 diffractometer in reflection geometry both equipped with Cu-K$_\alpha$-radiation ($\lambda = 1.540598$ Å). For temperature and time resolved X-ray powder diffraction the STADI P diffractometer is equipped with a graphite oven and a position sensitive detector (scan range: $5° - 50°$) from STOE & CIE. All temperature resolved X-ray powder experiments were performed in glass capillaries under a static air atmosphere.

Differential thermal analysis, thermogravimetry and mass spectroscopy

DTA-TG-MS measurements were performed simultaneously using the STA-409CD with Skimmer coupling from Netzsch, which is equipped with a quadrupol mass spectrometer QMA 400 (max. 512 amu) from Balzers. The MS measurements were performed in both analog and trend scan mode. All measurements were corrected for buoyancy and current effects and were performed using heating rates of 0.5, 1, 2, 3, 4, 8 and 16 K/min. in Al$_2$O$_3$ crucibles with and without capes under a dynamic nitrogen (purity: 5.0) or helium (purity 4.6) atmosphere (flow-rate: 75 ml/min.). The thermobalance was calibrated using standard reference materials.

Elemental analysis

C, H, N analysis was performed using a CHN-O-RAPID combustion analyser from Heraeus and EDX were performed using a Philips XL30 Environmental Scanning Electron Microscope (ESEM) which is equipped with an EDX system (Energy Dispersive X-Ray Analysis) from EDAX.

Results of the elemental analysis of the residues obtained during the thermal decomposition of **I**: Residue obtained after the first mass loss at 162 °C (**II**): C$_8$N$_4$H$_8$Cu$_2$ (275.26): calcd. C 33.4, N 19.5, H 2.8; found: C 33.2, N 19.4, H 2.7.

Residue obtained after the second mass loss at 200 °C: CuCN (89.56): calcd. C 13.4, N 15.6; found C 13.5, N 15.9.

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