

Synthesis, Crystal Structure and Properties of CuBr(2,3-dimethylpyrazine) Coordination Polymers

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Reaction of CuBr with an excess of 2,3-dimethylpyrazine in acetonitrile leads to the formation of the literature known ligand-rich 1 : 1 compound poly[μ_2 -bromo- μ_2 -2,3-dimethylpyrazine-N,N'-copper(I)] (**1**). On heating this compound in a thermobalance a transformation into the new ligand-deficient 2 : 1 compound poly[di- μ_3 -bromo- μ_2 -2,3-dimethylpyrazine-N,N'-dicopper(I)] (**3**) is observed, which later was also prepared in solution. This compound crystallizes in the monoclinic space group $P2_1/n$ with all atoms in general positions. In the crystal structure the Cu atoms are surrounded by three Br atoms and one 2,3-dimethylpyrazine ligand within a distorted tetrahedron. The tetrahedra are connected *via* common Br edges into CuBr double chains, which are connected by the ligands into layers located in the *ab* plane. The formation of compounds **1** and **3** was also investigated in solution. The results have shown that compound **1** can only be prepared if an excess of the ligand is used. If CuBr and the ligand are reacted in a ratio of 1 : 1, in the beginning the literature known ligand-deficient 3 : 2 intermediate catena[tribromo- μ_2 -bis(μ_2 -2,3-dimethylpyrazine-N,N')-tricopper(I)] (**2**) is obtained, which transforms within minutes into compound **3**. If a crystalline suspension of compound **1** is stirred in acetonitrile a transformation into the most stable compound **3** is also observed. The luminescence properties of compounds **1** and **3** were investigated. The complexes show differences mainly in the emission spectra.

Key words: Coordination Polymers, CuBr(2,3-dimethylpyrazine), Crystal Structures, Thermal Properties, Luminescence Properties

Introduction

In the last years we were interested in the synthesis, crystal structures and properties of coordination polymers based on transition metal (I) halides or *pseudo* halides and N donor ligands, with special attention to CuX compounds ($X = \text{Cl}, \text{Br}, \text{I}$). Several of these compounds are known and were structurally characterised [1–24]. For a certain copper(I) halide or *pseudo* halide and a specific nitrogen donor ligand in most cases several compounds of different stoichiometry were reported. We have found that on heating, most of the ligand-rich compounds transform into ligand-deficient intermediate compounds, which can be isolated in quantitative yield [11–21]. Therefore, thermal decomposition of suitable CuX precursor compounds is an alternative route for the discovery and preparation of new CuX coordination polymers.

In 2001 we reported on the crystal structure of the ligand-rich 1 : 1 compound poly[μ_2 -bromo- μ_2 -2,3-dimethylpyrazine-N,N'-copper(I)] (**1**) [22]. In this structure (CuBr)₂ dimers are connected by the 2,3-dimethylpyrazine ligands into layers (Fig. 1: left). Four years later Wells *et al.* reported on a second compound in this system, which was obtained by accident as a by-product in the synthesis of dibromo-2,3-dimethylpyrazine-copper(II) [23]. In the 3 : 2 compound catena[tribromo- μ_2 -bis(μ_2 -2,3-dimethylpyrazine-N,N')-tricopper(I)] (**2**) (CuBr)₃ six-membered rings are connected by the 2,3-dimethylpyrazine ligands into double chains (Fig. 1: right). For the corresponding CuCl₂-2,3-dimethylpyrazine system we have identified one ligand-rich 4 : 9 compound, two ligand-deficient polymorphic 1 : 1 compounds as well as ligand-deficient 3 : 2 and 2 : 1 compounds [24]. Therefore, we assumed that for the CuBr(2,3-dimethylpyrazine) system at least one additional ligand-

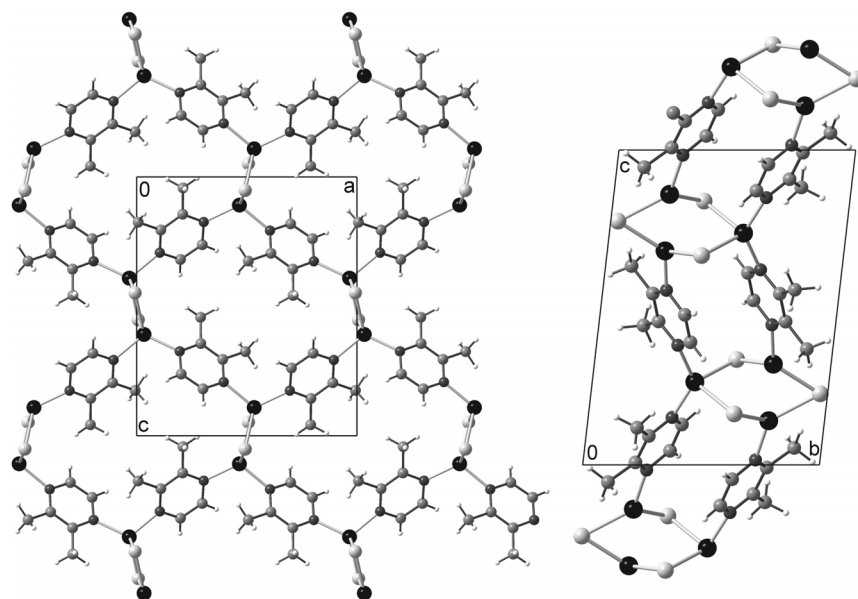


Fig. 1. Crystal structure of the literature known 1 : 1 compound **1** with view along the *b* axis (left) and of the literature known 3 : 2 compound **2** with view along the *a* axis (right).

deficient intermediate is still missing and investigated the ligand-rich 1 : 1 compound poly[μ_2 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-copper(I)] by thermal measurements. In these investigations we discovered one additional ligand-deficient compound of composition (CuBr)₂(2,3-dimethylpyrazine) (**2**), which can also be prepared in solution. Compounds **1** and **2** show strong luminescence and therefore, these properties were also investigated.

Results and Discussion

Thermal properties

The ligand-rich 1 : 1 compound poly[μ_2 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-copper(I)] (**1**) was investigated using differential thermoanalysis and thermogravimetry coupled to mass spectroscopy (DTA-TG-MS). Up to 330 °C two mass steps were observed, both accompanied by two endothermic events in the DTA curve (Fig. 2). The final product of this reaction was identified as CuBr by X-ray powder diffraction. The DTG curve shows that both events are well resolved, and from the MS trend scan curve it is obvious that in both steps only the 2,3-dimethylpyrazine ligand is emitted (Fig. 2). The experimental mass loss of 21.3 % is in good agreement with that calculated for the removal of half of the 2,3-dimethylpyrazine ligands (21.5 %). Therefore, it can be assumed that during thermal decomposition a new ligand-deficient compound

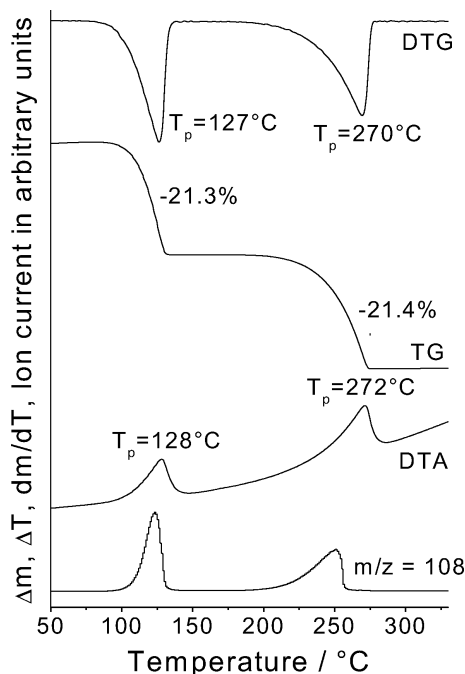


Fig. 2. DTA, TG, DTG and MS trend scan curves for poly[μ_2 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-dicopper(I)] (**3**) (T_p = peak temperature).

of composition (CuBr)₂(2,3-dimethylpyrazine) (**3**) was formed.

To prove this assumption a second TG experiment was performed and the residue obtained after

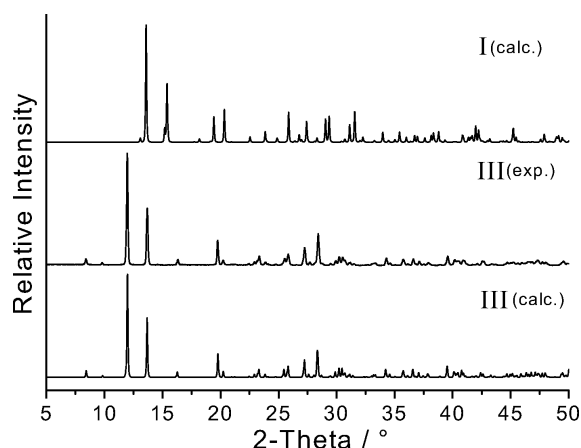


Fig. 3. Experimental X-ray powder pattern of the residue obtained after the first TG step in the thermal decomposition reaction of the ligand-rich 1 : 1 compound **1** (mid) and calculated pattern for **1** (top) and the ligand-deficient 2 : 1 compound **3** (bottom).

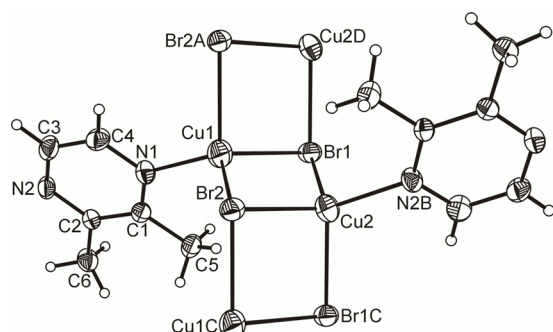


Fig. 4. Part of the crystal structure of poly[di- μ_3 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-dicopper(I)] **3** with labelling and displacement ellipsoids drawn at the 50 % probability level.

the first step was investigated by elemental analysis (see Experimental Section) and X-ray powder diffraction. The experimental pattern of the residue is completely different from that calculated for the ligand-rich 1 : 1 compound **1** and the results of the elemental analysis is in good agreement with that calculated for a ligand-deficient compound of composition $(\text{CuBr})_2(2,3\text{-dimethylpyrazine})$ (Fig. 3). On the basis of these results we tried to prepare this compound in solution and succeed in the preparation of single crystals of the new compound **3**. If afterwards the experimental pattern of the residue obtained in the DTA-TG-MS investigations is compared with that of compound **3** calculated from single crystal data, it is proven that **3** is an intermediate in the thermal decomposition reaction of compound **1** (Fig. 3).

Table 1. Selected bond lengths (Å) and angles (deg) for poly[di- μ_3 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-dicopper(I)] (**3**). (Symmetry transformations used to generate equivalent atoms: A: $x - 1, y, z$; B: $-x + 1/2, y - 1/2, -z + 3/2$; C: $x + 1, y, z$).

Cu(1)–N(1)	2.030(4)	Cu(2)–N(2B)	2.037(4)
Cu(1)–Br(2)	2.4774(9)	Cu(2)–Br(1C)	2.5175(8)
Cu(1)–Br(1)	2.5580(8)	Cu(2)–Br(1)	2.5205(9)
Cu(1)–Br(2A)	2.5726(8)	Cu(2)–Br(2)	2.5413(8)
N(1)–Cu(1)–Br(2)	113.36(12)	N(2B)–Cu(2)–Br(1C)	112.09(11)
N(1)–Cu(1)–Br(1)	117.37(10)	N(2B)–Cu(2)–Br(1)	102.80(11)
Br(2)–Cu(1)–Br(1)	113.28(3)	Br(1C)–Cu(2)–Br(1)	107.15(3)
N(1)–Cu(1)–Br(2A)	107.79(11)	N(2B)–Cu(2)–Br(2)	123.80(10)
Br(2)–Cu(1)–Br(2A)	106.77(3)	Br(1C)–Cu(2)–Br(2)	97.93(3)
Br(1)–Cu(1)–Br(2A)	96.10(3)	Br(1)–Cu(2)–Br(2)	112.39(3)
N(1)–Cu(1)–Cu(2)	140.21(12)	N(2B)–Cu(2)–Cu(1)	135.55(11)
Br(2)–Cu(1)–Cu(2)	57.29(2)	Br(1C)–Cu(2)–Cu(1)	111.84(3)
Br(1)–Cu(1)–Cu(2)	56.00(2)	Br(1)–Cu(2)–Cu(1)	57.29(2)
Br(2A)–Cu(1)–Cu(2)	111.90(3)	Br(2)–Cu(2)–Cu(1)	55.11(2)

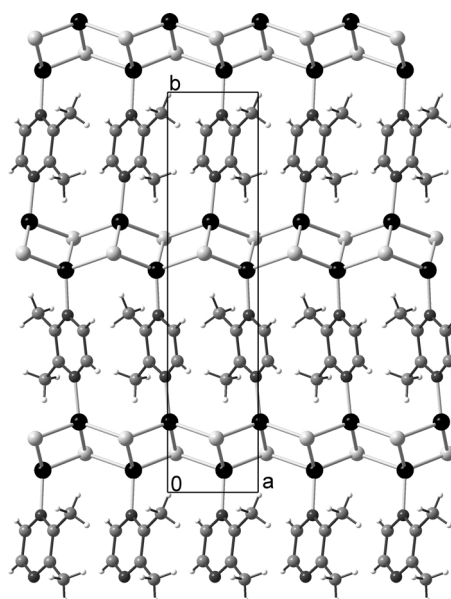


Fig. 5. Crystal structure of poly[di- μ_3 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-dicopper(I)] (**3**) with view in the direction of the *c* axis.

Crystal structure of poly[di- μ_3 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-dicopper(I)] (**3**)

The ligand-deficient 2 : 1 compound **3** crystallises in the monoclinic space group $P2_1/n$ with $Z = 4$ and all atoms in general positions. In the crystal structure the copper atoms are surrounded by three bromine atoms and one 2,3-dimethylpyrazine ligand in a distorted tetrahedral arrangement (Fig. 4 and Table 1). The Cu–N and Cu–Br distances for both crystallographically independent copper atoms are similar and

Table 2. Results of the crystallisation experiments in different solvents as a function of the molar ratio between copper(I) bromide and 2,3-dimethylpyrazine.

CuBr:Ligand	4:1	2:1	3:2	1:1	2:3	1 : 2	1:3	1:4	1:5	1:6
Water	—	(3)	—	(1)/(3)	—	—	—	(1)	—	—
Acetonitrile	—	(3)	—	(1)/(3)	—	—	—	(1)	—	—
Methanol	—	—	(3)	—	—	—	—	(1)	—	—

comparable to those in other CuBr coordination polymers retrieved from the literature.

The CuBr₃N tetrahedra are connected *via* common Br edges into CuBr double chains extending in the direction of the *a* axis (Fig. 5). These double chains are connected by the ligands into layers located in the *ab* plane. The topology of the coordination network of compound **3** is identical with that in the corresponding CuCl compound poly[di- μ_3 -chloro- μ_2 -2,3-dimethylpyrazine-*N,N'*-dicopper(I)], but the two compounds are not isotypic [23]. However, this arrangement is frequently found in 2:1 CuX coordination polymers (*X* = Cl, Br, I).

Investigations on the formation of compounds **1–3** in solution

The formation of these compounds was also investigated in solution. In these experiments copper(I) bromide and 2,3-dimethylpyrazine were mixed in different stoichiometric ratios in constant amounts of water, methanol and acetonitrile (Table 2). These crystalline suspensions were stirred for a week so that the thermodynamically most stable compounds were formed. Afterwards the products were identified by X-ray powder diffraction. These investigations have clearly shown that the ligand-rich compound **1** can only be prepared for example in acetonitrile if at least a 3-fold excess of the 2,3-dimethylpyrazine ligand is used, because otherwise the new ligand-deficient 2:1 compound **3** is obtained (Table 2). These findings are further supported by experiments where a suspension of the ligand-rich compound **1** is stirred in acetonitrile. After a few days a complete transformation into compound **3** is observed. These results also show that the equilibrium strongly depends on the solvent used in the synthesis (Table 2). In addition, it is proven that the literature known 3:2 compound **2** is metastable and cannot be prepared if the preparation is performed under thermodynamic control.

To investigate whether the ligand-deficient 3:2 intermediate **2** can also be prepared in solution, equimolar amounts of CuBr and the ligand were mixed and the

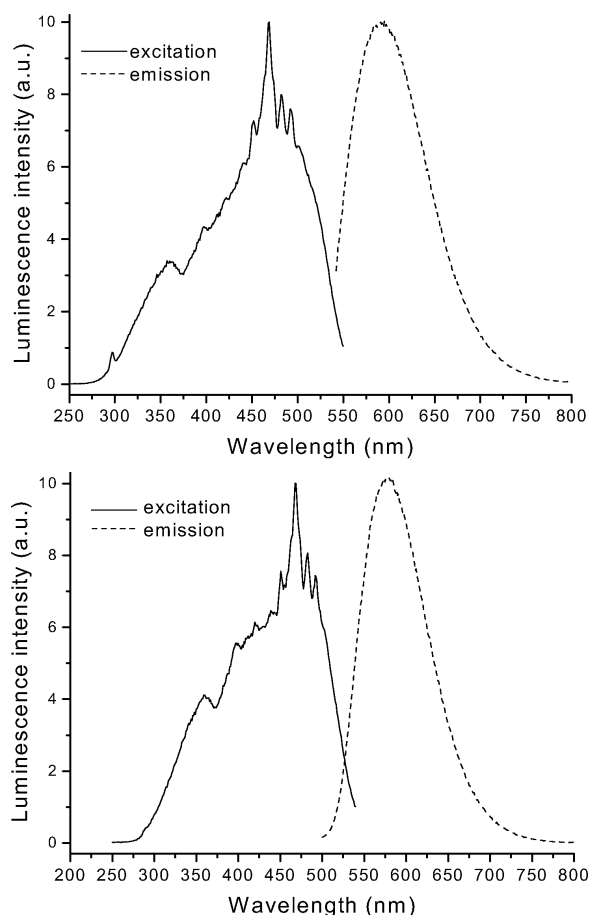


Fig. 6. Luminescence emission and excitation spectra of poly[μ_2 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-copper(I)] (**1**) (top) and poly[di- μ_3 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-dicopper(I)] (**3**) (bottom) in solid state at 298 K. The spectra are uncorrected and normalised.

precipitate formed was identified as a function of time using *ex situ* X-ray powder diffraction. These investigations have clearly shown, that at the beginning of this reaction compound **2** is formed, which transforms within about 1 h into the most stable compound **3**. However, compound **2** cannot be prepared in pure form in solution, because it is always contaminated with unreacted CuBr. Additional heating rate dependent TG measurements on compound **1** have also shown that the metastable compound **2** cannot be observed as an intermediate.

Luminescence measurements

Compound **1** and **3** show strong luminescent emission in the solid state after irradiation by light in the region between 300 and 550 nm (Fig. 6). Similar lumi-

Table 3. Luminescence properties of compounds **1** and **3** in the solid state at 298 K.

Compound	Excitation maximum (nm)	Emission maximum (nm)	Luminescence lifetime (μ s)
1	469	591	25.3
3	469	577	24.6

nescent properties of Cu(I) halide compounds were described by different authors and emission processes are usually explained as a result of metal centred transitions or halide to copper charge transfer [25, 26]. The emission maximum of compound **3** is shifted ($\Delta = 14$ nm) to higher wavelength in comparison with the emission maximum of compound **1** (Table 3). This observation confirms structural changes observed also by other techniques. Luminescence lifetime curves for each complex at r. t. are only single exponential. Differences in the lifetimes of compounds **1** and **3** seem to be insignificant (Table 3).

Conclusion

In the present work the thermal properties of a ligand-rich CuBr(2,3-dimethylpyrazine) compound were investigated, and the formation of a hitherto unknown ligand-deficient intermediate has been demonstrated. These findings clearly prove that thermal decomposition reactions of suitable ligand-rich precursor compounds offer an alternative route to new coordination polymers, which might be overlooked if the synthesis is performed in solution. Our investigations of solutions have also shown that different species are present and that the composition of the compounds obtained from solution depends on the nature of the solvent and the stability of these compounds. Therefore, a specific coordination polymer cannot be prepared by simple mixing of the reactands in a ratio given by the formula of the expected composition. To isolate specific compounds from solution, a large number of different experiments must be performed. In favourable cases, the synthesis can be accomplished much more easily by thermal decomposition reactions. Starting from the most ligand-rich compound, all ligand-deficient intermediates may be observed in one measurement. However, this is sometimes difficult to achieve if some of the compounds are metastable like in the present case, but we have shown previously that very often metastable compounds can also be prepared by thermal decomposition reactions if heating rate dependent TG measurements are used [13]. Investigation of the luminescence properties have shown only small

Table 4. Selected crystal data and results of the structure refinements for poly[di- μ_3 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-dicopper(1)] (**3**).

Formula	C ₆ H ₈ Br ₂ Cu ₂ N ₂
MW [g mol ⁻¹]	395.04
Crystal colour	yellow
Crystal size [mm ⁻¹]	0.3 × 0.1 × 0.1
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	4.0537(2)
<i>b</i> [Å]	17.936(2)
<i>c</i> [Å]	12.911(1)
β [deg]	92.95(1)
<i>V</i> [Å ³]	937.5(1)
Temperature [K]	293
<i>Z</i>	4
<i>D</i> _{calc.} [g cm ⁻³]	2.799
2 θ -Range [deg]	5–56
<i>hkl</i> ranges	–5/5, –23/23, –16/16
μ (MoK α) [mm ⁻¹]	13.001
Absorption corr.	numerical
Transmission min./max.	0.302/0.364
Refl. measured	8397
<i>R</i> _{int.}	0.0459
Refl. independent	2225
Refl. with <i>I</i> ≥ 2 σ (<i>I</i>)	1769
Parameters	112
<i>R</i> ₁ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0320
<i>wR</i> ₂ (all data)	0.0786
Goof	1.024
Residual electron density [e Å ⁻³]	0.53/–0.79

changes in the emission spectra in which the maximum of compound **3** is slightly shifted to higher wavelength compared to compound **1**. Small differences are also found for the luminescence lifetimes. Systematic studies on this topic will be the subject of further investigations.

Experimental Section

*Synthesis of poly[μ_2 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-copper(1)] (**1**)*

71.5 mg (0.5 mmol) of CuBr and 162.2 μ L (1.5) of 2,3-dimethylpyrazine were stirred in a glass container at r. t. in 2 mL of acetonitrile for 1 d. The orange precipitate was filtered off and washed with diethyl ether. Yield: 86.5 % based on CuBr. The homogeneity of the product was confirmed by comparison of the experimental and calculated X-ray powder patterns. Elemental analysis: calcd. C 28.5, H 3.2, N 11.0; found C 28.6, H 3.2, N 11.1.

*Synthesis of poly[di- μ_3 -bromo- μ_2 -2,3-dimethylpyrazine-*N,N'*-dicopper(1)] (**3**)*

Single crystals of compound **3** were prepared by hydrothermal reaction of 143.4 mg (1 mmol) of CuBr with

Table 5. Atomic coordinates [$\times 10^4$] isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for poly[di- μ_3 -bromo- μ_2 -2,3-dimethylpyrazine- N,N' -dicopper(I)] (**3**). (All atoms in position 4e; equivalent isotropic U calculated as a third of the trace of the orthogonalized U_{ij} tensors).

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cu(1)	1238(2)	4446(1)	7060(1)	40(1)
Cu(2)	5239(2)	3239(1)	7662(1)	39(1)
Br(1)	395(1)	3651(1)	8671(1)	30(1)
Br(2)	5932(1)	4025(1)	6050(1)	29(1)
N(1)	1022(10)	5570(2)	7226(3)	27(1)
C(1)	2406(11)	5954(2)	8031(3)	24(1)
C(2)	2015(11)	6735(2)	8096(3)	22(1)
N(2)	245(10)	7109(2)	7359(3)	27(1)
C(3)	−1083(13)	6716(3)	6552(3)	32(1)
C(4)	−713(12)	5958(3)	6483(3)	31(1)
C(5)	4276(13)	5523(3)	8860(4)	34(1)
C(6)	3513(13)	7173(3)	8987(3)	33(1)

54 μL (0.5 mmol) of 2,3-dimethylpyrazine in 3 mL of acetonitrile. The reactands were filled in a glas ampoule which was sealed and heated to 150 °C for 4 d. After cooling to r. t. light orange single crystals had formed which were suitable for single crystal X-ray analysis. The homogeneity of the product was confirmed by comparison of the experimental and calculated X-ray powder patterns.

Single crystal structure analysis

Data of **3** were measured using an Imaging Plate Diffraction System from STOE & CIE. Structure solutions were performed with Direct Methods using SHELXS-97 [27]. Structure refinement was carried out against F^2 using SHELXL-97 [27]. A numerical absorption correction was performed using X-RED and X-SHAPE [28]. 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. Selected crystal data and results of the structure refinement are shown in Table 4, atomic coordinates and equivalent isotropic displacement parameters are given in Table 5.

CCDC 628758 contains the supplementary crystallographic data for this paper. These data can be obtained free

of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-Ray powder diffraction

X-Ray powder diffraction experiments were performed using a STOE STADI P transmission powder diffractometer equipped with a position sensitive detector using $\text{CuK}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$).

Differential thermal analysis, thermogravimetry and mass spectrometry

DTA-TG-MS measurements were performed using the STA-409CD thermobalance with Skimmer coupling from Netzsch, equipped with a quadrupole mass spectrometer from Balzers. The MS measurements were performed in analog and trend scan mode, in Al_2O_3 crucibles under helium atmosphere (purity: 4.6) using heating rates of 4 °C/min. The instrument was calibrated using standard reference materials.

Elemental analysis

CHN analysis was performed using an EURO EA Elemental Analyser, from EURO VECTOR Instruments. Elemental analysis of the residue obtained after the first step in the thermal decomposition reaction of compound **1**: calcd. for the 2 : 1 compound **3**: C 18.2, H 2.0, N 7.1; found C 18.3, H 2.0, N 7.0.

Luminescence measurements

All luminescence measurements including lifetime decay curves, emission and excitation spectra were performed on a luminescence spectrometer Aminco-Bowman Series 2 (ThermoSpectronic, USA). The instrument is equipped with both a continuous Xe lamp (150 W) and a Xe flash lamp (7 W).

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