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Investigations on the Synthesis, Structures, and Properties of New Copper(I) 2,3-Dimethylpyrazine Coordination Compounds

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Five new coordination compounds were prepared, structurally characterized, and investigated for their thermal properties. In the structure of the ligand-rich 4:9 compound, tetra(μ_2-chloro)bis(μ_2-2,3-dimethylpyrazine-*N*,*N*′)tetrakis-(2,3-dimethylpyrazine-*N*)tetracopper(I) tris(2,3-dimethylpyrazine)solvate (**I**), discrete complexes are formed by build up of two $[(CuCl–(2,3\text{-dimethylpyrazine})_2]_2$ dimers, which are connected by two 2,3-dimethylpyrazine ligands via μ-N,N′ coordination. In the 1:1 compound poly[μ_2-chloro-μ_2-2,3-dimethylpyrazine-*N*,*N*′-copper(I)] (**II**), $(CuCl)_2$ dimers are found, which are connected by the 2,3-dimethylpyrazine ligands into layers. For this composition, a second polymorphic modification was found (**III**), which exhibits a different topology of the coordination network and a different packing of the layers. In the most stable 3:2 compound catena[tri(μ_2-chloro)bis(μ_2-2,3-dimethylpyrazine-*N*,*N*′)tricopper(I)] (**IV**), six-membered rings of $(CuCl)_3$ are found, which are connected by the 2,3-dimethylpyrazine ligands into chains. In the ligand-deficient 2:1 compound, poly[di(μ_3-chloro)(μ_2-2,3-dimethylpyrazine-*N*,*N*′)dicopper-(I)] (**V**), CuCl double chains are found, which are connected by the 2,3-dimethylpyrazine ligands into layers. On heating, compound **I** transforms quantitatively into the 3:2 compound **IV** without the formation of **II** or **III** as intermediates. Compound **IV** is also obtained by heating either the 1:1 compound **II** or **III**. On further heating, the 3:2 compound **IV** loses additional ligands, forming the ligand-deficient 2:1 compound **V**, which then decomposes into CuCl. The stability, thermal reactivity, and the transition behavior of all compounds were investigated using different thermoanalytical methods. These results are compared with those previously reported for the structurally similar CuCl(2-ethylpyrazine) coordination compounds. The formation and the stability of the different compounds in solution were also investigated.

Introduction

Recently, we investigated coordination compounds based on copper(I) halides or pseudohalides and N-donor ligands. In these compounds, typical CuX substructures are found that are connected by the ligands into one-, two-, or three-dimensional coordination polymers. For a certain copper(I) halide or pseudohalide and a given ligand, ligand-rich as well as ligand-deficient compounds of different stoichiometries are often observed, which cannot always be obtained in phase-pure form, if the reaction is performed in solution. Several of such compounds have been reported in the literature, but most of them were only structurally characterized.[1−29]

We have found that most of the ligand-rich compounds decompose into the ligand-deficient compounds on heating,

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whereas a few compounds transform directly to the pure copper(I) halides or pseudohalides.[14−29] A similar reactivity has also been observed for coordination compounds based on silver(I) or zinc(II) halides, and we have also shown that coordination polymers that exhibit cooperative magnetic interactions can be prepared by this route.[30−33] In almost all cases, ligand-deficient intermediates are formed in 100% yield and in a very pure form. Therefore, the controlled thermal decomposition of suitable precursor compounds is a convenient alternative for the discovery or synthesis of coordination polymers and inorganic−organic hybrid compounds, which cannot be prepared in solution or which are always obtained as mixtures. We have investigated such reactions in detail, and we have found that there exists no simple relationship between the crystal structures of the starting compounds and their thermal reactivity. On the other hand, for compounds with 2-ethylpyrazine as the ligand, we have observed that the occurrence of the ligand-deficient intermediate phases depends on the heating rate used in the experiment, indicating that compound formation depends on the kinetics of all reactions involved.[20] With this ligand, three different CuCl coordination polymers can be prepared: The amine-rich 1:1 compound poly[μ_2-chloro(μ_2-2-ethylpyrazine-*N*,*N*′)copper(I)], the intermediate 3:2 compound catena[tri-(μ_2-chloro)bis(μ_2-2-ethylpyrazine-*N*,*N*′)tricopper(I)], and the ligand-deficient 2:1 compound poly[di(μ_3-chloro)(μ_2-2-ethylpyrazine-*N*,*N*′)dicopper(I)]. In the 1:1 compound, CuCl chains are found and are connected by the 2-ethylpyrazine ligands into a three-dimensional coordination network. In the 3:2 compound, six-membered $(CuCl)_3$ rings occur and are connected into chains by the organic ligands. The ligand-deficient 2:1 compound consists of CuCl double chains, which are linked by the ligands into layers. Heating of the 1:1 compound in a thermobalance using a heating rate of 1 °C/min results in a transformation into the 2:1 compound. In contrast, heating of the ligand-rich 1:1 compound at 16 °C/min leads to the formation of the 3:2 compound as a pure intermediate. On further heating, this compound transforms into the 2:1 compound, which finally decomposes into CuCl on extended heating.[20]

To study such reactions systematically, we have synthesized and investigated several such compounds containing only pyrazine derivatives as ligands. The use of pyrazine derivatives was expected to result in similar topology of the coordination networks of these compounds, thus making the study advantageous for structure−property relationships. During these investigations, we have prepared compounds of CuCl with 2,3-dimethylpyrazine, which have an identical topology of the coordination network to those of the 2-ethylpyrazine compounds but a different thermal reactivity and thermodynamic stability. The results of these investigations are described herein.

Experimental Section

Synthesis. 2,3-Dimethylpyrazine and CuCl are commercially available. The purity of all compounds was checked by comparing the experimental powder patterns with those calculated from single-crystal data and by elemental analysis. In the following section, the preparation of crystals that are suitable for single-crystal X-ray diffraction is described. The preparation of large amounts of powders for most of the compounds is discussed in the Results and Discussion section.

Tetra(μ_2-chloro)bis(μ_2-2,3-dimethylpyrazine-*N*,*N*′)tetrakis-(2,3-dimethylpyrazine-*N*)tetracopper(I) tris(2,3-dimethylpyrazine)solvate (I). CuCl (99.0 mg, 1 mmol) and 2,3-dimethylpyrazine (324.4 mg, 3 mmol) were mixed in a glass container. After 3−4 days, orange crystals of **I** were obtained and used without any further purification. This compound decomposes within a few minutes into the 3:2 compound **IV**. Therefore, elemental analysis cannot be performed.

Poly[μ_2-chloro-μ_2-2,3-dimethylpyrazine-*N*,*N*′-copper(I)] (II). CuCl (99.0 mg, 1 mmol) and 2,3-dimethylpyrazine (432.6 mg, 4 mmol) was taken into an ampule, and water (2 mL) was added. The ampule was sealed and heated at 140 °C for 1 day. Afterward, the reaction mixture was maintained at 80 °C for 4 days and then cooled to room tempearture. By this procedure, a mixture of the orange-yellow 3:2 compound **IV** and the red 1:1 compound **II** was obtained and can be separated by hand. Elem anal. Calcd: C, 34.8; N, 13.5; H, 3.9. Found: C, 34.8; N, 13.3; H, 3.7.

Poly[μ_2-chloro-μ_2-2,3-dimethylpyrazine-*N*,*N*′-copper(I)] (III). CuCl (99.0 mg, 1 mmol) and 2,3-dimethylpyrazine (432.6 mg, 4 mmol) were reacted in methanol (2 mL) in a glass container at room temperature. Initially, phase-pure crystals of the 3:2 compound **IV** are formed, and they transform within 5 days into large red crystals of compound **III**. Elem anal. Calcd: C, 34.8; N, 13.5; H, 3.9. Found: C, 34.9; N, 13.4; H, 3.8.

Catena[tri(μ_2-chloro)bis(μ_2-2,3-dimethylpyrazine-*N*,*N*′)tricopper(I)] (IV). Compound **IV** was prepared using the same reaction conditions as those for compound **III**, but the product was isolated before the transformation into compound **III** occurred. Elem anal. Calcd: C, 28.1; N, 10.9; H, 3.1. Found: C, 27.9; N, 10.8; H, 3.1.

Poly[di(μ_3-chloro)(μ_2-2,3-dimethylpyrazine-*N*,*N*′)] (V). CuCl (99.0 mg, 1 mmol) and 2,3-dimethylpyrazine (54.1 mg, 0.5 mmol) were heated in a glass ampule at 140 °C for 3 days. Yellow needles

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Table 1. Crystal Data and Results of the Structure Refinement for Compounds **I**−**V**[a]

	compound				
	I	**II**	**III**	**IV**	**V**
formula	$C_{54}H_{72}Cl_4Cu_4N_{18}$	$C_6H_8N_2CuCl$	$C_6H_8N_2CuCl$	$C_{12}H_{16}N_4Cu_3Cl_3$	$C_6H_8Cl_2Cu_2N_2$
fw (g/mol)	1369.28	207.13	207.13	513.26	306.12
space group	$P\bar{1}$	*Pbca*	*C*2/*c*	$P\bar{1}$	*C*2/*c*
a (Å)	11.314(1)	11.588(1)	19.106(2)	7.219(1)	30.303(2)
b (Å)	11.688(1)	9.4479(5)	7.1485(3)	9.416(1)	3.9135(2)
c (Å)	13.977(1)	13.180(1)	12.558(1)	13.019(2)	15.194(1)
α (deg)	71.87(1)			82.89(2)	
β (deg)	75.41(1)		118.47(1)	85.62(2)	100.39(1)
γ (deg)	63.47(1)			81.97(2)	
V (Å^3)	1557.5(2)	1443.0(2)	1507.7(2)	868.0(2)	1772.4(2)
T (K)	200	293	200	293	293
Z	1	8	8	2	8
D_{calcd} (g/cm^3)	1.451	1.907	1.825	1.964	2.294
μ (mm^{-1})	1.570	3.311	3.168	4.102	5.339
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
R1 [$I > 2\sigma(I)$]	0.0378	0.0290	0.0257	0.0460	0.0363
wR2 [all data]	0.1014	0.0779	0.0693	0.1203	0.0921

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

of compound **V** were obtained. Elem anal. Calcd: C, 23.5; N, 9.1; H, 2.6. Found: C, 23.3; N, 8.9; H, 2.5.

Single-Crystal X-ray Structure Determination. All structure solutions were performed with direct methods using *SHELXS-97*.[34] The structure refinements were performed against F^2 using *SHELXL-97*.[34] For compounds **II**−**V**, a numerical absorption correction was applied using *X-Red*[35] and *X-Shape*.[36] All non-H atoms were refined using anisotropic displacement parameters. The H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding model. In compound **I**, one of the four crystallographically independent 2,3-dimethylpyrazine ligands is disordered around a center of inversion and was refined using a split model. The H atoms of this ligand were not considered in the structure refinement. Details of the structure determination are given in Table 1.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre [CCDC 614157 (**I**), CCDC 614158 (**II**), CCDC 614159 (**III**), CCDC 614160 (**IV**), and CCDC 614161 (**V**)]. Copies may be obtained free of charge upon application to the Director, CCDC, 12 Union Road, Cambridge CB2 1E2, U.K. (Fax int. code +(44)01223/3 36-033; e-mail deposit@chemcrys.cam.ac.uk).

X-ray Powder Diffraction. Powder diffraction experiments were performed using a STOE STADI P transmission powder diffractometer equipped with position-sensitive detectors (scan range: 5−45°) from STOE & Cie, using Cu Kα radiation (λ = 154.0598 pm).

Differential Thermal Analysis (DTA), Thermogravimetry (TG), and Mass Spectroscopy (MS). The DTA−TG−MS measurements were performed under a N_2 atmosphere (purity: 5.0) in Al_2O_3 crucibles using heating rates of 4 °C/min and a flow rate of 75 mL/min using a STA-409CD thermobalance from Netzsch. For the MS measurements, the instrument is connected to a quadrupole mass spectrometer from Balzers via Skimmer coupling from Netzsch. The MS measurements were performed in analogue and trend scan mode. All measurements were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

Elemental Analysis. CHN analysis was performed using an Euro EA elemental analyzer, from EuroVector Instruments and Software.

Elemental Analysis of the Residues Obtained in the Thermal Decomposition Reaction of Compounds I−V. (A) Isolated after the first mass step for compound **I** (%). Calcd for the 3:2 compound **III**: C, 28.1; H, 3.1; N, 10.9. Found: C, 27.9; H, 3.2; N, 11.0. (B) Isolated after the second mass step for compound **I** (%). Calcd for the 2:1 compound **IV**: C, 23.5; H, 2.6; N, 9.2. Found: C, 22.9; H, 2.5; N, 9.4. (C) Isolated after the first mass step for compound **II** (%). Calcd for the 3:2 compound **III**: C, 28.1; H, 3.1; N, 10.9. Found: C, 27.8; H, 3.1; N, 10.7. (D) Isolated after the second mass step for compound **II** (%). Calcd for the 2:1 compound **IV**: C, 23.5; H, 2.6; N, 9.2. Found: C, 23.0; H, 2.4; N, 8.9. (E) Isolated after the first mass step for compound **III** (%). Calcd for the 3:2 compound **III**: C, 28.1; H, 3.1; N, 10.9. Found: C, 28.2; H, 3.1; N, 10.7. (F) Isolated after the second mass step for compound **II** (%). Calcd for the 2:1 compound **IV**: C, 23.5; H, 2.6; N, 9.2. Found: C, 23.4; H, 2.5; N, 8.9. (G) Isolated after the first mass step for compound **IV** (%). Found: C, 23.3; H, 2.6; N, 9.3. Calcd for the 2:1 compound **IV**: C, 23.5; H, 2.6; N, 9.2.

Results and Discussion

Crystal Structures. The ligand-rich 4:9 compound **′I** crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell. In this compound, two symmetry-related $(CuCl)_2$ dimers are found that are connected by two symmetry-related 2,3-dimethylpyrazine ligands via μ-N,N′ coordination (Figure 1, top). Each of the four Cu atoms are additionally connected by one 2,3-dimethylpyrazine ligand within distorted tetrahedra. This ligand does not act as a bridging ligand (Table 2). From this arrangement, discrete building blocks are formed that are located on the centers of inversion. Bond lengths and angles are comparable to those in other CuCl coordination polymers that contain $(CuCl)_2$ dimers (Table 2).

In the crystal structure, the discrete complexes are packed in such a way that holes are formed, in which additional 2,3-dimethylpyrazine ligands are located (Figure 1, bottom).

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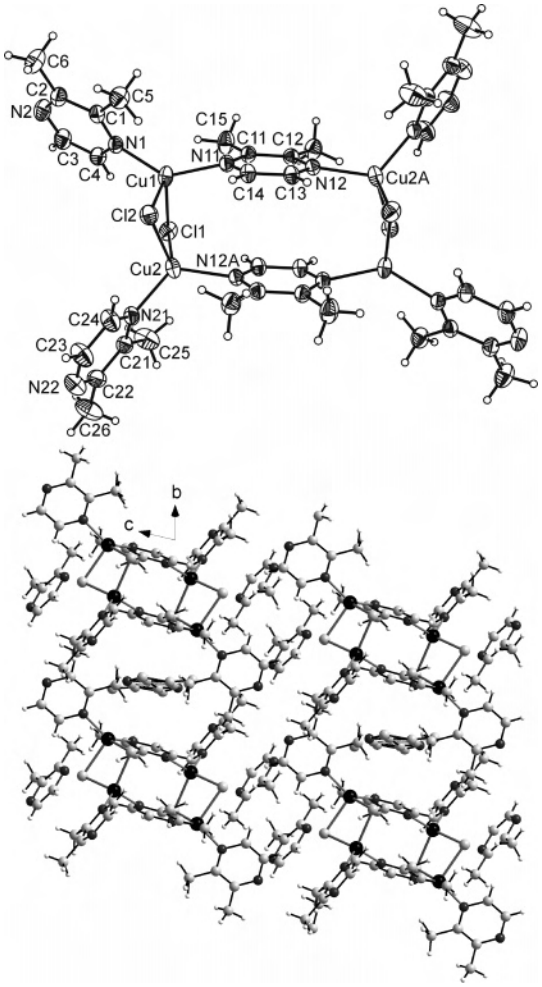

Figure 1. Crystal structure of the 4:9 compound **I** with labeling and displacement ellipsoids drawn at the 50% probability level (top; the solvate 2,3-dimethylpyrazine molecules are not shown for clarity) and crystal structure with a view along the *a* axis (bottom).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for the 4:9 Compound **I**[a]

Cu1−N1	2.005(2)	Cu2−N21	2.021(2)
Cu1−N11	2.0187(19)	Cu2−N12A	2.0492(19)
Cu1−Cl2	2.4140(8)	Cu2−Cl1	2.3976(8)
Cu1−Cl1	2.4724(7)	Cu2−Cl2	2.4573(7)
Cu1−Cu2	2.9742(6)		
N1−Cu1−N11	134.98(9)	N21−Cu2−N12A	121.17(9)
N1−Cu1−Cl2	108.30(6)	N21−Cu2−Cl1	116.11(6)
N11−Cu1−Cl2	103.50(6)	N12A−Cu2−Cl1	102.78(6)
N1−Cu1−Cl1	102.92(6)	N21−Cu2−Cl2	103.02(6)
N11−Cu1−Cl1	100.65(6)	N12A−Cu2−Cl2	109.41(6)
Cl2−Cu1−Cl1	102.00(3)	Cl1−Cu2−Cl2	102.92(3)
N1−Cu1−Cu2	127.90(6)	N21−Cu2−Cu1	134.83(6)
N11−Cu1−Cu2	96.66(6)	N12A−Cu2−Cu1	103.54(6)
Cl2−Cu1−Cu2	53.033(19)	Cl1−Cu2−Cu1	53.51(2)
Cl1−Cu1−Cu2	51.23(2)	Cl2−Cu2−Cu1	51.714(19)
Cu2−Cl1−Cu1	75.27(2)	Cu1−Cl2−Cu2	75.25(2)

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

One of these ligands is disordered around a center of inversion, and none of these ligands are coordinated to the Cu atoms.

The 1:1 compound ′**II** crystallizes in the orthorhombic space group *Pbca* with eight formula units in the unit cell. In this structure, $(CuCl)_2$ dimers are found in which each

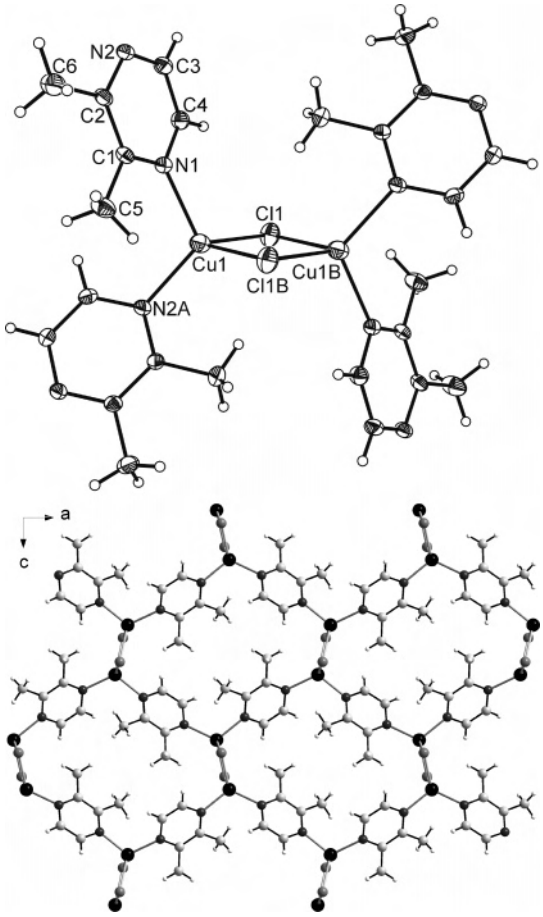

Figure 2. Crystal structure of the 1:1 compound **II** with labeling and displacement ellipsoids drawn at the 50% probability level (top) and with a view along the *b* axis (bottom).

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for the 1:1 Compound **II**[a]

Cu1−N2A	2.0803(17)	Cu1−Cl1B	2.5498(8)
Cu1−N1	2.0848(17	Cl1−Cu1B	2.5498(8)
Cu1−Cl1	2.3414(7)		
N2A−Cu1−N1	113.67(7)	N1−Cu1−Cl1B	101.79(5)
N2A−Cu1−Cl1	119.49(6)	Cl1−Cu1−Cl1B	95.35(2)
N1−Cu1−Cl1	111.82(5)	Cu1−Cl1−Cu1B	84.65(2)
N2A−Cu1−Cl1B	111.74(6)		

[a] Symmetry transformations used to generate equivalent atoms: A, $x - {}^1/_2$, y, $-z + {}^3/_2$; B, $-x + 1$, $-y + 1$, $-z + 1$.

Cu atom is coordinated by two symmetry-related Cl atoms and two N atoms of two symmetry-related 2,3-dimethylpyrazine ligands within distorted tetrahedra (Figure 2, top). Bond lengths and angles in compound **II** are comparable to those in compound **I** as well as those in other compounds that consist of $(CuCl)_2$ dimers (Table 3). In contrast to compound **I**, where the $(CuCl)_2$ dimers show a butterfly-like conformation, in compound **II** these dimers are coplanar (compare Figure 2, top, with Figure 1, top). In the crystal structure, the dimers are connected by the 2,3-dimethylpyrazine ligands via μ_2-N,N′ coordination into layers that are parallel to the crystallographic *ac* plane (Figure 3, bottom).

The second modification of the 1:1 compound (**III**) crystallizes in the monoclinic space group *C*2/*c* with eight formula units in the unit cell. As in compound **II**, coplanar

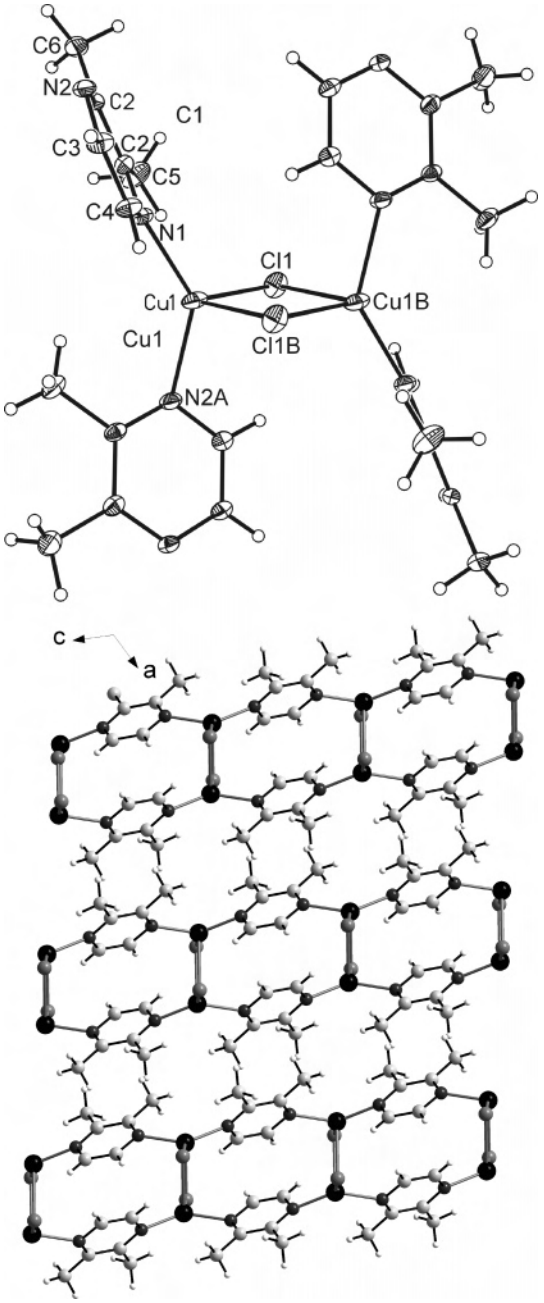

Figure 3. Crystal structure of the second modification of the 1:1 compound **III** with labeling and displacement ellipsoids drawn at the 50% probability level (top) and with a view along the *b* axis (bottom).

$(CuCl)_2$ dimers are found in which each Cu atom is coordinated by two symmetry-related Cl atoms and two N atoms of two symmetry-related 2,3-dimethylpyrazine ligands within distorted tetrahedra (Figure 3, top). In contrast to compound **II**, two of the four ligands are oriented nearly perpendicular to the others and, therefore, the topology of the coordination network is different. From this arrangement, 12-membered rings built up of two ligands and two $(CuCl)_2$ dimers, which are connected into layers, are formed (Figure 3, bottom). Bond lengths and angles in compound **III** are comparable to those in compounds **I** and **II** as well as those in other compounds that consist of $(CuCl)_2$ dimers (Table 4).

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for the 1:1 Compound **III**[a]

Cu1−N1	1.9956(15)	Cu1−Cl1	2.3492(6)
Cu1−N2A	2.0300(15)	Cu1−Cl1B	2.5203(6)
Cl1−Cu1B	2.5203(6)		
N1−Cu1−N2A	133.35(7)	N2A−Cu1−Cl1B	92.74(5)
N1−Cu1−Cl1	117.27(5)	Cl1−Cu1−Cl1B	99.124(17)
N2A−Cu1−Cl1	104.55(5)	Cu1−Cl1−Cu1B	80.876(17)
N1−Cu1−Cl1B	99.78(5)		

[a] Symmetry transformations used to generate equivalent atoms: A, x, $-y+1$, $z-{}^1/_2$; B, $-x+{}^1/_2$, $-y+{}^1/_2$, $-z$.

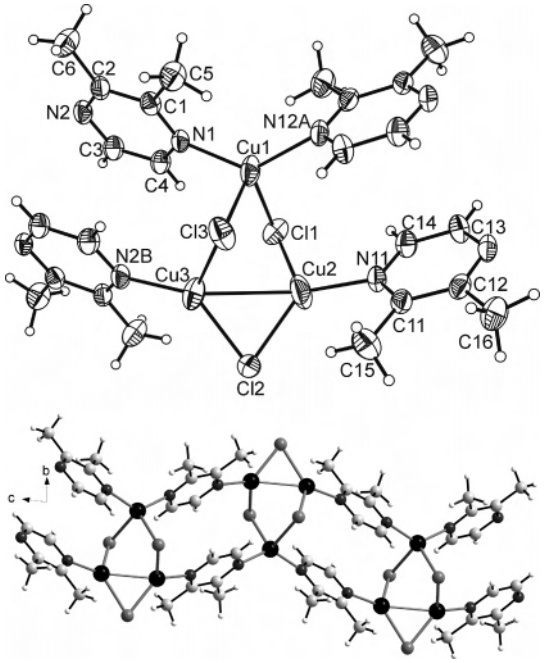

Figure 4. Crystal structure of the 3:2 compound **IV** with labeling and displacement ellipsoids drawn at the 50% probability level (top) and with a view along the *a* axis (bottom).

The 3:2 compound **′IV** crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. In its crystal structure, distorted $(CuCl)_3$ six-membered rings are found in which one Cu atom is coordinated by two Cl atoms and two 2,3-dimethylpyrazine ligands within distorted tetrahedra, whereas two Cu atoms are only 3-fold-coordinated by two Cl atoms and one 2,3-dimethylpyrazine ligand (Figure 4, top). However, between the two 3-fold-coordinated Cu atoms, a very short Cu−Cu distance of 2.635(1) Å occurs that is indicative of $d^{10}-d^{10}$ interactions[37] (Figure 4, top, and Table 5). In contrast to compounds **I** and **II**, large differences in the CuCl bond lengths are found (Table 5). The $(CuCl)_3$ rings are each connected by two 2,3-dimethylpyrazine ligands into chains that elongate along the *c* axis (Figure 4, bottom).

The ligand-deficient 2:1 compound **′V** crystallizes in the monoclinic space group $C2/c$ with eight formula units in the unit cell. In its structure, each Cu atom is coordinated by three Cl atoms and one N atom of a 2,3-dimethylpyrazine ligand within distorted tetrahedra (Figure 5, top, and Table 6). The Cu atoms are each connected via two μ_3-Cl atoms into corrugated CuX double chains, which elongate in the

(37) Jansen, M. *Angew. Chem.* **1987**, *99*, 1136−1154; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098−1116 and references cited therein.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for the 3:2 Compound **IV**[a]

Cu1−N1	2.018(4)	Cu1−N12A	2.026(4)
Cu1−Cl1	2.380(2)	Cu1−Cl3	2.493(2)
Cu2−N11	1.978(4)	Cu2−Cl2	2.243(2)
Cu2−Cl1	2.367(2)	Cu2−Cu3	2.635(1)
Cu3−N2B	1.984(4)	Cu3−Cl2	2.270(2)
Cu3−Cl3	2.332(2)		
N1−Cu1−N12A	131.7(2)	N1−Cu1−Cl1	104.8(2)
N12A−Cu1−Cl1	108.2(2)	N1−Cu1−Cl3	103.5(2)
N12A−Cu1−Cl3	102.7(2)	Cl1−Cu1−Cl3	102.5(1)
N11−Cu2−Cl2	133.6(2)	N11−Cu2−Cl1	113.6(2)
Cl2−Cu2−Cl1	108.3(6)	N11−Cu2−Cu3	152.1(2)
Cl2−Cu2−Cu3	54.76(5)	Cl1−Cu2−Cu3	78.7(1)
N2B−Cu3−Cl2	132.0(2)	N2B−Cu3−Cl3	111.9(2)
Cl2−Cu3−Cl3	114.9(1)	N2B−Cu3−Cu2	155.2(2)
Cl2−Cu3−Cu2	53.8(1)	Cl3−Cu3−Cu2	74.2(1)

[a] Symmetry transformations used to generate equivalent atoms: A, $-x + 1, -y + 1, -z + 2$; B, $-x, -y + 1, -z + 1$.

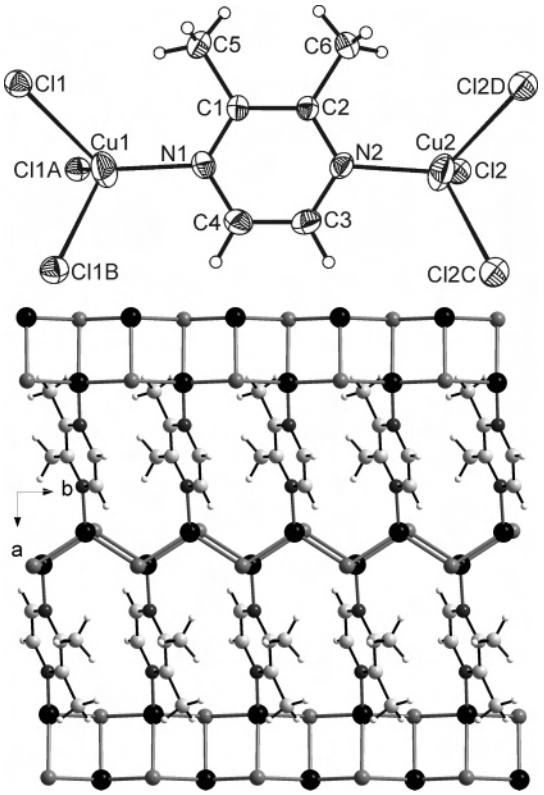

Figure 5. Crystal structure of compound **V** with labeling and displacement ellipsoids drawn at the 50% probability level (top) and with a view along the *c* axis (bottom).

direction of the crystallographic *b* axis (Figure 5, bottom). The CuCl double chains are linked by the 2,3-dimethylpyrazine ligands via μ-N,N′ coordination into layers that are located in the crystallographic *ab* plane (Figure 5, bottom). The orientation of neighboring double chains changes in the direction of the *a* axis (Figure 5, bottom).

Thermoanalytical Investigations. All compounds were investigated by simultaneous DTA and TG coupled to MS (DTA−TG−MS). On heating, the 4:9 compound **I** starts decomposing at room temperature. Until 275 °C, three mass steps are observed, accompanied by four endothermic signals in the DTA curve (Figure 6). The differential thermogravimetry (DTG) curve shows that all mass steps are well resolved

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for the 2:1 Compound **V**[a]

Cu1−N1	2.011(3)	Cu1−Cl1A	2.363(1)
Cu1−Cl1B	2.403(1)	Cu1−Cl1	2.484(1)
Cu2−N2	2.017(3)	Cu2−Cl2	2.376(1)
Cu2−Cl2C	2.381(1)	Cu2−Cl2D	2.506(1)
N1−Cu1−Cl1A	113.24(9)	N1−Cu1−Cl1B	110.55(9)
Cl1A−Cu1−Cl1B	110.42(4)	N1−Cu1−Cl1	125.15(8)
Cl1A−Cu1−Cl1	98.46(3)	Cl1B−Cu1−Cl1	97.39(3)
N2−Cu2−Cl2	108.16(9)	N2−Cu2−Cl2C	113.56(9)
Cl2−Cu2−Cl2C	110.71(4)	N2−Cu2−Cl2D	120.02(8)
Cl2−Cu2−Cl2D	108.31(3)	Cl2C−Cu2−Cl2D	95.48(3)

[a] Symmetry transformations used to generate equivalent atoms: A, $-x + 3/2, y - 1/2, -z + 1/2$; B, $-x + 3/2, y + 1/2, -z + 1/2$; C, $x, y + 1, z$; D, $-x + 1, -y + 1, -z + 1$.

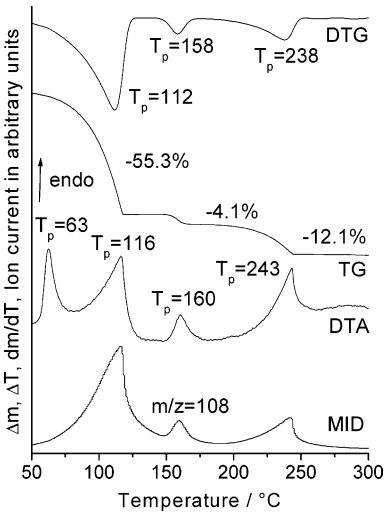

Figure 6. DTA, TG, DTG, and MS trend scan curve for the ligand-rich compound **I** [heating rate, 4 °C/min; $m/z = 108$ (2,3-dimethylpyrazine); given are the mass changes (%) and the peak temperatures T_p (°C)].

and the MS trend scan curve shows that only 2,3-dimethylpyrazine ($m/z = 108$) is emitted. The experimental mass loss in the first step of 55.3% is in good agreement with that calculated for the formation of the 3:2 compound **III** ($\Delta m_{theo} = -55.5\%$), and the mass loss of 4.1% in the second step corresponds to that expected for the formation of the 2:1 compound **IV** ($\Delta m_{theo} = -4.05\%$). On further heating, the remaining ligands are emitted, and the final product was identified as CuCl by X-ray powder diffraction. Interestingly, no mass step that can be assigned to the formation of the 1:1 compound **II** is observed in the beginning. The observation of two endothermic signals in the DTA curve indicates a more complex reaction (Figure 6).

To prove the formation of the 3:2 (**IV**) and 2:1 (**V**) compounds as intermediate phases, additional TG measurements were performed in which the residues after the first and second TG steps were isolated and investigated by X-ray powder diffraction as well as elemental analysis (Figure 7A−D). A comparison of the experimental X-ray powder patterns of these residues with those calculated for the 3:2 compound **IV** and the 2:1 compound **V** clearly shows that compounds **IV** and **V** have formed in the first and second TG step, respectively (Figure 7). These results are in good agreement with the elemental analysis of the corresponding residues (see the Experimental Section).

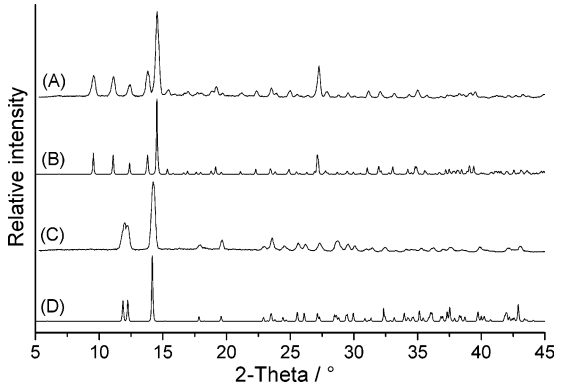

Figure 7. Experimental powder pattern of the residue isolated after the first TG step at 125 °C (A) and after the second TG step at 170 °C (C) in the thermal decomposition reaction of compound **I** and the calculated pattern for the 3:2 compound **IV** (B) and the 2:1 compound **V** (D).

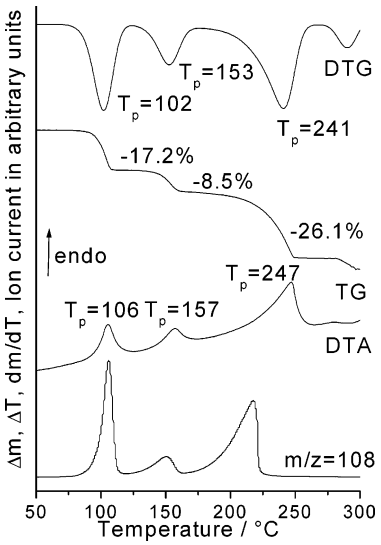

Figure 8. DTA, TG, DTG, and MS trend scan curve for the 1:1 compound **II** [heating rate, 4 °C/min; m/z = 108 (2,3-dimethylpyrazine); given are the mass changes (%) and the peak temperatures T_p (°C)].

The DTA−TG−MS curves of the 1:1 compound **II** exhibit three well-resolved mass steps in which only 2,3-dimethylpyrazine (m/z = 108) is emitted (Figure 8). The experimental mass loss in the first TG step of 17.2% is in good agreement with that expected for the removal of one-third of the 2,3-dimethylpyrazine ligands (Δm_{theo} = −17.4%), which should lead to the 3:2 compound **IV** (Figure 8). In the next TG step, the ligand-deficient 2:1 compound **V** should have formed (Δm_{theo} = −8.7%), whereas in the last TG step, the remaining 2,3-dimethylpyrazine ligands are emitted. The final product was identified as CuCl by X-ray powder diffraction.

In additional TG experiments, the residue formed after the first and second TG step was isolated and investigated by X-ray powder diffraction and elemental analysis. A comparison of the powder pattern of these residues with those calculated from single-crystal data unambiguously proves that the 3:2 compound **IV** and the ligand-deficient 2:1 compound **V** are formed in the first and second steps, respectively (see the Supporting Information). In addition, the results of the elemental analysis of these residues are in good agreement with this reaction pathway (see the Experimental Section).

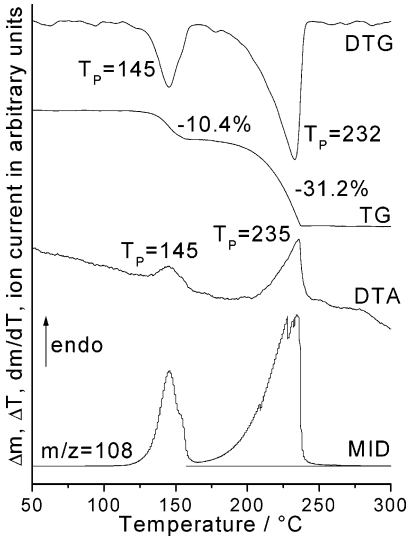

Figure 9. DTA, TG, DTG, and MS trend scan curve for the 1:1 compound **IV** [heating rate, 4 °C/min; m/z = 108 (2,3-dimethylpyrazine); given are the mass changes (%) and the peak temperatures T_p (°C)].

The TG−DTA thermograms of the second modification **III** of the 1:1 compound indicate a behavior similar to that for compound **II** (see the Supporting Information). There are no significant differences in the thermal stability of both compounds. An examination of the residues obtained in the first and second TG steps by elemental analysis and X-ray powder diffraction shows that the 3:2 compound **IV** and the 2:1 compound **V** are formed in the first and second TG steps, respectively (see the Supporting Information and Experimental Section).

For the 3:2 compound **IV**, two mass steps are observed in the TG curve, of which the first step corresponds to the formation of the 2:1 compound **V** (Δm_{theo} = −10.5%) and the second step corresponds to the formation of CuCl (Δm_{theo} = −31.6%) (Figure 9, the Supporting Information, and the Experimental Section). The DTA−TG curves of the 2:1 compound **V** exhibit a single mass step as expected, in which all ligands are emitted (see the Supporting Information).

Investigations in Solution and in the Solid State. The stabilities of all of the compounds **I**−**V** in the solid state were investigated by time-dependent X-ray powder diffraction. This shows that compounds **II**−**V** are stable over several days, whereas the ligand-rich compound **I** decomposes into the 3:2 compound **IV** even at room temperature within a few hours.

The formation of these compounds was also investigated in solution. In these experiments, copper(I) chloride and 2,3-dimethylpyrazine were mixed in different stoichiometric ratios and constant amounts of water, methanol, and ethanol were added (Table 7). These crystalline suspensions were stirred for 1 week so that the thermodynamically most stable compounds were formed. Afterward, the products were identified by X-ray powder diffraction.

In all, only three of the five compounds are obtained under these conditions. These investigations clearly show that the 1:1 compound **II** is the thermodynamically more stable form than the 1:1 compound **III** but compound **II** can be obtained pure only if a 5- or 6-fold excess of 2,3-dimethylpyrazine is

Table 7. Results of the Crystallization Experiments in Different Solvents as a Function of the Molar Ratio between Copper(I) Chloride and 2,3-Dimethylpyrazine

	CuCl:ligand									
	4:1	2:1	3:2	1:1	2:3	1:2	1:3	1:4	1:5	1:6
water		**V** (2:1)				**IV** (3:2)			**II** (1:1)	
methanol		**V** (2:1)				**IV** (3:2)			**II** (1:1)	
ethanol		**V** (2:1)			**IV** (3:2)				**II** (1:1)	

used in the synthesis. The use of a 3-fold excess of ligand leads to the formation of only the 3:2 compound **IV**. Interestingly, this compound cannot be obtained by reacting copper(I) chloride with 2,3-dimethylpyrazine in a molar ratio as given by the formula of this compound. From this reaction, the ligand-deficient 2:1 compound **V** is obtained.

To determine the thermodynamically most stable form of the 1:1 compounds at room temperatuer, a crystalline suspension of an equimolar mixture of both forms was stirred in water and ethanol. Because the 1:1 compounds will transform into the 2:1 compound **V** under these conditions (see Table 7), a 5-fold excess of ligand was added. An investigation of the residue formed after 1 week revealed that all the reflections of the second form **III** have disappeared and the powder pattern was identical with that of compound **II** calculated from single-crystal data. Therefore, form **II** is the thermodynamically most stable form at room temperature.

Structure−Property Relationships. As mentioned in the Introduction, we have previously reported on some coordination polymers with 2-ethylpyrazine, which have exactly the same composition as the compounds described here, with one exception.[20] The analogous ligand-rich 4:9 compound of Cu with 2-ethylpyrazine cannot be prepared. It must also be mentioned that the structures of these compounds are not isotypic. From a comparison of the structures of the 2-ethylpyrazine compounds with those of the 2,3-dimethylpyrazine compounds, it is obvious that the topology of the coordination network of both 3:2 and 2:1 compounds are identical and that the topology of the 1:1 compound with 2-ethylpyrazine corresponds exactly to that of the thermodynamically most stable 1:1 modification **II**.[20] Interestingly, the thermal reactivity of the ligand-rich 1:1 compounds and the thermal stability of the 3:2 compounds with 2-ethylpyrazine and 2,3-dimethylpyrazine are completely different. As mentioned earlier, the 3:2 compound with 2-ethylpyrazine can only be obtained by thermal decomposition at relatively fast heating rates, but in any case, the TG curve is not well resolved.[20] Therefore, it is really difficult to isolate this compound in phase-pure form. Slow heating rates resulted in the formation of the ligand-deficient 2:1 compound. In contrast, for the present compounds with 2,3-dimethylpyrazine, a completely different behavior is observed. The 3:2 compound **IV** is always obtained in the first step, irrespective of the actual heating rate. In addition, the stability range of this compound is much larger than that of the corresponding 2-ethylpyrazine coordination polymer. A similar behavior is observed with the 2:1 compound **V**, which also shows a larger stability range compared to that of the 2:1 2-ethylpyrazine coordination polymer.[20] These results clearly show that no simple relationship exists between the topologies of the coordination networks and the thermal reactivity and stability in such compounds.

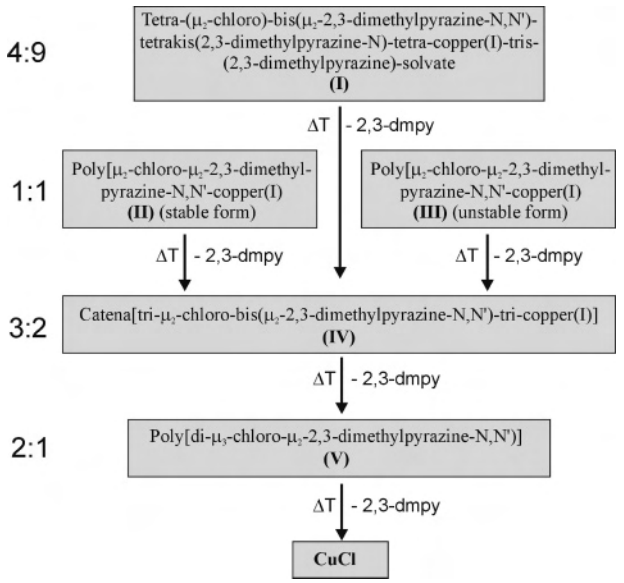

Figure 10. Schematic representation of the thermal transformation of compounds **I**−**V**.

Conclusions

In the present contribution, we describe five new coordination polymers based on copper(I) chloride and 2,3-dimethylpyrazine including a pair of polymorphic modifications. Whereas the ligand-rich 4:9 compound is built up of discrete building blocks, all other ligand-deficient compounds represent coordination polymers with one- or two-dimensional structures. Thermoanalytical measurements reveal that the ligand-deficient 3:2 and 2:1 compounds can be prepared very pure by thermal decomposition reaction of the 4:9 compound (Figure 10). Interestingly, during this process, the 1:1 compounds are not formed as intermediates, indicating their lower stability as compared to those of the other ligand-deficient compounds. For the 1:1 compounds, two different polymorphic modifications are obtained, differing in the topology of the coordination network. A thermal investigation of the thermodynamically metastable and stable forms reveals no differences. A comparison of the thermal properties of these compounds with those of other compounds exhibiting an identical topology of the coordination network shows significant differences, indicating that no simple structure−property relationships can be drawn in this class of compounds. However, these investigations also show that thermal decomposition reactions offer an easy, rapid, and convenient method for the discovery and synthesis of several new ligand-deficient coordination polymers, by the decomposition of ligand-rich compounds. Investigations in solution show that most of the compounds are in equillibria and that not all of them are thermodynamically stable. Moreover, these compounds cannot be prepared in solution by mixing stoichiometric amounts of the educts, because their stability is quite dependent on the actual composition of the

solution. In the present case, an excess of ligand must be generally used for the preparation of a particular compound in pure form. These investigations also show that in the beginning of the reaction different compounds are formed and transform within some time into the thermodynamically most stable compounds. Therefore, the reactions in solution are much more complicated than was expected for such simple compounds.

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Supporting Information Available: Lists with details of the structure determination, atomic coordinates, isotropic and anisotropic displacement parameters, as well as CIF files, experimental and calculated X-ray powder patterns for compounds **I**−**V**, DTA−TG curve for compounds **II** and **V**, and experimental X-ray powder patterns for the residues isolated in the thermal decomposition reaction of compounds **III**−**V**. This material is available free of charge via the Internet at http://pubs.acs.org.

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