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On the Preparation of Coordination Polymers by Controlled Thermal Decomposition: Synthesis, Crystal Structures, and Thermal Properties of Zinc Halide Pyrazine Coordination Compounds

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The five zinc(II) halide pyrazine coordination compounds poly-bis(μ_2-pyrazine)-dichloro-zinc(II) (**I**), poly-(μ_2-pyrazine-*N*,*N*′)-dichloro-zinc(II) (**II**), poly-bis(μ_2-pyrazine-*N*,*N*′)-dibromo-zinc(II) (**III**), catena-(μ_2-pyrazine-*N*,*N*′)-dibromo-zinc(II) (**IV**), and catena-(μ-pyrazine)-diiodo-zinc(II) (**V**) were prepared by the reaction of ZnX_2 (X = Cl, Br, I) with pyrazine in acetonitrile. In the crystal structure of compound **I**, the zinc atoms are coordinated by two chlorine atoms and two pyrazine ligands within distorted tetrahedra. The zinc atoms are linked by the N-donor ligands into layers. The crystal structure of compound **III** is very similar to that of compound **I**. The structure of compound **III** was originally reported in space group *Ccca* with similar *a* and *b* axes, but it was proved that the correct space group is *I*4/*mmm*. Ligand-poor compound **V** is isotypic to compound **IV**, in which ZnX_2 units (X = Br, I) are connected by the pyrazine ligands into chains. It was originally reported in the noncentrosymmetric space group $P2_1$, but we found that the correct space group is $P2_1/m$. If ligand-rich 1:2 compounds **I** and **III** are heated in a thermobalance, different mass steps are observed. We have proven that in the first step, ligand-poor compounds **II** and **IV** are formed in quantitative yields. On further heating, a second mass step occurs that leads to the formation of two new compounds of composition $(ZnCl_2)_2$(pyrazine) (**VI**) and $(ZnBr_2)_2$(pyrazine) (**VII**). However, the mass step is not well-resolved. and the new compounds are not phase-pure after the thermal event. If ligand-poor 1:1 compound **V** is investigated by thermogravimetry, a not-well-resolved single mass step is observed in which new ligand-poor 2:1 compound $(ZnI_2)_2$(pyrazine) (**VIII**) is formed. On further heating, all 2:1 compounds lose their remaining ligands and transform into the pure zinc(II) halides.

Introduction

In the past few years, numerous investigations on the synthesis, structures, and properties of new coordination polymers have been reported.[1−10] The major goal in this area is the preparation of new coordination compounds with well-defined physical properties. To reach this goal, researchers have to overcome several problems. First of all, strategies for a more-directed design of their crystal structures are needed; second, structure property relationships have to be investigated. However, for the investigations of the properties of compounds, we need large and pure amounts, which in the case of coordination polymers is sometimes difficult to achieve. In practically all cases, such compounds are prepared in a solution in which different compounds are in equilibrium, and therefore, mixtures of different solids are frequently obtained that have to be separated by hand. Moreover, some

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compounds cannot be prepared in solution or are overlooked, especially if these compounds are thermodynamically metastable. Therefore, alternative routes for the discovery and preparation of pure new or known coordination polymers are really needed.

In our own investigations, we have investigated coordination polymers on the basis of copper(I) halides and different N-donor ligands.[11−22] For one specific halide atom and one specific ligand, several compounds of a different ratio between the copper halide and the ligand are frequently observed and therefore ligand-rich and ligand-poor compounds can be prepared. We found that most of the ligand-rich coordination polymers can be transformed into ligand-poor coordination polymers on heating before decomposition into the pure copper(I) halides is observed.[11−22] In most cases, the ligand-poor intermediates are obtained very pure and always in quantitative yields. Only in some minor cases is no ligand-poor intermediate observed at all.[14] We have also found that coordination polymers on the basis of copper(I) pseudohalides react in a similar way[23−25] and that ligand-poor compounds on the basis of silver(I) halides can also be prepared.[26] Especially the copper(I) pseudohalides are of interest, because most of them show luminescence or thermoluminescence properties.[23] To understand such reactions in more detail, we have started systematic investigations on the thermal behavior of these compounds. We found, for example, that in some cases, several ligand-poor intermediates can be obtained and that the reactivity can be influenced by mixed-crystal formation.[15] We have also demonstrated that the product formation depends on the kinetics of all reactions involved, and therefore, different products can be prepared by heating-rate-dependent measurements.[17] During these investigations, we identified different isomers and polymorphic modifications; as one of the major results of the experiments, no simple relationship between the structures of these compounds and their thermal reactivity or thermodynamic stability could be established.[18−20] Because the dimensionality of the coordination networks increases in the direction of the ligand-poor compounds, we applied this method to the preparation of coordination polymers that exhibit cooperative magnetic properties.[27]

Table 1. Crystal Data and Results of the Structure Refinement for Compounds **I**, **III**, and **V**

	I	**III**	**V**
chemical formula	$C_8H_8Cl_2N_4Zn$	$C_8H_8N_4Br_2Zn$	$C_4H_3N_2I_2Zn$
fw	296.46	375.35	399.26
space group	*Ccca*	*I*4/*mmm*	$P2_1/m$
a (Å)	10.1630(11)	7.1969 (8)	6.3113 (8)
b (Å)	10.6042(15)	7.1969 (8)	9.8980 (13)
c (Å)	10.1858(10)	11.1356(15)	7.4380 (9)
β (deg)			109.871 (14)
V (Å^3)	1097.7(2)	576.77(12)	436.98 (10)
T (°C)	20	20	20
Z	4	2	2
D_{calcd} (g cm^{-3})	1.794	2.058	3.034
μ (mm^{-1})	2.693	9.014	9.798
l (Å)	0.71073	0.71073	0.71073
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0260	0.0228	0.0357
$wR_2{}^a$ [all data]	0.0725	0.0552	0.0933

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$.

However, to investigate if the preparation of coordination polymers can be widely used as a preparative tool or for the discovery of new compounds, we have started systematic investigations of the thermal properties of other coordination compounds. In the beginning, we decided to investigate coordination polymers on the basis of zinc halides and N-donor ligands.[28] Only a few of such compounds were reported in the literature, but the analysis of their structures has shown that the topologies of their coordination networks are very often similar to that of the copper(I) coordination polymers.[29−34] In addition, in contrast to copper(I), in zinc compounds, octahedral coordination can also be found, which increases the structural diversity dramatically. Therefore, for zinc halides, ligand-rich and ligand-poor compounds can be expected, which might show a thermal reactivity similar to that of the copper(I) coordination compounds. Because we are predominantly interested in the thermal reactivity, we decided to first investigate compounds for which at least some coordination compounds were reported. This is the case for the Zn halide coordination polymers with the diazine ligand pyrazine. Altogether, four different compounds were structurally characterized: ligand-rich compound poly-bis-(μ_2-pyrazine-*N*,*N*′)-dibromo-zinc(II) (**III**)[32] and ligand-poor compounds poly-(μ_2-pyrazine-*N*,*N*′)-dichloro-zinc(II) (**II**),[33] catena-(μ_2-pyrazine-*N*,*N*′)-dibromo-zinc(II) (**IV**),[32] and catena-(μ_2-pyrazine-*N*,*N*′)-diiodo-zinc(II) (**V**).[34] The crystallographic data reported for compounds **III** and **V** highly suggest that the structure determinations were not correctly performed. Therefore, we redetermined these structures in

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the beginning. In addition, for $ZnCl_2$ and ZnI_2, no ligand-rich compounds were reported until now, which is surprising because one would expect a ligand-rich coordination polymer for at least one of these compounds. For zinc chloride, we identified, prepared, and structurally characterized such a ligand-rich coordination polymer. Finally, all compounds were investigated with respect to their thermal properties, which shows that the ligand-rich compounds transform into the ligand-poor coordination polymers and that there are additional ligand-poor samples that were not expected in the beginning. Here, we report on these investigations.

Experimental Section

Synthesis. All compounds were prepared by stirring the reactants in acetonitrile for 2 days. The residues were filtered off and washed with diethyl ether. The purity of these compounds was checked by X-ray powder diffraction (see the Supporting Information).

Synthesis of Poly-bis(μ_2-pyrazine)-dichloro-zinc(II) (I). Crystalline powder of compound **I** was prepared by the reaction of 0.5 mmol (68.1 mg) $ZnCl_2$ and 5.0 mmol (400.4 mg) pyrazine in 2.0 mL of acetonitrile. Yield: 90.4% (134.0 mg) on the basis of $ZnCl_2$. CHN anal. Calcd for $C_8H_8Cl_2N_4Zn$: C, 32.41; H, 2.72; N, 18.90. Found: C, 32.68; H, 2.52; N, 18.57. IR (KBr, cm^{-1}): 3106 (w), 1483 (w), 1415 (s), 1377 (w), 1155 (m), 1118 (m), 1053 (s), 992 (w), 818 (m), 790 (m), 427 (s), 446 (w). Preparation of single crystals: 0.5 mmol (68.09 mg) $ZnCl_2$ was mixed with 5.0 mmol (400.4 mg) pyrazine in 3.0 mL of acetone. After slow evaporation of the solvent, colorless crystals are obtained within about 1 week.

Synthesis of Poly(μ_2-pyrazine-*N*,*N*′)-dichloro-zinc(II) (II). Crystalline powder of compound **II** was prepared by the reaction of 0.5 mmol (68.1 mg) $ZnCl_2$ and 0.5 mmol (40.0 mg) pyrazine in 2.0 mL of acetonitrile. Yield: 52.6% (56.9 mg). CHN anal. Calcd for $C_4H_4Cl_2N_2Zn$: C, 22.20; H, 1.86; N, 12.95. Found: C, 22.32; H, 1.93; N, 13.17. IR (KBr, cm^{-1}): 3114 (w), 1483 (w), 1417 (s), 1168 (m), 1118 (m), 1054 (s), 790 (m), 466 (s), 446.3 (w).

Synthesis of Poly-bis(μ_2-pyrazine-*N*,*N*′)-dibromo-zinc(II) (III). Crystalline powder of compound **III** was prepared by the reaction of 1.0 mmol (225.2 mg) $ZnBr_2$ and 2.0 mmol (160.2 mg) pyrazine in 2.0 mL of acetonitrile. Yield: 88.7% (341.8 mg). CHN anal. Calcd for $C_8H_8Br_2N_4Zn$: C, 24.93; H, 2.09; N, 14.54. Found: C, 24.92; H, 2.08; N, 14.13. IR (KBr, cm^{-1}): 3106 (w), 3088 (w), 1963 (w), 1428 (m), 1409 (s), 1375 (m), 1155 (m), 1118 (s), 1053 (s), 992 (m), 817 (s), 463 (s). Preparation of single crystals: 0.1 mmol (22.5 mg) $ZnBr_2$ was mixed with 1.0 mmol (80.1 mg) pyrazine in 3.0 mL of methanol. After slow evaporation of the solvent, colorless crystals are obtained within about 1 week.

Synthesis of Catena(μ_2-pyrazine-*N*,*N*′)-dibromo-zinc(II) (IV). Crystalline powder of compound **IV** was prepared by the reaction of 1.0 mmol (225.2 mg) $ZnBr_2$ and 1.0 mmol (80.1 mg) pyrazine in 2.0 mL of acetonitrile. Yield: 89.0% (271.7 mg). CHN anal. Calcd for $C_4H_4Br_2N_2Zn$: C, 15.74; H, 1.32; N, 9.18. Found: C, 15.89; H, 1.31; N, 9.13. IR (KBr, cm^{-1}): 3124 (m), 3088 (m), 3042 (m), 2999 (w), 2923 (w), 1943 (w), 1880 (w), 1774 (w), 1496 (w), 1427 (s), 1165 (s), 1123 (s), 1112 (m), 1063 (s), 984 (w), 815 (S), 469 (s), 446 (s).

Synthesis of Catena(μ-pyrazine)-diiodo-zinc(II) (V). Crystalline powder of compound **V** was prepared by the reaction of 1.0 mmol (319.2 mg) ZnI_2 and 1.0 mmol (80.1 mg) pyrazine in 2.0 mL of acetonitrile. Yield: 91.9% (366.9 mg). CHN anal. Calcd for $C_4H_4I_2N_2Zn$: C, 12.03; H, 1.01; N, 7.02. Found: C, 12.12; H, 0.96; N, 8.29. IR (KBr, cm^{-1}): 3117 (m), 3075 (w), 3036 (m), 1875 (w), 1769 (w), 1492 (w), 1424 (s), 1165 (s), 1121 (s), 1062 (s), 814 (s), 468 (s), 444 (s). Preparation of single crystals: 0.05 mmol (15.95 mg) ZnI_2 was mixed with 0.05 mmol (4.00 mg) pyrazine in 0.3 mL of water. After slow evaporation of the solvent, colorless crystals were obtained within about 2 weeks.

CHN Analysis of the Residues Obtained in the Thermal Decomposition of Compounds I−V. (A) Isolated after first heating step for compound **I** (%). Found: C, 22.22; H, 1.75; N, 12.86. Calcd for compound **II**: C, 22.20; H, 1.86; N, 12.95. (B) Isolated after first heating step for compound **II** (%). Found: C, 13.44; H, 1.38; N, 7.68. Calcd for **VI**: C, 13.62; H, 1.14; N, 7.94. (C) Isolated after first heating step for compound **III** (%). Found: C, 15.91; H, 1.32; N, 10.23. Calcd for compound **IV**: C, 15.74; H, 1.32; N, 9.18. (D) Isolated after first heating step for compound **IV** (%). Found: C, 8.96; H, 0.79; N, 5.14. Calcd for compound **VII**: C, 9.06; H, 0.76; N, 5.28. (E) Isolated after first heating step for compound **V** (%). Found: C, 5.49; H, 0.35; N, 3.19. Calcd for compound **VIII**. C, 6.69; H, 0.56; N, 3.90.

Single-Crystal Structure Analysis. All investigations were performed with an imaging plate diffraction system (IPDS-1) from STOE & CIE. The structure solutions were performed with direct methods using SHELXS-97,[35] and structure refinements were performed against F^2 using SHELXL-97.[36] For all structures, a numerical absorption correction was applied using X-Red[37] and X-Shape.[38] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters ($U_{eq}(H) = 1.2U_{eq}(C)$) using a riding model with $d\mathrm{C{-}H} = 0.95$ Å. Details of the structure determination are given in Table 1 and in the Supporting Information.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC602639 (**I**), CCDC602640 (**III**), and CCDC602641(**V**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, U.K. (fax: 44-(0)1223-336033 or e-mail: deposit@ccdc.ca.ac.uk).

X-ray Powder Diffraction. Powder-diffraction experiments were performed using a STOE STADI P transmission powder diffractometer with Cu Kα radiation ($\lambda = 154.0598$ pm) that is equipped with a position-sensitive detector (scan range: 5−45°) from STOE & CIE.

Differential Thermal Analysis, Thermogravimetry, and Mass Spectroscopy. The heating-rate-dependent DTA-TG measurements were performed in a nitrogen atmosphere (purity: 5.0) in Al_2O_3 crucibles using a STA-409CD instrument from Netzsch. The DTA-TG-MS measurements were performed with the same instrument, which 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 in Al_2O_3 crucibles in a dynamic nitrogen atmosphere (purity: 5.0) using heating rates of 4 °C/min. All measurements were performed with a flow rate of 75 mL/min and were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

Elemental Analysis. CHN analysis has been performed using

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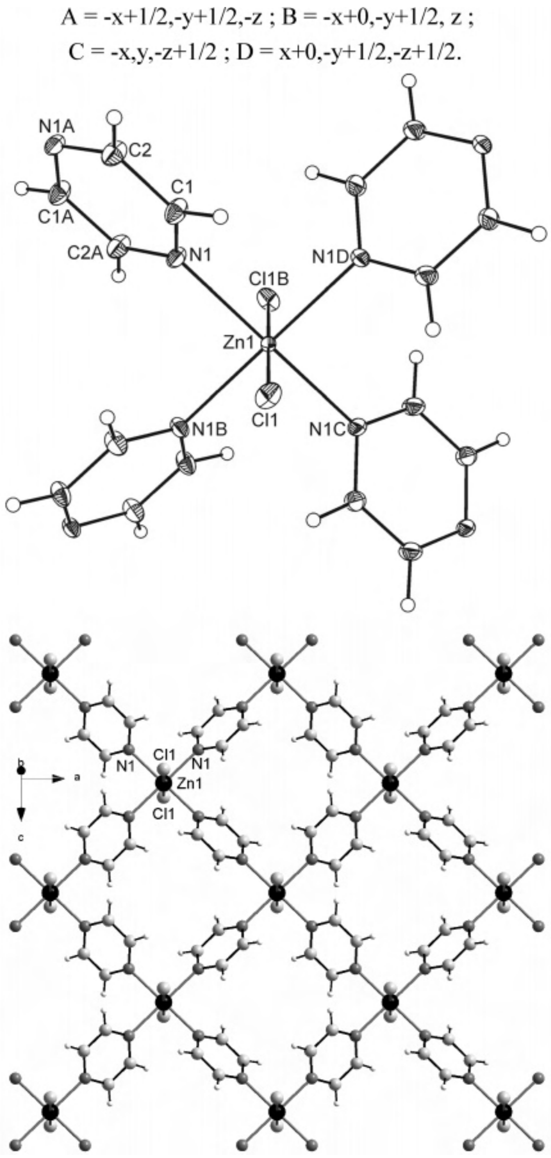

Figure 1. Crystal structure of compound **I** with view of the coordination sphere of the zinc cations with labeling and displacement ellipsoids drawn at the 50% probability level (top) and view of the structure approximately in the direction of the crystallographic *b* axis (bottom). Symmetry codes: A = $-x + {}^1/_2$, $-y + {}^1/_2$, $-z$; B = $-x + 0$, $-y + {}^1/_2$, z; C = $-x$, y, $-z + {}^1/_2$; D = $x + 0$, $-y + {}^1/_2$, $-z + {}^1/_2$.

an EURO EA elemental analyzer, fabricated by EURO VECTOR Instruments and Software.

Results and Discussion

Synthetic Aspects. The formation of all compounds was investigated in solution using ex situ time-dependent X-ray powder diffraction. Compounds **II**−**V** can be prepared phase-pure by reacting stoichiometric amounts of the reactants in acetonitrile. However, if zinc(II) chloride is reacted with pyrazine in a 1:2 ratio, which should lead to the formation of ligand-rich compound **I**, ligand-poor 1:1 compound **II** is obtained as phase-pure material. Compound **I** can be prepared only if a 5-fold excess of pyrazine is used in the synthesis, which might be the reason that this compound was overlooked in previous reports. However, both ligand-rich compounds are not stable as solids. In solution, ligand-rich compound **I** transforms into ligand-poor 1:1 compound **II** within a few days. If ligand-rich compound **III** is prepared by the reaction of $ZnBr_2$ with pyrazine in acetonitrile, it also transforms into the ligand-poor compound; however, the decomposition is much slower than for the $ZnCl_2$ compound **I**, which shows that the stability of the ligand-rich compounds increases from chlorine to bromine. However, it can also be assumed that the stability of the ligand-poor 1:1 compounds increases from chlorine to iodine, which would explain why no ligand-rich compound with ZnI_2 and pyrazine can be prepared. In our thermal investigations, we proved that there exist additional ligand-poor compounds of composition $(ZnX_2)_2$(pyrazine) (X = Cl, Br, I) (see thermoanalytical investigations). Therefore, we tried to prepare these compounds in solution as well. But, if the zinc(II) halides and pyrazine are mixed in a 2:1 molar ratio, only ligand-poor 1:1 compounds **II**, **IV**, and **V** are obtained, which demonstrates that the 1:1 coordination polymers represent the thermodynamically most stable compounds in this system. This is somewhat surprising, because one can expect that in the ligand-poor 2:1 compounds, a more-condensed coordination network with condensed $(ZnX_2)_n$ substructures (X = Cl, Br, I) can be found.

Table 2. Bond Lengths (Å) and Angles (deg) for Compound **I**[a]

Zn(1)−N(1D)	2.2053(15)	Zn(1)−N(1)	2.2053(15)
Zn(1)−N(1B)	2.2053(15)	Zn(1)−Cl(1)	2.4143(7)
Zn(1)−N(1C)	2.2053(15)	Zn(1)−Cl(1B)	2.4143(7)
N(1D)−Zn(1)−N(1B)	179.36(6)	N(1C)-Zn(1)−Cl(1)	90.32(3)
N(1D)−Zn(1)−N(1C)	90.16(8)	N(1)−Zn(1)−Cl(1)	90.32(3)
N(1B)−Zn(1)−N(1C)	89.84(8)	N(1D)−Zn(1)−Cl(1B)	90.32(3)
N(1D)−Zn(1)−N(1)	89.84(8)	N(1B)−Zn(1)−Cl(1B)	90.32(3)
N(1B)−Zn(1)−N(1)	90.16(8)	N(1C)−Zn(1)−Cl(1B)	89.68(3)
N(1C)−Zn(1)−N(1)	179.36(6)	N(1)−Zn(1)−Cl(1B)	89.68(3)
N(1D)−Zn(1)−Cl(1)	89.68(3)	Cl(1)−Zn(1)−Cl(1B)	180.0
N(1B)−Zn(1)−Cl(1)	89.68(3)		

[a] Symmetry transformations used to generate equivalent atoms: A = $-x + {}^1/_2$, $-y + {}^1/_2$, $-z$; B = $-x + 0$, $-y + {}^1/_2$, z; C = $-x$, y, $-z + {}^1/_2$; D = $x + 0$, $-y + {}^1/_2$, $-z + {}^1/_2$.

Crystal Structures. Compound **I** crystallizes in orthorhombic space group *Pmma* with 4 formula units in the unit cell. In the crystal structure, the zinc atoms are each coordinated by two symmetry-related chlorine atoms and four symmetry-equivalent pyrazine ligands within slightly distorted octahedra (Figure 1, top, and Table 2).

The nitrogen atoms are located in the basal plane, whereas the chlorine atoms occupy the apical positions. The zinc atoms are connected by the pyrazine ligands by μ-*N*,*N*′ coordination into layers that are parallel to the *a*−*b* plane (Figure 1, bottom). These layers are stacked in the direction of the crystallographic *c* axis, with the zinc atoms and pyrazine ligands arranged in separate columns.

The crystal structure of compound **III** was originally reported in orthorhombic space group *Cmmm* with $a = 10.1904(4)$, $b = 10.1981(6)$, and $c = 11.1516(7)$.[32] In this structure, the pyrazine ligands are disordered in two different orientations because of symmetry. The similarity of the *a* and *b* axes as well as the disorder of the ligands give strong hints that either the structure will crystallize tetragonal or the cell parameters are wrong, maybe because super structure reflections were overlooked. We redetermined the structure

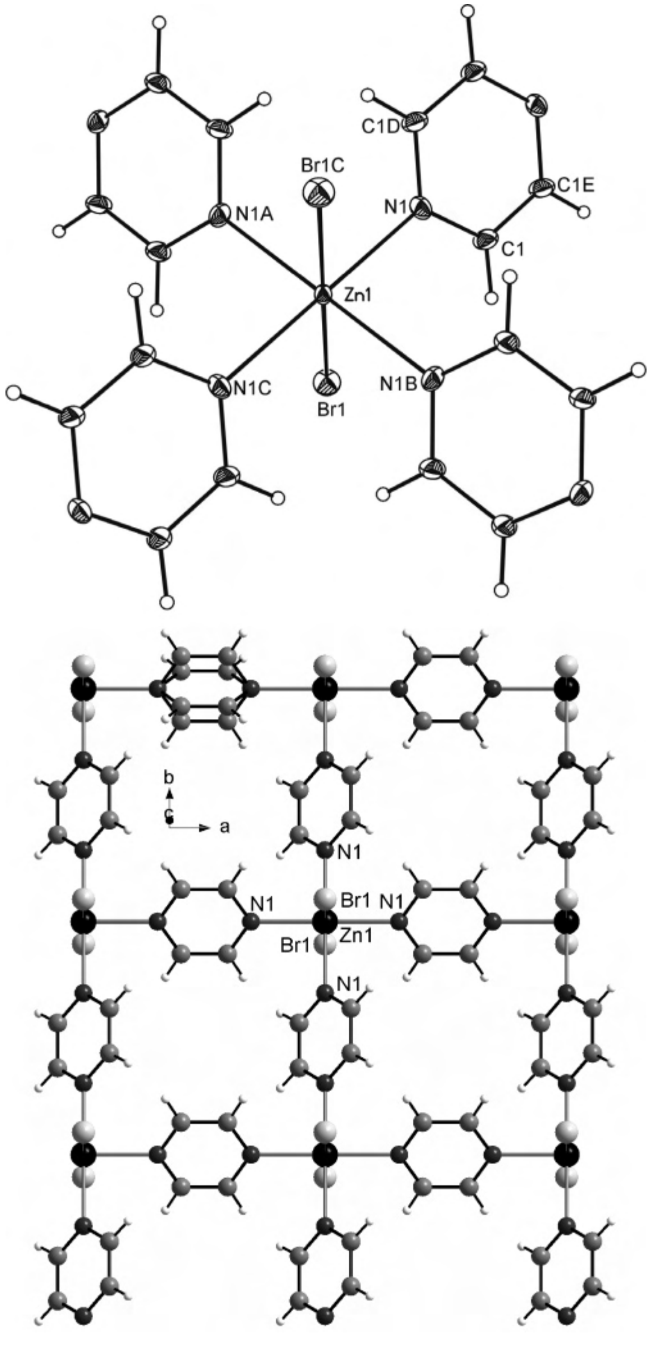

Figure 2. Crystal structure of compound **III** with view of the coordination sphere of the zinc cations with labeling and displacement ellipsoids drawn at the 70% probability level (top) and view of the structure approximately in the direction of the crystallographic *c* axis (bottom). Symmetry codes: A = y, $-x + 1$, $-z + 1$; B = $-y + 1$, *x*, *z*; C = $-x + 1$, $-y + 1$, $-z + 1$; D = $-x + 1$, *y*, $-z + 1$; E = *x*, $-y + 2$, *z*. For clarity, the disorder of the pyrazine ligand is shown for only one ligand.

Table 3. Bond Lengths (Å) and Angles (deg) for Compound **III**[a]

Zn(1)−N(1A)	2.206(3)	Zn(1)−Br(1C)	2.5782(5)
Zn(1)−N(1B)	2.206(3)	Zn(1)−N(1C)	2.206(3)
Zn(1)−N(1)	2.206(3)	Zn(1)−Br(1)	2.5782(5)
N(1A)−Zn(1)−N(1B)	180.0	N(1A)−Zn(1)−Br(1C)	90.0
N(1)−Zn(1)−N(1C)	180.0	N(1B)−Zn(1)−Br(1C)	90.0
N(1A)−Zn(1)−N(1)	90.000(1)	N(1)−Zn(1)−Br(1C)	90.0
N(1B)−Zn(1)−N(1C)	90.000(1)	N(1C)−Zn(1)−Br(1C)	90.0
N(1A)−Zn(1)−Br(1)	90.0	N(1B)−Zn(1)−N(1)	90.0
Br(1)−Zn(1)−Br(1C)	180.0	N(1A)−Zn(1)−N(1C)	90.0
N(1)−Zn(1)−Br(1)	90.0	N(1B)−Zn(1)−Br(1)	90.0
N(1C)−Zn(1)−Br(1)	90.0		

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

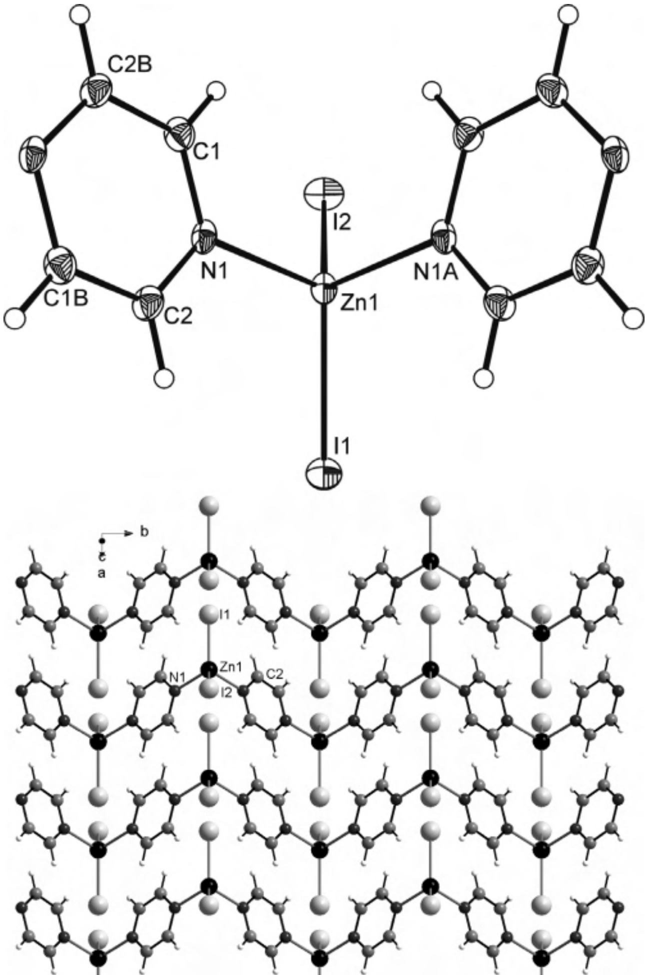

Figure 3. Crystal structure of compound **V** with view of the coordination sphere of the zinc cations with labeling and displacement ellipsoids drawn at the 50% probability level (top) and view of the structure in the direction of approximately the crystallographic *c* axis (bottom). Symmetry codes: A = *x*, $-y + {}^1/_2$, *z*; B = $-x$, $-y$, $-z + 1$.

and found no hints for super structure reflections, but the structure can easily be refined in the tetragonal space group *I*4/*mmm*. In this space group, the disorder of the pyrazine ligands is still present. The zinc atoms are located on 4/*mmm* sites, the bromine atom on the 4 *mm* position, and the pyrazine ligand on sites with symmetry *mmm*.

In the crystal structure, the zinc atoms are coordinated by two symmetrically related bromine atoms and four symmetry equivalent pyrazine ligands within a distorted octahedron. (Figure 2, top, and Table 3). The zinc atoms are connected by the pyrazine ligands into chains, which are further joined by ligands into layers that are parallel to the *a*−*b* axis (Figure 2, bottom).

Compound **V** crystallizes in monoclinic space group $P2_1/m$ with 2 formula units in the unit cell and is isotypic to bromine compound **IV**. This structure was previously reported in noncentrosymmetric space group $P2_1$;[34] however, the cell parameters are very similar to those of compound **IV**, and it

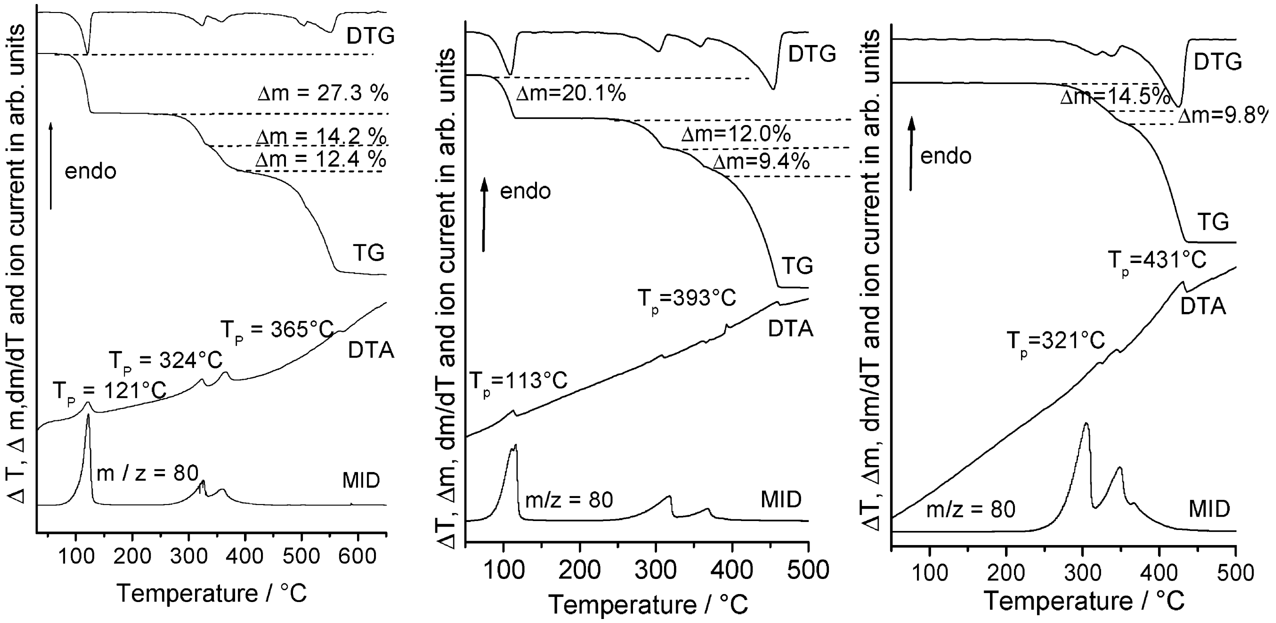

Figure 4. DTA, TG, DTG, and MS trend scan curve for compound **I** (left), **III** (middle), and **V** (right). Heating rate = 4 °C/min; $m/z = 80$ (pyrazine); given are the mass changes (%) and the peak temperatures T_P (°C).

Table 4. Bond Lengths (Å) and Angles (deg) for Compound **V**[a]

I(1)−Zn(1)	2.5194(11)	Zn(1)−N(1)	2.082(4)
I(2)−Zn(1)	2.5193(10)	Zn(1)−N(1A)	2.082(4)
N(1)−Zn(1)−N(1A)	94.3(2)	N(1)−Zn(1)−I(1)	110.23(13)
N(1)−Zn(1)−I(2)	109.11(13)	N(1A)−Zn(1)−I(1)	110.23(13)
N(1A)−Zn(1)−I(2)	109.11(13)	I(2)−Zn(1)−I(1)	120.64(3)
C(2)−N(1)−Zn(1)	121.0(3)	C(1)−N(1)−Zn(1)	120.9(4)

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

is obvious that the structure was refined in a wrong space group. In the crystal structure, the zinc atoms are each coordinated by two symmetry-related iodine atoms and two symmetry-equivalent pyrazine ligands (Figure 3, top, and Table 4). The zinc atoms as well as the two crystallographically independent iodine atoms are located on a mirror plane, whereas the pyrazine ligand is situated on a center of inversion. The ZnI_2 units are connected by the pyrazine ligands by μ-*N*,*N′* coordination into chains that elongate in the direction of the crystallographic *b* axis (Figure 3, bottom).

Thermoanalytic Investigations. On heating 1:2 compound **I** to 650 °C, four mass steps are observed in the TG curve that are accompanied with endothermic events in the DTA curve (Figure 4, left). From the MS trend scan curve, it is obvious that the ligand ($m/z = 80$) is emitted during only the first three mass steps. The mass loss in the first step of 27.3% is in good agreement with that calculated for the removal of half of the ligands, 27.0%. Therefore, one can assume that during this thermal reaction, ligand-poor compound **II** has been formed. From the DTG curve, it is obvious that the second mass step is not well-resolved, and therefore, the mass loss is difficult to estimate (Figure 4, left). However, the experimental mass loss of this step of about 14.2% is in reasonable agreement with that calculated for the removal of an additional half a ligand ($\Delta m_{\text{theo}}(-{}^1/_2$ pyrazine) = 13.5%), which may lead to a new ligand-poor 2:1 compound of composition $(ZnCl_2)_2$(pyrazine). On further heating, the remaining ligands are emitted; this leads to the formation of $ZnCl_2$, which vaporizes on further heating (Figure 4, left).

If the ligand-rich 1:2 compound $ZnBr_2$(pyrazine)$_2$ (**III**) is heated, a similar behavior as for compound **I** is observed (Figure 4, middle). Compared to those in compound **I**, all decomposition temperatures are shifted to higher values. The experimental mass loss observed in the first TG step of 20.1% is in reasonable agreement with that expected for the removal of half of the ligands ($\Delta m_{\text{theo}}(-1$ pyrazine) = 20.7%). As for the thermal decomposition of compound **I**, the second TG step cannot be resolved successfully (Figure 4, middle). However, the estimated mass loss of about 12.0% is in rough agreement with that calculated for the formation of a ligand-poor 2:1 compound ($\Delta m_{\text{theo}}(-{}^1/_2$ pyrazine) = 10.3%).

For ZnI_2, no ligand-rich 1:2 compound can be prepared; therefore, ligand-poor 1:1 compound **V** was investigated. The curves are similar to those obtained for compounds **I** and **III**, starting after the first TG step (Figure 4, right). The experimental mass loss during the first TG step of 14.5% is in rough agreement with that expected for the formation of a ligand-poor 2:1 compound of 10.0%.

From the DTA-TG-MS measurements, there are hints that ligand-rich 2:1 compounds **I** and **III** decompose in the first step into ligand-poor 1:1 compounds **II** and **IV**. To prove these assumptions, we performed additional TG measurements and stopped after the first TG step. Afterward, the residues were investigated by X-ray powder diffraction (Figure 5). Comparing the powder patterns of these residues with those calculated for 1:1 compounds **II** and **IV** from single-crystal data, it is obvious that these phases were formed in the thermal decomposition reaction. In addition, the residues were investigated by elemental analysis, demonstrating that the compositions are in good agreement with those calculated for 1:1 compounds **II** and **IV** (see Experimental Section).

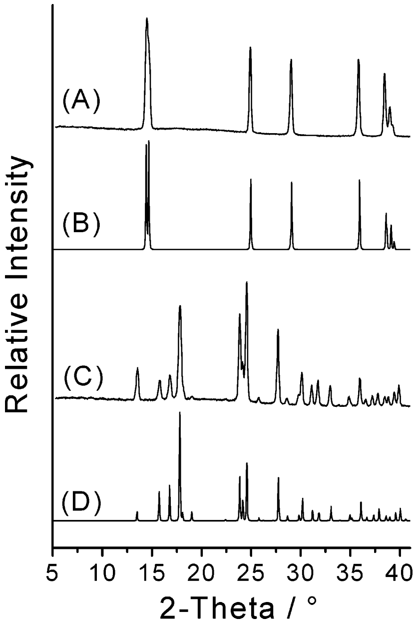

Figure 5. Experimental X-ray powder patterns of the residues obtained during the thermal decomposition of ligand-rich compounds **I** (A) and **III** (C) at 160 °C and calculated patterns for ligand-poorer compounds **II** (B) and **IV** (D).

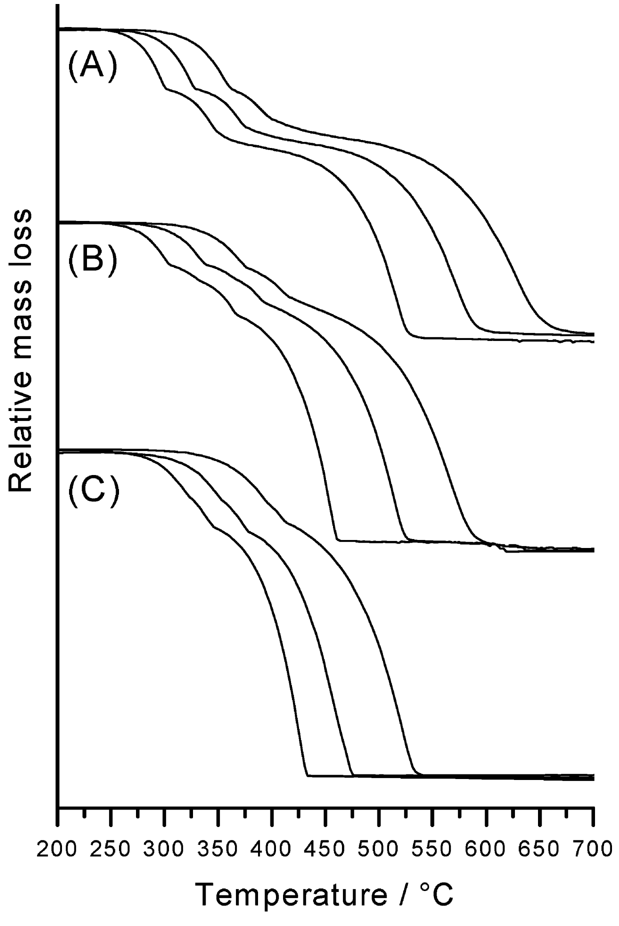

Figure 6. Heating-rate-dependent measurements for ligand-poor compounds **II** (A), **IV** (B), and **V** (C); heating rates = 1, 4, and 16 K/min, from left to right.

From the investigations described above, there are hints for the formation of ligand-poor 2:1 intermediate compounds (Figure 4). But the TG curves are not well-resolved, and therefore, isolation of such intermediates will be difficult. To check whether the resolution can be improved, we performed heating-rate-dependent measurements for ligand-poor 1:1 compounds **II**, **IV**, and **V** with 1, 4, and 16 K/min. (Figure 6). For chlorine compound **II**, it is obvious that the resolution can be significantly improved using lower heating rates (Figure 6A). The same improvement is observed for compound **IV**, whereas the resolution of the TG step during the thermal decomposition of compound **V** cannot be improved (Figure 6B,C).

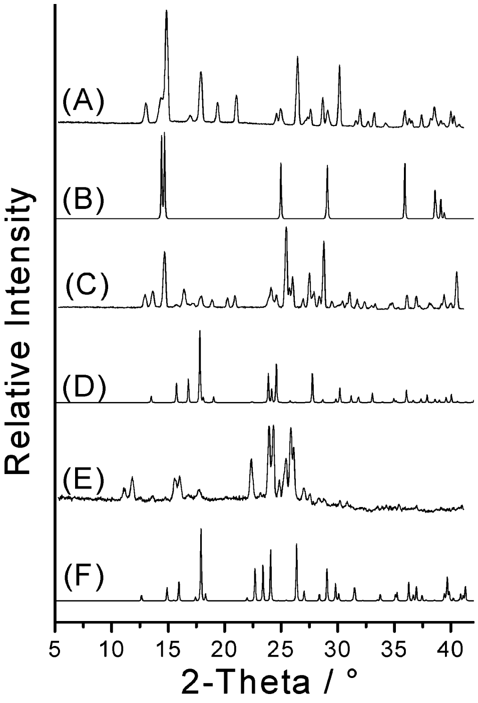

Figure 7. Experimental X-ray powder patterns of the residues obtained after the first TG step during the thermal decomposition of ligand-poor 1:1 compounds at 345 °C for compound **II** (A), at 345 °C for compound **IV** (C), and at 373 °C for compound **IV** (E), together with calculated X-ray powder patterns for compounds **II** (B), **IV** (D), and **V** (F).

To prove whether an additional ligand-poor 2:1 intermediate compound has formed during the thermal decomposition reaction of compounds **II**, **IV**, and **V**, we performed additional TG measurements with lower heating rates of 1 K/min that were stopped after the first TG step. The residues obtained in this experiment were investigated by X-ray powder diffraction (Figure 7A−F). The powder pattern of the intermediate of chlorine compound **II** is different from that of the pristine material. A detailed analysis shows there are no reflections of compound **II** or $ZnCl_2$, which is the final product of the thermal decomposition reaction (Figure 7A,B). Therefore, one can assume that the intermediate compound obtained is very pure. Elemental analysis of the intermediate yields a composition that is in reasonable agreement with that calculated for a ligand-poor compound of composition $(ZnCl_2)_2$(pyrazine) (see Experimental Section). Similar results were obtained for the residues isolated during the thermal decomposition of compounds **IV** (Figure 7C,D) and **V** (Figure 7E,F). The X-ray powder patterns gave evidence that the ligand-poor intermediates are not isotypic (compare Figure 7A with Figure 7C,E). In addition, the ligand-poor compound with ZnI_2 cannot be obtained as phase-pure material.

Conclusion

In the present work, we have shown for the first time that even ligand-poor zinc halide coordination polymers can be prepared by controlled thermal decomposition of ligand-rich precursor compounds. Despite the fact that the ligand-poor 1:1 compounds presented in this paper are the thermodynamically most stable compounds in this system and therefore can also be prepared in solution by applying stoichiometric amounts of the reactants, we demonstrated impressively that controlled thermal decomposition can be an alternative tool for the preparation of pure and quantitative amounts of coordination polymers. In any case, we demonstrated that thermal decomposition reactions are suitable for discovering additional ligand-poor phases, independent of whether they can be isolated as pure compounds, which might depend on the actual system investigated. The results of thermal decomposition experiments show that the overall thermal reactions are frequently much more complicated than expected. Therefore, detailed investigations of the thermal behavior using different methods gave much more insight into the chemical reactivity and mechanisms of the thermal reactions of a given class of compounds. However, the results presented in this paper are only a first report. Similar coordination polymers have to be investigated in the future. From such investigations, we expect a large number of new compounds.

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Supporting Information Available: List with details of the structure determination, atomic coordinates, and isotropic and anisotropic displacement parameters, as well as CIF files and drawings of the two structures. Experimental and calculated X-ray powder patterns as well as IR and Raman spectra of compounds **I**−**V**. This material is available free of charge via the Internet at http://pubs.acs.org.

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