

Synthesis, Crystal Structure and Thermal Reactivity of [ZnX₂(2-chloropyrazine)] (X = Cl, Br, I) Coordination Compounds

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Reaction of zinc(II) halides with 2-chloropyrazine in different solvents leads to the formation of five new coordination compounds that contain either only 2-chloropyrazine or additional water molecules as donor ligands. In the ligand-rich 1:2 compound catena[bis(2-chloropyrazine-N)]di-μ-chloro-zinc(II) (**1**) the zinc atom is coordinated by two 2-chloropyrazine ligands and four chlorine atoms in an octahedral fashion. The zinc atoms are connected by the chloride atoms forming linear chains. In the isotypic ligand-rich 1:2 compounds bis(2-chloropyrazine-N)dibromozinc(II) (**2**) and bis(2-chloropyrazine-N)diiodozinc(II) (**3**) discrete complexes are found in which each zinc atom is coordinated by two 2-chloropyrazine ligands and two halide atoms within distorted tetrahedra. The 1:1 compounds aqua-(2-chloropyrazine-N)di-

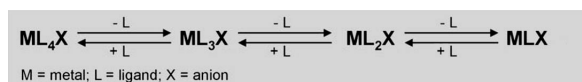
bromozinc(II) (**4**) and aqua-(2-chloropyrazine-N)diiodozinc(II) (**5**) are also isotypic and form discrete complexes in which the zinc atoms are surrounded by two halide atoms, one 2-chloropyrazine ligand and one water molecule. Upon heating, compounds **1–5** form ligand-deficient 1:1 and 2:1 compounds of composition [ZnX₂(2-chloropyrazine)] (X = halide) and [(ZnX₂)₂(2-chloropyrazine)]. X-ray powder diffraction shows that identical ligand-deficient intermediates are obtained on decomposition of either [ZnX₂L₂] (L = 2-chloropyrazine) or the [ZnX₂L(H₂O)] complexes. DFT calculations suggest that the formation of the [ZnX₂L(H₂O)] complex is energetically favoured for the heavier halide anions. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

Recently the preparation of new coordination compounds like coordination polymers, inorganic–organic hybrid compounds or metal organic frameworks has become of increasing interest because of their potential applications as conducting, porous, magnetic, catalytic or NLO materials.^[1–11] For any application or investigation of the properties of such compounds, pure samples are required in large amounts, which sometimes can be difficult to achieve if the syntheses are performed in solution. Different stable and metastable compounds exist in equilibria in solution, often leading to mixtures of different compounds. In view of stability constraints, certain compounds cannot be prepared or metastable compounds are overlooked in solution.

In recent work we have demonstrated that novel coordination compounds can be conveniently prepared by the thermal decomposition reactions of suitable ligand-rich precursor compounds based on Cu^I or Zn^{II} halides and mostly aromatic diazine ligands like pyrazine or substituted pyrazines. In this method several ligand-deficient intermediates can be obtained in phase pure form in quantitative

yields.^[12–21] During the thermal reaction the equilibrium is shifted irreversibly in the direction of the ligand-deficient compounds, leading to the isolation of metastable compounds, which normally cannot be prepared in solution or which are always obtained as mixtures otherwise (Scheme 1).



Scheme 1.

It is to be noted that in all thermal reactions ligand-rich precursor compounds are transformed into ligand-deficient products and that a part of the ligand is irreversibly emitted. In certain cases, depending on the stability of the intermediate phases, some of the mass steps are not well resolved, indicating that not all of the compounds can be prepared in phase pure form. Therefore, we have started investigations on the thermal decomposition reactions of precursors that contain additional volatile sacrificial donors like CH₃CN, which can be removed first such that the desired amine ligands are retained, as shown previously.^[22] In this context it must be pointed out that ligand-rich precursor compounds that contain additional water molecules as donors can also be prepared. We have found this, for example, for the compounds based on Zn^{II} halides and 2-chloropyrazine. Upon thermal decomposition the water is removed first and, therefore, the stoichiometry of the ligand-

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deficient coordination compound is predefined in the precursor compound. The product of this reaction is the same as expected for the decomposition of a ligand-rich precursor compound that contains only 2-chloropyrazine as ligand, as shown in this work.

Results and Discussion

Crystal Structures

The ligand-rich 1:2 compound **1** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 2$ with the zinc atoms in special and all other atoms in general positions. In the crystal structure the zinc atoms are coordinated by four symmetry-equivalent chloride atoms and two nitrogen atoms of

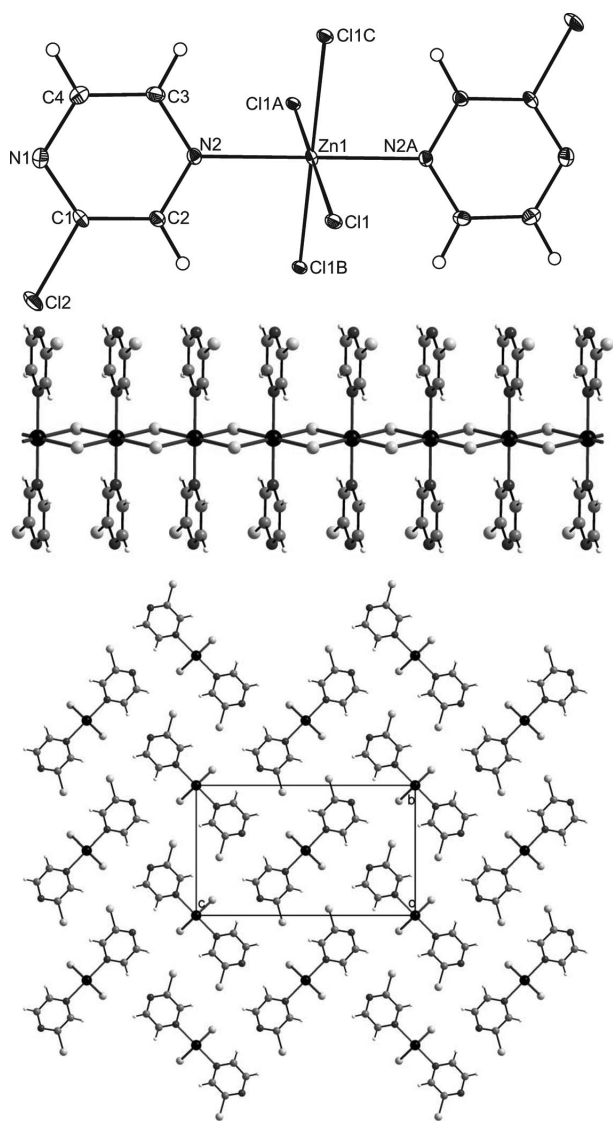


Figure 1. Crystal structure of compound **1** with a view of the coordination sphere of the zinc atoms with labelling and displacement ellipsoids drawn at the 50% probability level (top), with a view of the linear $ZnCl_2(2\text{-chloropyrazine})$ chains (mid) and with a view along the crystallographic a axis (bottom). Symmetry codes: A: $-x + 1, -y + 1, -z + 1$; B: $-x + 2, -y + 1, -z + 1$; C: $3x - 1, y, z$.

two symmetry-equivalent 2-chloropyrazine ligands within slightly distorted octahedra (Figure 1, top, and Table 1). Bond lengths and angles are in rough agreement with those retrieved from the literature for hexacoordinate zinc(II) atoms ($Zn-Cl$: 2.476–2.516 Å and $Zn-N$: 2.145–2.188 Å).^[23–25] Interestingly, two of the four $Zn-Cl$ bond lengths are significantly elongated (Table 1).

Table 1. Bond lengths [Å] and angles [°] for compounds **1**, **2** and **3**.

Compound	1 (X = Cl)	2 (X = Br)	3 (X = I)
Zn1–N2	2.2055(12)	2.076(3)	2.091(2)
Zn1–X1A	2.4388(4)	2.3380(5)	2.5324(3)
Zn1–X1	2.4388(4)	2.3380(5)	2.5324(3)
Zn1–X1C	2.5001(4)	–	–
N2–Zn1–N2A	180.000(1)	99.82(17)	96.96(12)
N2–Zn1–X1A	89.29(3)	105.21(9)	107.33(6)
N2–Zn1–X1	90.71(3)	108.92(9)	109.64(6)
X1A–Zn1–X1	180.000(12)	125.82(3)	122.88(2)
X1–Zn1–X1B	86.662(12)	–	–
N2–Zn1–X1C	89.74(3)	–	–
X1–Zn1–X1C	93.338(12)	–	–
X1B–Zn1–X1C	180.0	–	–
N2–Zn1–X1B	90.26(3)	–	–

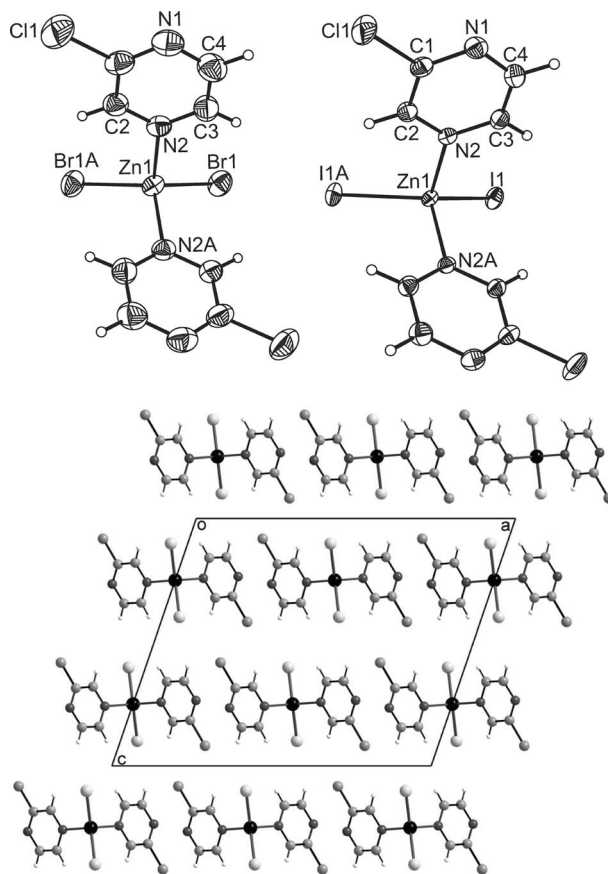


Figure 2. Crystal structure of compounds **2** (top left) and **3** (top right) with a view of the coordination sphere of the zinc atoms with labelling and displacement ellipsoids drawn at the 50% probability level and a view of the structure along the crystallographic b axis for compound **3** as a representative (bottom). Symmetry codes: A: $-x + 1, y, -z + 5/2$.

The zinc atoms are connected by the chloride atoms by common edges to form linear chains (Figure 1, mid), which elongate in the direction of the crystallographic *a* axis (Figure 1, bottom). The 2-chloropyrazine ligands are coordinated to the zinc atoms through the nitrogen atom, which is away from the bulky chlorine, and thus function as monodentate terminal ligands.

The ligand-rich 1:2 compounds bis(2-chloropyrazine-*N*)-dibromozinc(II) (**2**) and bis(2-chloropyrazine-*N*)diiodozinc(II) (**3**) are isotypic and crystallize in the monoclinic space group *C2/c* with four formula units in the unit cell. The halide atoms and the 2-chloropyrazine ligands are located in general positions whereas the zinc atoms occupy special positions. In contrast to compound **1**, discrete complexes are found, with the zinc atoms coordinated by two symmetry-related halide atoms and two nitrogen atoms of two symmetry-related 2-chloropyrazine ligands. As in compound **1**, the 2-chloropyrazine ligand coordinates with the nitrogen atom, which is away from the bulky chlorine substituent (Figure 2, top, and Table 1). The Zn–N bond lengths in compounds **2** and **3** are comparable and significantly shorter than in compound **1**. In the crystal structure the discrete complexes are stacked into columns that elongate in the direction of the *b* axis (Figure 2, bottom).

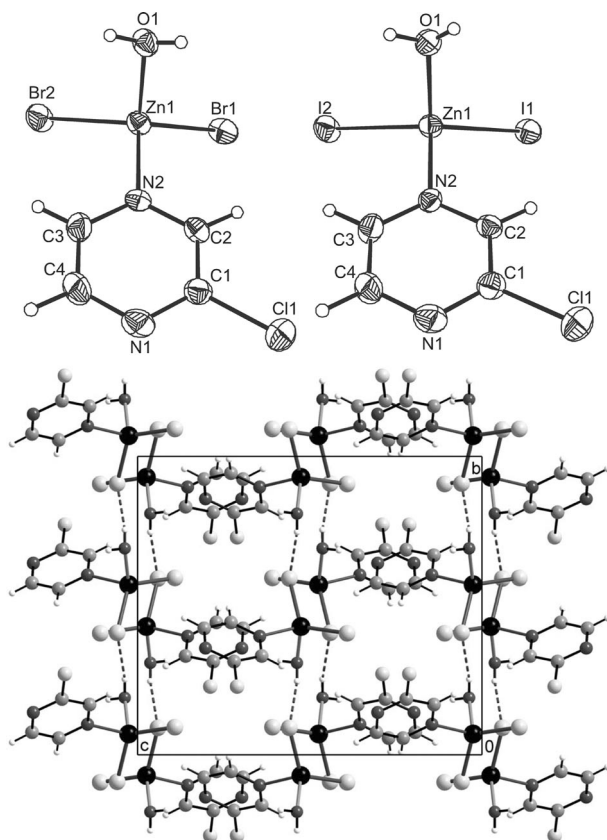


Figure 3. Crystal structure of compounds **4** (top left) and **5** (top right) with a view of the coordination sphere of the zinc atoms with labelling and displacement ellipsoids drawn at the 50% probability level and a view of the structure along the crystallographic *a* axis (bottom). Hydrogen bonding is shown as dashed lines.

The 1:1 compounds aqua-(2-chloropyrazine-*N*)dibromozinc(II) (**4**) and aqua-(2-chloropyrazine-*N*)diiodozinc(II) (**5**) are isotypic and crystallize in the orthorhombic space group *Pbca* with eight formula units in the unit cell and all atoms in general positions. Their crystal structures are similar to those of compounds **2** and **3**, but one of the two 2-chloropyrazine ligand is exchanged by a water molecule. Discrete complexes are found, with the zinc tetrahedrally coordinated by two halide atoms, one 2-chloropyrazine ligand and one water molecule (Figure 3, top, and Table 2). The Zn–N and Zn–X bond lengths are comparable to those in compounds **2** and **3**, but the tetrahedra are more distorted than those in the anhydrous compounds (compare Tables 1 and 2).

Table 2. Bond lengths [Å] and angles [°] for compounds **4** and **5**.

Compound	4 (X = Br)	5 (X = I)
Zn1–N2	2.074(3)	2.084(3)
Zn1–X1	2.3273(7)	2.5219(4)
Zn1–X2	2.3576(7)	2.5468(5)
Zn1–O1	2.034(3)	2.026(3)
N2–Zn1–X1	109.34(10)	109.22(8)
O1–Zn1–N2	99.25(13)	99.43(10)
O1–Zn1–X1	111.17(8)	110.47(6)
O1–Zn1–X2	104.32(9)	104.34(7)
N2–Zn1–X2	106.13(10)	106.57(8)
X1–Zn1–X2	123.79(3)	123.99(2)

In the crystal structure the discrete complexes are connected through O–H...N hydrogen bonds between the water molecules and the nitrogen atoms of the 2-chloropyrazine ligands, which are not involved in metal coordination (Table 3). Additional hydrogen bonding is also found between the water hydrogen atoms and the halide atoms (Table 3 and Figure 3).

Table 3. Hydrogen-bonding parameters for compounds **4** and **5**.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	∠(DH...A)	<i>d</i> (D...A)
Compound 4				
O1–H1O1...N1A ^[a]	0.840	1.983	169.33	2.812
O1–H2O1...Br2B	0.840	2.523	163.37	3.337
Compound 5				
O1–H1O1...N1A	0.840	1.993	171.78	2.827
O1–H2O1...I2B	0.840	2.855	143.60	3.566

[a] A = *x* + 1/2, *y*, –*z* + 1/2; B = –*x* + 3/2, *y* + 1/2, *z*.

Differential Thermoanalysis and Thermogravimetry (DTA-TG)

Compounds **1–5** are suitable ligand-rich precursor compounds for the preparation of new ligand-deficient intermediate compounds. Thus, their thermal reactivity was investigated using simultaneous differential thermoanalysis and thermogravimetry (DTA-TG).

The ligand-rich 1:2 dichloro compound **1** exhibits three mass steps up to 400 °C in the TG curves accompanied with endothermic events in the DTA curve (Figure 4). The experimental mass loss in the first TG step of 31.2% is in

good agreement with that calculated for the removal of a 2-chloropyrazine ligand [$\Delta m_{\text{theo1}}(-1 \text{ 2-chloropyrazine}) = 31.3\%$], whereas the second mass loss corresponds to the emission of two-thirds of a 2-chloropyrazine ligand [$\Delta m_{\text{theo2}}(-2/3 \text{ 2-chloropyrazine}) = 20.9\%$] (Figure 4, left). Similar observations were made for the corresponding 1:2 dibromo compound **2** [$\Delta m_{\text{theo1}}(-1 \text{ 2-chloropyrazine}) = 25.2\%$; $\Delta m_{\text{theo2}}(-2/3 \text{ 2-chloropyrazine}) = 16.8\%$] and the diiodo compound **3** [$\Delta m_{\text{theo1}}(-1 \text{ 2-chloropyrazine}) = 20.9\%$; $\Delta m_{\text{theo2}}(-2/3 \text{ 2-chloropyrazine}) = 13.9\%$], but for the latter the second TG step is not well resolved (Figure 4). The final products at the end of this reaction were identified as ZnCl_2 , ZnBr_2 and ZnI_2 . The above data can be attributed to the formation of the new ligand-deficient 1:1 compounds $\text{ZnX}_2(2\text{-chloropyrazine})$ ($X = \text{Cl}, \text{Br}, \text{I}$) in the first TG step. In the second TG step a transformation of the 1:1 compounds into more ligand-deficient products of composition $(\text{ZnX}_2)_3(2\text{-chloropyrazine})$ ($X = \text{Cl}, \text{Br}, \text{I}$) occurs. This is in agreement with the results from elemental analysis (see Experimental Section).

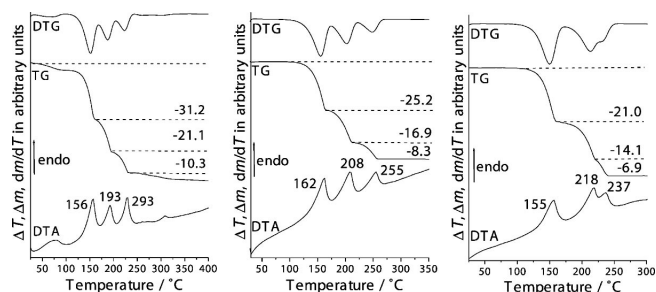


Figure 4. DTA, TG and DTG curves for compounds **1**, **2** and **3** (the mass loss in % and the peak temperatures in °C are given).

The TG-DTA thermogram of the 1:1 compound [$\text{ZnBr}_2(2\text{-chloropyrazine})(\text{H}_2\text{O})$] (**4**) exhibits three TG steps. The first step corresponds to the removal of the water molecule [$\Delta m_{\text{theo}}(-\text{H}_2\text{O}) = 5.0\%$], whereas the mass loss in the second step agrees with the emission of two-thirds of the 2-chloropyrazine ligands [$\Delta m_{\text{theo}}(-2/3 \text{ 2-chloropyrazine}) = 21.3\%$] (Figure 5).

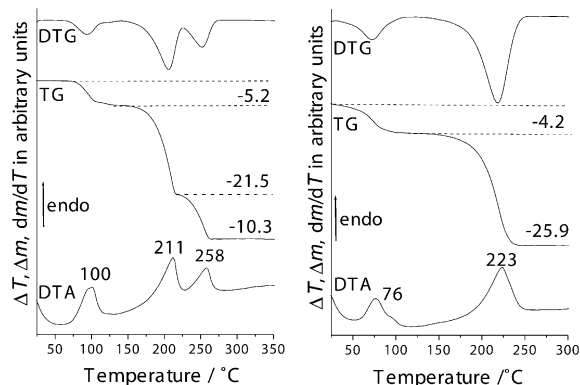


Figure 5. DTA, TG and DTG curves for compounds **4** and **5** (% mass loss and peak temperatures [°C] are given).

In contrast, for [$\text{ZnI}_2(2\text{-chloropyrazine-N})(\text{H}_2\text{O})$] (**5**) only two mass steps are observed, the first of which corresponds to the emission of the water molecules [$\Delta m_{\text{theo}}(-\text{H}_2\text{O}) = 4.0\%$], whereas the second TG step agrees with the removal of the 2-chloropyrazine ligands [$\Delta m_{\text{theo}}(-2\text{-chloropyrazine}) = 26.2\%$] (Figure 5). Based on these results it can be rationalized that in the first TG step the 1:1 compounds [$\text{ZnX}_2(2\text{-chloropyrazine})$] ($X = \text{Br}, \text{I}$) are formed, which in the case of the dibromide transforms into a ligand-deficient compound of composition [$(\text{ZnBr}_2)_3(2\text{-chloropyrazine})$]. The elemental analyses add further credence to these findings (see Experimental Section).

In order to prove the formation of ligand-deficient compounds, additional TG experiments were performed, which were stopped after the first mass loss. The residues obtained in this way were then investigated by X-ray powder diffraction (Figure 6). These investigations clearly show that new ligand-deficient 1:1 compounds of composition [$\text{ZnX}_2(2\text{-chloropyrazine})$] have formed. All powder patterns are different from those calculated for compounds **1–5**. It is interesting to note that the decomposition of the [ZnX_2L_2] compounds ($X = \text{Br}, \text{I}; \text{L} = 2\text{-chloropyrazine}$) as well as the [$\text{ZnX}_2\text{LH}_2\text{O}$] compounds leads to the formation of the same 1:1 compound (compare parts B/C and D/E of Figure 6). The low crystallinity of the 1:1 compounds as well as the hygroscopic nature of the ligand-deficient dibromo and diiodo compounds preclude further investigations.

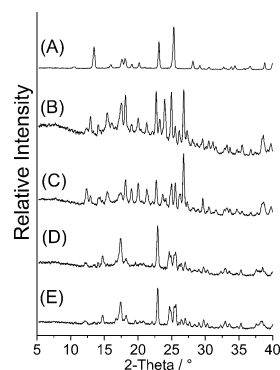


Figure 6. Experimental X-ray powder pattern of the residues obtained after the first TG step in the thermal decomposition reaction of compounds **1** (A), **2** (B), **3** (D), **4** (C) and **5** (E).

The residues formed in the second TG step, which correspond to ligand-deficient 3:1 compounds, are extremely hygroscopic and transform into a liquid within a few minutes. Therefore, elemental analysis was not performed. However, X-ray powder diffraction clearly shows that the patterns are different from those of the 1:1 compounds and from those of the pure Zn^{II} halides.

Calculations

As mentioned above, [$\text{ZnX}_2(2\text{-chloropyrazine})(\text{H}_2\text{O})$] compounds were obtained for $X = \text{Br}$ and I in which one 2-chloropyrazine ligand is replaced by a water molecule. In

contrast, for $X = \text{Cl}$ such a compound cannot be prepared. These results suggest that the exchange of 2-chloropyrazine against water is energetically favoured for the ZnBr_2 - and ZnI_2 -based coordination compounds. To get more insight into this phenomenon, theoretical calculations on the B3LYP/TZVP level were performed for the two following reactions, in which all species were fully optimized (Table 4).

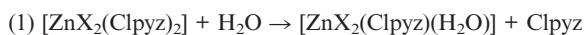


Table 4. Results of the calculations for reactions 1 and 2.

Complex	ΔE [kcal/mol]	ΔH [kcal/mol]	ΔG [kcal/mol]	K_{eq} (r.t.) ^[a]
Reaction 1				
$X = \text{Cl}^-$	+1.70	+1.94	0.00	1.00
$X = \text{Br}^-$	+0.95	+1.19	-0.78	3.73
$X = \text{I}^-$	+0.40	+0.59	-1.46	11.77
Reaction 2				
$X = \text{Cl}^-$	+3.8	+3.9	+1.4	0.094
$X = \text{Br}^-$	+3.2	+3.2	+0.9	0.22
$X = \text{I}^-$	+2.7	+2.8	+0.2	0.71

[a] $\Delta G = -RT \ln K = -592.183 \ln K$ ($T = 298 \text{ K}$).

In these calculations, solvation effects were neglected, because it can be assumed that the solvation energies should only affect the absolute reaction energies (ΔE), but not the relative energies of the different systems ($\Delta\Delta E$). In other words, addition of solvation energies will cause a linear shift of all three reaction energies by approximately the same amount.

From Table 4, an interesting trend can be derived where the exchange of the first 2-chloropyrazine against water (reaction 1) becomes more favourable with increasing size of the anion X . This means that in aqueous solution, the equilibrium according to reaction 1 is more and more shifted toward the water-containing species with increasing size of X (cf. K_{eq} values in Table 4, top). Although the energy differences are small, this can at least be counted as evidence to explain the experimental observation that the water-containing species can be prepared for $X = \text{Br}$ and I , whereas this compound cannot be obtained for $X = \text{Cl}$. In addition, whereas the first exchange of 2-chloropyrazine against water (reaction 1) is thermodynamically neutral to exergonic, the exchange of the second 2-chloropyrazine against water (reaction 2) becomes unfavourable. Correspondingly, the 2-chloropyrazine-free compounds with two water molecules bound could not be accessed from the solutions. Interestingly, the same trend is observed for reaction 2, that is, the exchange of water is more favourable with increasing size of the halide anion X (cf. Table 4, bottom). In summary, the calculations provide some evidence to understand the experimental observation that with ZnBr_2 and ZnI_2 , 2-chloropyrazine coordination compounds are accessible with one additional water in the coordination sphere, whereas for ZnCl_2 , this species seems less stable.

Conclusions

In the present work we have prepared several new coordination compounds of Zn halides with 2-chloropyrazine, which form ligand-deficient zinc(II)halide compounds upon thermal decomposition. The same ligand-deficient compounds are obtained irrespective of the thermal decomposition of $[\text{ZnX}_2\text{L}_2]$ ($L = 2\text{-chloropyrazine}$) or the $[\text{ZnX}_2\text{L}(\text{H}_2\text{O})]$ complexes. In this context the $[\text{ZnX}_2\text{L}(\text{H}_2\text{O})]$ complexes are of special interest because by thermal decomposition the water is removed first and the N-donor ligand is retained. Although not all of the ligand-deficient compounds can be obtained in a pure form, our investigations clearly show that such compounds can be prepared. It must be noted that the water-containing complexes can only be prepared with ZnBr_2 or ZnI_2 and 2-chloropyrazine. These experimental observations are in agreement with our theoretical calculations, which indicate that the formation of the $[\text{ZnX}_2\text{L}(\text{H}_2\text{O})]$ complexes is energetically favoured only for the bromide and iodide compounds.

Experimental Section

Synthesis of Compounds 1–3: ZnCl_2 , ZnBr_2 or ZnI_2 (1.0 mmol) and 2-chloropyrazine (2.0 mmol, 216.28 mg) were stirred in hexane (2.0 mL) for 2 d. The colorless precipitates were filtered off and washed with diethyl ether. $\text{C}_8\text{H}_6\text{Cl}_4\text{N}_4\text{Zn}$ (**1**): calcd. C 26.30, H 1.66, N 15.33; found C 26.1, H 1.69, N 15.40. $\text{C}_8\text{H}_6\text{Br}_2\text{Cl}_2\text{N}_4\text{Zn}$ (**2**): calcd. C 21.15, H 1.33, N 12.33; found C 21.12, H 1.36, N 12.45. $\text{C}_8\text{H}_6\text{Cl}_2\text{I}_2\text{N}_4\text{Zn}$ (**3**): calcd. C 17.53, H 1.10, N 10.22; found C 17.47, H 1.05, N 10.16. Single crystals were prepared by dissolving ZnCl_2 , ZnBr_2 or ZnI_2 (0.25 mmol) and 2-chloropyrazine (0.25 mmol) in ethanol (1.0 mL). On slow evaporation of the solvent, single crystals of compounds **1**, **2** and **3** grew within 1 week.

Synthesis of Compounds 4 and 5: ZnBr_2 or ZnI_2 (1.0 mmol) and 2-chloropyrazine (1.0 mmol) were stirred in hexane (2.0 mL) for 2 d. The colorless precipitates were filtered off and washed with diethyl ether. $\text{C}_4\text{H}_5\text{Br}_2\text{ClN}_2\text{OZn}$ (**4**): calcd. C 13.43, H 1.41, N 7.83; found C 13.36, H 1.32, N 7.75. $\text{C}_4\text{H}_5\text{ClI}_2\text{N}_2\text{OZn}$ (**5**): calcd. C 10.64, H 1.12, N 6.20; found C 10.57, H 1.09, N 6.11. Single crystals were prepared by dissolving ZnBr_2 or ZnI_2 (0.25 mmol) and 2-chloropyrazine (0.25 mmol) in ethanol (2.0 mL) (**4**) or acetonitrile (0.5 mL) and water (0.2 mL) (**5**). On slow evaporation of the solvent, single crystals of compounds **4** and **5** grew within 1 week.

Single-Crystal Structure Analysis: The data were measured using an IPDS-1 from STOE, Germany. All structure solutions were performed with direct methods using SHELXS-97.^[26] Structure refinement was done against F^2 using SHELXL-97.^[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. The C–H hydrogen atoms were positioned with idealized geometry and were refined with isotropic displacement parameters using a riding model. The data were corrected for absorption using X-RED^[28] and X-SHAPE.^[29] Selected crystal data and results of the structure refinement are shown in Table 5.

CCDC-662623 (for **1**), -662624 (for **2**), -662625 (for **3**), -662626 (for **4**) and -662627 (for **5**) contain the supplementary crystallographic data (excluding structure factors) 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.

Table 5. Selected crystal data and results of the structure refinements for compounds 1–5.

Compound	1	2	3	4	5
Formula	C ₈ H ₆ Cl ₄ N ₄ Zn	C ₈ H ₆ Br ₂ Cl ₂ N ₄ Zn	C ₈ H ₆ Cl ₂ I ₂ N ₄ Zn	C ₄ H ₅ Br ₂ ClN ₂ OZn	C ₄ H ₅ ClI ₂ N ₂ OZn
Formula mass [g/mol ¹]	365.34	454.26	548.24	357.74	451.72
Crystal color	colorless	colorless	colorless	colorless	colorless
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> [Å]	3.5928(3)	17.9491(15)	16.8523(14)	11.2591(7)	11.4595(8)
<i>b</i> [Å]	9.8030(6)	5.6817(5)	6.0972(4)	12.2488(6)	12.9539(7)
<i>c</i> [Å]	16.5933(14)	14.6824(11)	15.1299(13)	14.1375(7)	14.4758(8)
<i>α</i> [°]	–	–	–	–	–
<i>β</i> [°]	94.185(10)	108.853(9)	105.413(10)	–	–
<i>γ</i> [°]	–	–	–	–	–
<i>V</i> [Å ³]	582.86(8)	1417.0(2)	1498.7(2)	1949.71(2)	2148.9(2)
Temperature [K]	170.0	220	170.0	220.0	220.0
<i>Z</i>	2	4	4	8	8
<i>D</i> _{calcd} [g/cm ³]	2.082	2.129	2.430	2.437	2.793
<i>F</i> (000)	360	864	1008	1344	1632
2 θ range [°]	4.82–56.02	4.80–56.04	5.58–56.02	5.7–56.14	5.52–56.01
<i>h</i> / <i>k</i> / <i>l</i> ranges	–4/4	–23/23	–21/22	–14/14	–15/11
	–12/12	–7/7	–7/7	–16/16	–15/17
	–21/21	–19/19	–19/19	–18/18	–19/19
μ (Mo- <i>K</i> α) [mm ^{–1}]	3.00	7.73	6.10	10.94	8.23
Absorption correction	numerical	numerical	numerical	numerical	numerical
Min./max. transmission	0.6068/0.6898	0.1065/0.4909	0.2845/0.5756	0.1111/0.3304	0.1983/0.3629
Measured reflections	5475	6595	6849	17607	13377
<i>R</i> _{int}	0.0231	0.0699	0.0373	0.0966	0.0455
Independent reflections	1366	1644	1762	2358	2581
Reflections with <i>I</i> > 2 σ (<i>I</i>)	1284	1239	1577	1874	2078
Parameters	80	79	79	101	101
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0209	0.0354	0.0232	0.0378	0.0230
<i>wR</i> ₂ [all data]	0.0560	0.0877	0.0602	0.1013	0.0519
Gof	1.095	1.025	1.039	1.026	0.975
Residual electron density [e/Å ³]	0.384/–0.477	0.415/–0.451	0.844/–0.845	0.578/–0.904	0.643/–0.770

X-ray Powder Diffraction: X-ray powder diffraction experiments were performed using a STOE STADI P transmission powder using Cu-*K* α radiation (λ = 1.540598 Å).

Differential Thermal Analysis, Thermogravimetry and Mass Spectrometry: DTA-TG measurements were performed using the STA-409CD in Al₂O₃ crucibles under nitrogen (purity: 5.0). 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: C,H,N analysis was performed using a CHN-O-RAPID combustion analyzer from Heraeus.

CHN Analysis of the Residues Obtained in the Thermal Decomposition of Compounds 1–5: (A) Isolated after the first TG step for compound 1: C₄H₃Cl₃N₂Zn (250.82): calcd. C 19.15, H 1.21, N 11.17; found C 19.01, H 1.10, N 10.93. (B) Isolated after the first heating step for compound 2: C₄H₃Br₂ClN₂Zn (339.72): calcd. C 14.14, H 0.89, N 8.25; found C 13.98, H 0.78, N 8.14. (C) Isolated after the first heating step for compound 3: C₄H₃N₂ClI₂Zn (433.71): calcd. C 11.08, H 0.70, N 6.46; found C 10.98, H 0.62, N 6.39. (D) Isolated after the first heating step for compound 4: C₄H₃Br₂ClN₂Zn (339.72): calcd. C 14.14, H 0.89, N 8.25; found C 14.01, H 0.81, N 8.19. (E) Isolated after the first heating step for compound 5: C₄H₃ClI₂N₂Zn (433.71): calcd. for C 11.08, H 0.70, N 6.46; found C 10.93, H 0.64, N 6.32.

Calculations: Spin-unrestricted DFT calculations using Becke's three-parameter hybrid functional with the correlation functional of Lee, Yang and Parr (B3LYP)^[30] were performed with the pro-

gram package Gaussian 03.^[31] For all calculations, the TZVP basis set^[32] was applied as implemented in G03. The structures of the complexes [ZnX₂(Clpyz)₂], [ZnX₂(Clpyz)(H₂O)] and [ZnX₂(H₂O)₂] (X[–] = Cl[–], Br[–], I[–]) were fully optimized. Frequency calculations performed on these structures yielded no imaginary modes, which shows that true energy minima have been located in all cases. From the calculated frequencies, the thermodynamic corrections for enthalpy and the entropies of all species have been obtained as implemented in G03 (cf. Table 4). The obtained structures are in general very close to tetrahedral for all three types of complexes, which is significantly different from the crystal structures where significant distortions toward a planar geometry are observed (vide supra). These distortions can therefore be attributed to crystal packing effects in the solid state.

Supporting Information (see also the footnote on the first page of this article): Figures with experimental and calculated X-ray powder patterns for compounds 1–5.

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