Synthesis, Crystal Structures, and Thermal Properties of New Zinc(II) Thiocyanato Coordination Compounds

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Abstract. Reaction of zinc(II) thiocyanate with pyrazine, pyrimidine, pyridazine, and pyridine leads to the formation of new zinc(II) thiocyanato coordination compounds. In bis(isothiocyanato-*N*)-bis(μ_2 -pyrazine-*N*,*N*) zinc(II) (1) and bis(isothiocyanato-*N*)-bis(μ_2 -pyrimidine-*N*,*N*) zinc(II) (2) the zinc atoms are coordinated by four nitrogen atoms of the diazine ligands and two nitrogen atoms of the isothiocyanato anions within slightly distorted octahedra. The zinc atoms are connected by the diazine ligands into layers, which are further linked by weak intermolecular S···S interactions in 1 and by weak intermolecular C-H···S hydrogen bonding in 2. In bis(isothiocyanato-*N*)-bis(pyridazine-*N*) (3) discrete complexes are found, in which the zinc atoms are coordinated by two nitrogen atoms of the isothiocyanato ligands and two nitrogen atoms of the isothiocyanato soft he pyridazine ligands. The crystal structure of bis(isothiocyanato-*N*)-tetrakis(pyridine-*N*) (4) is known and consists of

Introduction

Recently, numerous investigations on the synthesis, structures and properties of coordination polymers, inorganic-organic hybrid compounds, or metal organic frameworks have been reported [1-10]. One important goal in this field comprised the preparation of compounds with useful physical properties. Most of these compounds are prepared in solution, which frequently leads to mixtures that sometimes have to be separated by hand. Therefore, a few years ago we started systematic investigations on the preparation of coordination polymers by thermal decomposition reactions. By this method ligand-rich precursor compounds are thermally decomposed, which frequently leads to the formation of ligand-deficient compounds in pure form and quantitative yields. We firstly investigated the synthesis of coordination compounds on the basis of copper(I) and zinc(II) halides and N-donor ligands [11-20].

Comparison of the crystal structures of the ligand-rich precursors and the ligand-deficient intermediates proves that in

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discrete complexes, in which the zinc atoms are octahedrally coordinated by two thiocyanato anions and four pyridine molecules. Investigations using simultaneous differential thermoanalysis and thermogravimetry, X-ray powder diffraction and IR spectroscopy prove that on heating, the ligand-rich compounds **1**, **2**, and **3** decompose without the formation of ligand-deficient intermediate phases. In contrast, compound **4** looses the pyridine ligands in two different steps, leading to the formation of the literature known ligand-deficient compound bis(isothiocyanato-*N*)-bis(pyridine-*N*) (**5**) as an intermediate. The crystal structure of compound **5** consists of tetrahedrally coordinated zinc atoms which are surrounded by two isothiocyanato anions and two pyridine ligands. The structures and the thermal reactivity are discussed and compared with this of related transition metal isothiocyanates with pyrazine, pyrimidine, pyridazine, and pyridine.

the course of such reactions more condensed networks are formed. This was the origin of further investigations that should show if paramagnetic transition metal compounds with terminally bonded small-sized ligands like e.g. thio- or selenocyanates can be transformed into new compounds with bridging anions that show a modified magnetic behavior [15, 21– 28]. In the meantime we have found several examples for such a behavior and in the following we also have started investigations on the thermal properties of Zn^{II} and Cd^{II} thiocyanates in order to prove if a similar thermal reactivity is observed.

A search in the Cambridge Structural Database for zinc(II) thiocyanates with N-donor ligands leads to about 170 hits [29, 30]. In practically all of them the thiocyanato anions are only terminal bonded and selected examples are given in references [31–38]. In only one of these structures the anions are connected by the sulfur atom to the zinc(II) atom but no space group and coordinates are given [39]. Interestingly, in only three structures the metal atoms are connected by the thiocyanato anion in μ -1,3-coordination [40–42]. Therefore, the question raises if bridged zinc(II) thiocyanates can be prepared by thermal decomposition reactions.

In the beginning, we investigated zinc(II) thiocyanates with pyridine, pyrazine, pyrimidine, and pyridazine as neutral coligands, for which according to the CCDC only crystal structures with pyridine were reported. With pyrazine only a structure of the ligand rich 1:4 compound (1:4 = ratio between metal and neutral N-donor coligand) bis(isothiocyanato-*N*)(tetrakis(pyrazine-*N*) zinc(II) was published in 2007 but retracted



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in 2010 [43]. With pyridine a ligand-rich 1:4 compound of composition $[Zn(NCS)_2(pyridine)_4]$ [44] and a ligand-deficient 1:2 compound of composition $[Zn(NCS)_2(pyridine)_2]_n$ [45] is known and therefore, it can be easily proved if this 1:2 compound occurs as an intermediate in the thermal decomposition reaction of the 1:4 compound. Herein we report on our investigations.

Results and Discussion

Crystal Structures

The 1:2 compound bis(isothiocyanato-*N*)-bis(μ_2 -pyrazine-*N*,*N*) zinc(II) (1) crystallizes in the monoclinic space group *C*2/*m* with two formula units in the unit cell and is isotypic to its manganese [46], iron [47], cobalt [48], and nickel [49] analogues reported recently. The zinc atoms are located on position 2/*m*, the isothiocyanato ligands on a mirror plane and the pyrazine ligand on a center of inversion (Figure 1). Each zinc atom is coordinated by four nitrogen atoms of the pyrazine ligands and two nitrogen atoms of the isothiocyanato ligands within a slightly distorted octahedral arrangement (Figure 1 and Table 1). The isothiocyanato ligands are *trans*oriented and are only terminally bonded.



Figure 1. Crystal structure of compound **1** with labelling and displacement ellipsoids drawn at the 50 % probability level. Symmetry transformations used to generate equivalent atoms: A: -x, -y+1, -z; B: x, -y+1, z; C: -x, y, -z; D: -x+1/2, -y+3/2, -z.

Table 1. Selected bond lengths	s /Å and angles /° for 1
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Zn(1)–N(1)	2.060(3)
Zn(1)–N(11)	2.2486(17)
N(1)-Zn(1)-N(1)A	180.0
N(1)-Zn(1)-N(11)	89.43(7)
N(1)-Zn(1)-N(11)	90.57(7)
N(11)–Zn(1)–N(11)C	88.59(9)
N(11)-Zn(1)-N(11)B	91.41(9)

Symmetry codes: A: -*x*, -*y*+1, -*z*; B: *x*, -*y*+1, *z*; C: -*x*, *y*, -*z*; D: -*x*+1/2, -*y*+3/2, -*z*.

The zinc atoms are connected by the pyrazine ligands in μ -N,N' coordination into layers, which are stacked in the direction of the crystallographic *c* axis (Figure 2). These layers are further linked by weak intermolecular S···S interactions between the sulfur atoms of the isothiocyanato ligands. The S···S distance amounts to 3.5 Å, which is slightly shorter than the sum of the van der Waals radii [50].



Figure 2. Crystal structure of compound **1** with view onto the layers (black = metal, dark-grey = nitrogen, grey = carbon, light-grey = sulfur, white = hydrogen).

The 1:2 compound bis(isothiocyanato-*N*)-bis(μ_2 -pyrimidine-*N*,*N*) zinc(II) (**2**) crystallizes in the orthorhombic space group *Cmca* with four formula units in the unit cell and is isotypic to its manganese [51], iron [51], cobalt [46, 52] and nickel [22] analogues reported recently. The zinc atom is located on position 2/*m*, the isothiocyanato ligand on a mirror plane and the pyrimidine ligand on a twofold rotation axis (Figure 3). The zinc atom is coordinated by four nitrogen atoms of the pyrimidine ligands and two nitrogen atoms of the isothiocyanato ligands within slightly distorted octahedral arrangement (Figure 3 and Table 2). As in compound **1**, the isothiocyanato ligands are *trans*-configured and act only as terminal ligands through the nitrogen atoms.



Figure 3. Crystal structure of compound **2** with labelling and displacement ellipsoids drawn at the 50 % probability level. Symmetry transformations used to generate equivalent atoms: A: -x+1, -y+1, -z; B: x, -y+1, -z; C: -x+1, y, z; D: -x+3/2, y, -z+1/2.



Table 2. Selected bond lengths /Å and angles /° for 2.

-	-	
Zn(1)–N(1)	2.2929(12)	
Zn(1)-N(2)	2.0331(18)	
N(1) - Zn(1) - N(1)C	88.72(6)	
N(2)–Zn(1)–N(1)A	89.83(5)	
N(2)-Zn(1)-N(1)	90.17(5)	
N(1)A-Zn(1)-N(1)C	91.28(6)	
N(2)–Zn(1)–N(2)A	180.0	

Symmetry codes: A: -*x*+1, -*y*+1, -*z*; B: *x*, -*y*+1, -*z*; C: -*x*+1, *y*, *z*; D: -*x*+3/2, *y*, -*z*+1/2.

The zinc atoms are connected by the pyrimidine ligands in μ -*N*,*N* coordination into layers, which are located in the a/c plane (Figure 4).



Figure 4. Crystal structure of compound 2 with view in the direction of the *b* axis (black = metal, dark-grey = nitrogen, grey = carbon, light-grey = sulfur, white = hydrogen).

Compound **3** crystallizes in the monoclinic space group C2/c with four formula units in the unit cell. The isothiocyanato anions and the pyridazine ligands occupy general positions, whereas the zinc atoms are located on twofold rotation axis (Figure 5). In contrast to compounds **1** and **2**, in **3** the zinc atoms are only tetrahedrally coordinated by two nitrogen atoms



Figure 5. Crystal structure of compound **3** with labelling and displacement ellipsoids drawn at the 50 % probability level. Symmetry transformation used to generate equivalent atoms: A : -x+1, y, -z+1/2.

from the isothiocyanato anions and two nitrogen atoms from the pyridazine ligand (Figure 5 and Table 3). Because the two nitrogen atoms are neighbored, no extended structures can be formed.

Table 3. Selected bond	lengths /Å	and angles /°	for 3 .
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Symmetry codes: A: -x+1, y, $-z+\frac{1}{2}$.

In the crystal structure the complexes are connected by weak intermolecular C–H···N and C–H···S interactions into layers that are located in the a/c plane (Figure 6).



Figure 6. Crystal structure of compound **3** with view along the crystallographic *b* axis. Intermolecular C–H···N and C–H···N interactions are shown as dashed lines (black = metal, dark-grey = nitrogen, grey = carbon, light-grey = sulfur, white = hydrogen).

Thermoanalytical Investigations

On heating, compounds 1, 2, and 3 in a thermobalance decomposition starts at about 200 °C for 1 and at about 150 °C for 2 and 3 (Figure S5–S7 in the Supporting Information). For all compounds a continuous mass loss is observed without the occurrence of distinct steps. From the experimental mass loss it is obvious that the complete ligands are removed in one step and that also the decomposition of the isothiocyanato anion cannot be distinguished. Therefore, no ligand deficient intermediates can be observed in the thermal decomposition reaction of compounds 1-3.

If the 1:4 compound **4** is heated two different mass steps are observed, that are accompanied with endothermic events in the DTA curve at 96 °C and 183 °C (Figure 7). From the DTG curve it is obvious that the two steps are well resolved and the experimental mass loss in the first step of 31.5 % is in perfect agreement with the removal of half of the pyridine ligands

 $(\Delta m_{\text{calcd.}} = -31.4 \%)$. Therefore, it can be assumed that in the first step a ligand-deficient 1:2 compound of composition $\text{Zn}(\text{SCN})_2(\text{pyridine})_2$ (5) is formed that decomposes on further heating.



Figure 7. DTG, TG, and DTA curves for compound **4**. Heating rate = $4 \, ^{\circ}\text{C-min}^{-1}$; given are the mass changes /% and the peak temperatures $T_{\text{P}} \, /^{\circ}\text{C}$.

To prove this assumption a second TG experiment was performed, in which the residue formed after the first mass loss was isolated. The result of an elemental analysis of this residue is in good agreement with that calculated for a 1:2 compound (see Experimental Section). Moreover, if the residue is investigated by X-ray powder diffraction it is proven that the 1:2 compound bis(isothiocyanato-*N*)-bis(pyridine-*N*) zinc(II) (5) is formed, that consists of discrete complexes, in which the zinc(II) atom is coordinated by two N-bonding isothiocyanato anions and two pyridine ligands within a slightly distorted tetrahedron (Figure 8) [45].



Figure 8. Experimental XRPD patterns of the residues obtained after the first heating step in the thermal decomposition reaction of 4 (top) and XRPD pattern for the 1:2 compound 5 calculated from single crystal data.

Additional investigations show that compound **4** is not very stable at room temperature and decomposes within two hours. To prove the identity of all intermediates experiments using time-dependent X-ray powder diffraction were performed (Figure 9). This experiment clearly shows that within about 1 h at room temperature a transformation only into the ligand-deficient 1:2 compound **5** is observed.



Figure 9. Time dependent XRPD patterns of compound 4 measured at room temperature.

Spectroscopy

All compounds were additionally investigated by IR and Raman spectroscopy because the coordination mode of the isothiocyanato anion can easily be determined from their vibrational spectra (see Figures S7–S10 in the Supporting Information). Due to the transformation of compound **4** into compound **5** even at room temperature, for **4** only a Raman spectrum could be measured in glass capillaries.

In general the three normal vibrational modes of the linear isothiocyanato anion include the pseudo-asymmetric stretching vibration $v_1[v(CN)]$, the bending mode $v_2[\delta(NCS)]$ and the pseudo-symmetric stretching vibration $v_3[v(CS)]$. All three bands can be used to diagnose the coordination mode of the isothiocyanato anion but the most interesting band is the very strong C–N stretching vibration v_1 , which is shifted only by a few wavenumbers in terminal N-bonded isothiocyanato compounds relative to that in the reference compound potassium thiocyanate ($v_1 = 2053 \text{ cm}^{-1}$) [53, 54]. In contrast, in μ_2 -N,S bridging isothiocyanato compounds v1 occurs above 2100 cm⁻¹ and in μ_2 -N bridging isothiocyanato compounds v_1 is found near or just below 2000 cm^{-1} . In compounds 1–3, and 5 values of 2065, 2055, 2084/2099, and 2071/2097 cm⁻¹ are found for v_1 , which is in agreement with the presence of Nbonded isothiocyanato anions (see Supporting Information) (Table 4).

Table 4. Stretching vibration $v_1[v(CN)]$ in the infrared (4000–400 cm⁻¹) and Raman spectra (3500–100 cm⁻¹) for the thiocyanato anions in compounds 1–5.

Compound	IR bands /cm ⁻¹	Raman bands /cm ⁻¹
1	2065	2062
2	2055	2062, 2054
3	2099, 2084	2093
4	-	2069
5	2097, 2071	2084, 2068

For molecules with a center of symmetry the complementariness of the Raman and infrared spectra implies only one infrared active $[v_{as}(CN)]$ and one Raman active $[v_{sym}(CN)]$ band, as it should be the case for compounds 1, 2, and 4. For compounds 3 and 5 $[v_{as}(CN)]$ and $[v_{sym}(CN)]$ should be infrared and Raman active. For compounds 1, 4, and 5 the experimental measurements are in agreement with this rule. For compound 2 two bands are observed in the Raman spectra, but only one broad band in the infrared spectra. In contrast, for compound 3 two bands are observed in the infrared spectra and only one broadened band in the Raman spectra. Repeated measurements of different batches for these compounds support this observation and we have really no explanation for it.

Conclusions

In this contribution four zinc(II) thiocyanates were prepared and investigated for their thermal properties. It was found that the 1:2 compounds 1-3 decompose in one step without the formation of ligand-deficient intermediates. This is a bit surprising because recently we investigated the corresponding compounds with the transition metals manganese, iron, cobalt, and nickel, which in the case of e.g. pyrazine as coligand shows the same topology of the coordination network [15, 49]. If these compounds are heated a transformation into liganddeficient 1:1 compounds is observed, in which the metal atoms are bridged by the isothiocyanato anions and the octahedral coordination is retained. In compounds 1 and 2 also octahedral coordination is present and it could be assumed that zinc is as chalcophilic as the elements manganese, iron, cobalt, and nickel in order that also intermediates with bridging isothiocyanato anions are formed, which is not the case here. In this context it must also be mentioned that similar 1:2 compounds can also be prepared with e.g. zinc halides and pyrazine that shows the same topology of the coordination network as compound 1 [18]. If e.g. the chloro compound is heated, a structure is formed, in which the zinc atoms are octahedrally coordinated and connected into chains by the chlorine atoms, which are further linked by the pyrazine ligands into layers [18].

For the ligand-rich 1:4 compound 4 a ligand-deficient 1:2 intermediate 5 is observed on thermal decomposition, but the structure of this compound is different from that what we expected in the beginning because the octahedral coordination is transformed into a tetrahedral coordination, in which the isothiocyanato anions are always N-bonded. We also investigated similar compounds of composition $M(NCS)_2(pyridine)_4$ (M = Mn, Fe, Co, and Ni) that also consist of discrete complexes, in which the metal atoms are coordinated by two N-bonded isothiocyanato anions and four pyridine ligands and which are isotypic to compound 4 [55-59]. If these compounds are heated, also 1:2 intermediates can be isolated, but in contrast to compound 5 the octahedral coordination is retained and the metal atoms are bridged by the isothiocyanato anions into chains [60-62]. Obviously, in the case of zinc the tetrahedral coordination with N-bonded isothiocyanato anions is more stable than the octahedral coordination with µ-1,3 bridging anions. These observations clearly show that the situation is sometimes more complex and the prediction of the existence and structures of ligand-deficient intermediates based on the structures of the ligand-rich precursors is only possible to some

Finally, it must be mentioned that because of the structural similarities between compounds **4** and **5**, in which always discrete complexes are formed it could be expected that even for the compound with pyridazine a ligand-rich discrete 1:4 complex must exist. However, we performed several experiments to prepare this compound but it has not formed even if a large excess of pyridazine was used or the reaction was performed in pure ligand. In any case only the 1:2 compound **3** was obtained.

Experimental Section

Syntheses

extent.

Zn(NCS)₂: Ba(NCS)₂·3H₂O (3.0755 g, 10 mmol) and ZnSO₄·H₂O (1.61434 g) were stirred in water (100 mL). The colorless precipitate of BaSO₄ was filtered off and the water was removed from the filtrate by heating. The final product was dried by 80 °C. The homogeneity of the product was investigated by X-ray powder diffraction.

Compounds 1–3: $Zn(NCS)_2$ (181.5 mg) and pyrazine, pyrimidine, or pyridazine (160.2 mg) were stirred in acetonitrile (2 mL) for 1 d. The precipitates were filtered off and washed with ethyl ether. On slow evaporation of the acetonitrile from the filtrate crystals are obtained, which are suitable for single-crystal X-ray diffraction. The purity was checked by XRPD (see Figure S1–S3 in the Supporting Information) and elemental analysis. $C_{10}H_8N_6S_2Zn$ (341.71): calcd. C 35.15, H 2.36, N 24.59 %; found C 35.23, H 2.38, N 24.49 % (1); C 35.05, H 2.29, N 24.43 % (2); C 35.28, H 2.21, N 24.42 % (3).

Compound 4: The literature known compound **4** was prepared according to a different procedure by the reaction of $ZnCl_2$ (136.3 mg) KNCS (194.4 mg) and pyridine (1 mL) in water (2 mL). The colorless precipitate was filtered off and washed with pyridine. The purity was checked by XRPD (see Figure S4 in the Supporting Information). $C_{12}H_{10}N_4S_2Zn$ (337.73): calcd. C 42.42, H 2.97, N 16.49, S 18.88 %; found C 42.45, H 3.15, N 16.78, S 19.12 %.

Elemental Analysis

CHNS analysis was performed with an EURO EA elemental analyzer, fabricated by EURO VECTOR Instruments and Software.

Spectroscopy

Fourier transform IR spectra were recorded with a Genesis series FTIR spectrometer from ATI Mattson in KBr pellets. Raman-spectra were recorded with a Bruker ISF66 FRA106 between 3500–100 cm⁻¹ in a closed glass tube.

Differential Thermal Analysis and Thermogravimetry

The DTA-TG measurements were performed in nitrogen atmosphere (purity: 5.0) in Al_2O_3 crucibles using a STA-409CD thermobalance from Netzsch. All measurements were performed with a flow rate of 75 mL·min⁻¹ and were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

Single-Crystal Structure Analysis

All investigation was performed with an imaging plate diffraction system (IPDS-1) with Mo- K_{α} -radiation from STOE & CIE. The structure solution was performed with direct methods using SHELXS-97 [63], and structure refinements were performed against F^2 using SHELXL-97 [63]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters $[U_{iso}H) = -1.2 \cdot U_{eq}(C)]$ using a riding model. Details of the structure determination are given in Table 5.

Table 5. Selected crystal data and details on the structure determina-tions for compounds 1, 2, and 3.

	1	2	3
formula	C ₁₀ H ₈ N ₆ S ₂ Zn	C ₁₀ H ₈ N ₆ S ₂ Zn	C ₁₀ H ₈ N ₆ S ₂ Zn
MW /g·mol ⁻¹	341.71	341.71	341.71
crystal system	monoclinic	orthorhombic	monoclinic
space group	C2/m	Cmca	C2/c
<i>a</i> /Å	10.2096(10)	9.6383(7)	14.7258(12)
b /Å	10.4294(8)	15.6599(13)	5.5843(3)
c /Å	7.1818(8)	8.4943(8)	17.3102(15)
$\beta /^{\circ}$	118.94(1)	90.0	96.89(1)
$V/Å^3$	669.2(1)	1282.1(2)	1413.2(2)
T/K	293	170	170
Ζ	2	4	4
$D_{\rm calc} / \text{g} \cdot \text{cm}^{-3}$	1.696	1.770	1.606
μ / mm^{-1}	2.114	2.234	2.027
$\theta_{\rm max}$ / deg	28.00	27.95	27.98
measured refl.	3244	7021	7734
R _{int}	0.0559	0.0741	0.0347
unique reflns.	849	815	1694
refl.[$F_{o} > 4\sigma(F_{o})$]	812	772	1433
parameters	51	52	88
$R_1 [F_0 > 4\sigma(F_0)]$	0.0382	0.0293	0.0327
wR_2 [all data]	0.1039	0.0756	0.0938
GOF	1.099	1.027	1.006
$\Delta \rho_{\rm max/min}/{\rm e} \cdot {\rm \AA}^{-3}$	0.65/ -0.68	0.45/-1.27	0.37/-0.50

CCDC-779206 (1), CCDC-779208 (2), and CCDC-779207(3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336-033; or E-Mail: deposit@ccdc.cam.ac.uk).

X-ray Powder Diffraction (XRPD)

XRPD experiments were performed using a Stoe Transmission Powder Diffraction System (STADI P) with Cu- K_{α} radiation ($\lambda = 154.0598$ pm) that is equipped with a linear position-sensitive detector (Delta $2\theta = 6.5-7^{\circ}$ simultaneous; scan range overall = 2–130°) from STOE & CIE and an Image Plate Detector (scan range overall = 0–127°).

Supporting Information (see footnote on the first page of this article): Experimental and calculated XRPD pattern for compounds 1–4. DTA, TG, and DTG curves for compounds 1–3. IR spectra for compounds 1–5. Details on the structure determinations for compounds 1–3.

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