Synthesis, Structures, and Physical Properties of Thiocyanate Coordination Compounds with 3-Hydroxymethylpyridine

Tristan Neumann,^[a] Cesar dos Santos Cunha,^[a] Huayna Terraschke,^[a] Luzia S. Germann,^[b] Robert E. Dinnebier,^[b] Inke Jess,^[a] and Christian Näther^{*[a]}

Dedicated to Professor Wolfgang Schnick on the Occasion of his 60th Birthday

Abstract. The reaction of $Cd(NCS)_2$ with 3-hydroxymethylpyridine (3-HMPy) leads to the formation of compounds with the composition $Cd(NCS)_2(3-HMPy)_4(1-Cd),Cd(NCS)_2(3-HMPy)_2(2-Cd)(Cd(NCS)_2)_2-(3-HMPy)_3$ (3-Cd), and $(Cd(NCS)_2)_3(3-HMPy)_4$ (4-Cd). Compound 1-Cd consists of discrete complexes and in 2-Cd the Cd cations are linked into chains by the anionic and the organic co-ligands. In 3-Cd as well as 4-Cd the Cd cations are connected into chains by the thiocy-anate anions, which are further linked into layers by the 3-HMPy co-ligands. In contrast, with Zn only one compound with the composition Zn(NCS)_2(3-HMPy)_2'H_2O (1-Zn-H_2O) was characterized by single-

Introduction

Thiocyanate and selenocyanate anions have been widely used for the synthesis of new coordination compounds and polymers, hence they are showing a variety of coordination modes, which can lead to coordination networks of different topologies including polymorphic and isomeric modifications.^[1–12] In this context, compounds, in which the paramagnetic metal cations are linked by bridging ligands, are of special interest, because they can show cooperative magnetic phenomena.^[13-20] On the other hand, also compounds based on diamagnetic Zn^{II} and Cd^{II} are of interest, because they can exhibit luminescence properties with a variety of ligands.^[1-3,21-27] In most cases Zn compounds show a tetrahedral coordination, but there are also a number of compounds in which they possess a trigonal-bipyramidal, a square pyramidal, or an octahedral coordination arrangement, even if these modes are relatively rare compared to the tetrahedral coordination. For Cd^{II}-thiocyanates, most compounds show octahedral coordination environment, whereas four- or fivefold coordination is rarely observed.

- E-Mail: cnaether@ac.uni-kiel.de [a] Institute of Inorganic Chemistry Christian-Albrechts-University of Kiel Max-Eyth-Strasse 2
- 24118 Kiel, Germany
- [b] Max Planck Institute for Solid State Research Heisenbergstrasse 1 70569 Stuttgart, Germany
- Supporting information for this article is available on the WWW
- under http://dx.doi.org/10.1002/zaac.201700251 or from the author.

crystal X-ray diffraction, which shows a tetrahedral coordination of the Zn cations by two thiocyanate anions and two 3-HMPy ligands. The discrete complexes are arranged to form channels, in which the water molecules are embedded. **1-Zn-H₂O** cannot be obtained phase pure and detailed investigations reveal, that additional Zn compounds with the composition $Zn(NCS)_2(3-HMPy)_2 \cdot xH_2O$ including an anhydrate (**1-Zn**) can be obtained, which possesses a similar X-ray powder diffraction (XRPD) pattern. **1-Zn** was characterized using X-ray powder diffraction analysis. Most compounds were investigated by thermoanalysis, IR and Raman as well as luminescence spectroscopy.

Because Zn^{II} is less chalcophilic, in practically all cases the thiocyanate anions are only N-terminally coordinated to the cations and there are only very few examples, in which they are linked by μ -1,3-thiocyanate ligands into dimers or polymers.^[28–34] In contrast, in most of the Cd compounds the cations are linked into coordination polymers by bridging anionic ligands and such compounds show a variety of stoichiometries and topologies of the coordination networks. Compared to Zn^{II}, the synthesis of Cd^{II} compounds with only terminal N-bonded thiocyanate anions is sometimes more difficult.

In our ongoing investigations in this field, we are especially interested in transition metal thio- and selenocyanate coordination compounds, in which Mn^{II}, Fe^{II}, Co^{II}, or Ni^{II} cations are linked by the anionic ligands into coordination networks.^[35–41] Unfortunately, these metal cations are not very chalcophilic and therefore, the bridging compounds are frequently difficult to obtain. In some cases, they can be synthesized from solution using an excess of the metal thiocyanate but there are many examples in which such compounds cannot be obtained as phase pure samples or are not accessible from solution. As an alternative, precursor compounds with terminal coordinated anionic ligands can be heated. This leads frequently to a stepwise removal of the N-donor co-ligands and to a transformation into new compounds, in which the metal cations are linked by the anionic ligands into coordination polymers. Following this procedure, only microcrystalline powders are obtained, which cannot be characterized by single-crystal X-ray diffraction but X-ray powder diffraction (XRPD) analysis. In this case, corresponding compounds with Cd^{II} can be prepared, which easily crystallize from solution and which are very often isotypic to the paramagnetic counter parts and thus, the struc-

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^{*} Prof. Dr. C. Näther

ture determination of the latter can be performed by Rietveld refinements.^[42] In the same way, Zn compounds can be used to identify intermediates with a tetrahedral coordination, which can form if, e.g., Co^{II} precursors are annealed. This is one of the main reasons, why we are also interested in the structural chemistry of Zn^{II} and Cd^{II} compounds.

However, in the course of our project, we became interested in 3-hydroxymethylpyridine (3-HMPy) as ligand, for which no Cd^{II} and Zn^{II} thiocyanate compounds are reported in the Cambridge Structural Database (CSD). There is only one compound with Fe^{II}, in which the cations are octahedrally coordinated by four terminal N-bonded thiocyanate anions and two monodentate 3-HMPy ligands.^[43,44] Charge balance is achieved by an additional 3-HMPy ligand that is protonated at the N atom. It is also noted, that one compound with the composition $[Cd(N_3)_2(3-HMPy)_2]$ is reported, in which the Cd cations are octahedrally coordinated by four azide anions and two terminal N-bonded 3-HMPy ligands and are linked by pairs of µ-1,3-bridging anionic ligands into chains.^[45] This is also a very common motif for thiocyanate coordination compounds, in which the ratio between the metal thiocyanate and a monodentate co-ligand is 1:2. However, even if in most cases 3-HMPy is coordinated only with the pyridine N atom to the central metal atoms, some structures are known, in which the metal cations are linked by μ -1,5(N,O) bridging ligands into coordination polymers.^[46–48]

Results and Discussion

Synthetic Aspects

Reaction of $Cd(NCS)_2$ and $Zn(NCS)_2$ in different molar ratios and different solvents leads to the formation of suitable crystals of the following compounds that were characterized by single-crystal X-ray diffraction and XRPD analysis (*) (see Experimental Section):

 $\begin{array}{l} Cd(NCS)_{2}(3\text{-}HMPy)_{4} \ (1\text{-}Cd)\\ Cd(NCS)_{2]}(3\text{-}HMPy)_{2} \ (2\text{-}Cd)\\ (Cd(NCS)_{2})_{2}(3\text{-}HMPy)_{3} \ (3\text{-}Cd)\\ (Cd(NCS)_{2})_{3}(3\text{-}HMPy)_{4} \ (4\text{-}Cd)\\ Zn(NCS)_{2}(3\text{-}HMPy)_{2}\text{\cdot}H_{2}O \ (1\text{-}Zn\text{-}H_{2}O)\\ Zn(NCS)_{2}(3\text{-}HMPy)_{2} \ (1\text{-}Zn) \ (*) \end{array}$

Based on the structural data, XRPD patterns were calculated and compared with the experimental pattern, which proves that all Cd^{II} compounds were obtained as pure phases (Figures S1 and S2, Supporting Information). Comparison of the calculated XRPD pattern of **1-Zn-H₂O** with that measured for the batch from which the crystal of **1-Zn-H₂O** was selected, shows that a mixture of the monohydrate and a further crystalline phase was obtained. Therefore, several experiments were performed using different ratios between Zn(NCS)₂ and 3-HMPy to obtain **1-Zn** as a pure phase or to obtain single crystals of the new phase. The powder patterns of most of these batches are identical and correspond to a further crystalline phase (Figure S3, Supporting Information). Interestingly, the powder pattern of this crystalline phase is very similar to that of Zn(NCS)₂-(3-methylpyridine)₂ reported recently (Figure S4, Supporting Information), indicating that the anhydrate (**1-Zn**) has formed, which was confirmed by Rietveld analysis (Figure S5, Supporting Information).^[49] **1-Zn** was obtained as a pure phase (Figure S6, Supporting Information) as confirmed by XRPD.

The experimental XRPD patterns of some other batches, in which $Zn(NCS)_2$ and 3-HMPy was reacted in a 1:2 ratio, show minor but significant differences indicating the presence of an additional crystalline phase (Figure S7, Supporting Information). If **1-Zn** is stored in a humid atmosphere a crystalline phase is obtained, that is also formed if this compound is stored on air for several days (Figure S8, Supporting Information). DTA-TG measurements of this phase show a small weight loss below 100 °C, indicating that a hydrate has formed, that contains approximately one water molecule per formula unit. It is therefore assumed that different hydrates with similar powder patterns form upon different reaction or storage conditions. Summarizing, different crystalline phases are obtained with Zn(NCS)₂, that are hygroscopic and that show very similar XRPD patterns.

Crystal Structures

 $Cd(NCS)_2(3-HMPy)_4$ (1-Cd) crystallizes in the orthorhombic space group *Pbcn* with four formula units in the unit cell. The asymmetric unit consists of one metal cation, which is located on a center of inversion and one thiocyanate anion as well as two 3-HMPy ligands on general positions (Figure S9, Supporting Information). The crystal structure consists of discrete complexes, in which the Cd^{II} cations are coordinated by two terminal N-bonded thiocyanate anions and four 3-HMPy ligands that are linked with the pyridine N atom to the central metal atoms (Figure 1 top). The coordination polyhedra around the metal atoms can be described as a slightly distorted octahedra. The Cd-N distances range from 2.274(2) to 2.419(2) Å and correspond to that observed in similar compounds (Table S1, Supporting Information). The N-Cd-N angles within the equatorial plane are between 77.88(7) and 92.26(8)° (Table S1).

In the crystal structure of **1-Cd**, the discrete complexes are linked into layers by intermolecular O–H···O hydrogen bonding between the hydroxyl hydrogen atom of one complex and the hydroxyl O atom of a neighbored complex that acts as an acceptor. These layers are parallel to the *ac* plane (Table 1 and Figure 1 bottom). There are additional short contacts between some of the C–H hydrogen atoms and the thiocyanate sulfur atoms, an indication for weak C–H···S interactions (Table 1).

Cd(NCS)₂(3-hydroxymethylpyridine)₂ (**2-Cd**) crystallizes in the triclinic space group $P\bar{1}$ with all atoms located on general positions. The Cd^{II} cations are octahedral coordinated by two N- and one O-bonding 3-HMPy ligand as well as one S- and two N-bonding thiocyanate anions, of which one is only terminally bonded (Figure S10, Supporting Information). Because of the irregular coordination, the coordination sphere is more distorted than that in **1-Cd** (Table S2, Supporting Information). Each two cations are linked by centrosymmetric pairs of thiocyanate anions into dimers, that are further linked by pairs of N,O-bridging 3-hydroxymethylpyridine ligands into







Figure 1. Crystal structure of **1-Cd** view of the Cd coordination sphere (top) and along the crystallographic *b* axis (bottom) with intermolecular O–H···O hydrogen bonding shown as dashed lines (Cd: orange; S: yellow; N: blue; C: dark grey; O: red; H: light grey). An ORTEP plot of **1-Cd** can be found in Figure S9 (Supporting Information).

Table 1. Hydrogen bonding /Å,° for 1-Cd and 2-Cd.

D–H•••A	<i>d</i> (H••• <i>A</i>)	$d(D \cdot \cdot \cdot A)$	< <i>D</i> –H••• <i>A</i>
1-Cd			
O(11)–H(11)•••O(21)	1.97	2.755(3)	160.2
O(21)–H(21A)•••O(11)	1.96	2.770(3)	167.2
C(16)–H(16B)•••S(1)	2.97	3.883(3)	157.2
C(26)–H(26B)•••S(1)	3.00	3.752(3)	134.8
C(25)-H(25)-S(1)	2.95	3.620(3)	130.1
2-Cd			
O(21)–H(21A)•••O(11)	1.87	2.697(3)	168.0
O(11)-H(11A)-S(1)	2.42	3.223(2)	160.9
C(14)–H(14)•••O(11)	2.92	3.750(3)	146.5

chains, that elongate in the direction of the c axis (Figure 2 top). The chains are further linked into layers by an intermolecular O–H···O hydrogen network (Figure 2 bottom and Table 1). The layers are additionally connected by intermolecular O–H···S hydrogen bonding between the thiocyanate S atoms and the hydroxyl hydrogen atoms that are not involved in O–H···O hydrogen bonding (Table 1). There are also some



Figure 2. Crystal structure of **2-Cd** with view of a chain (top) and onto the layers along the *a* axis with intermolecular O–H···O hydrogen network shown as dashed lines (bottom). An Ortep plot of **2-Cd** can be found in Figure S10 (Supporting Information) (Cd: orange; S: yellow; N: blue; C: dark grey; O: red; H: light grey).

intermolecular C-H···O contacts, indicating weak intermolecular interactions (Table 1).

The crystal structures of $(Cd(NCS)_2)_2(3-HMPy)_3$ (3-Cd) and of $(Cd(NCS)_2)_3(3-HMPy)_4$ (4-Cd) are strongly related to each other. 3-Cd crystallizes in the monoclinic space group $P2_1/n$, whereas **4-Cd** crystallizes in the triclinic space group $P\bar{1}$. In both compounds all atoms are located on general positions. The asymmetric unit of each compound contains two crystallographically independent Cd^{II} cations that are each coordinated by two S and two N atoms of thiocyanate anions and two trans-coordinating 3-HMPy ligands and are linked into chains by pairs of anionic ligands (Figure 3 and Figures S11, Supporting Information). However, one of the cations (Cd1) is coordinated by both the pyridine N atoms, whereas the second (Cd2) is coordinated to one ligand via the N and the other by the O atom (Figure 3). The different coordination is accompanied by a different orientation of the anionic ligands, because the two S, respectively two N atoms of the thiocyanate

anions are in *cis* position for the Cd^{II} cation that is coordinated by one N and one O atom of the neutral ligands and *trans* for that cation, which is only coordinated by two pyridine N atoms (Figure 3).



Figure 3. Crystal structure of **3-Cd** (top) and **4-Cd** (bottom) with view of the $Cd(NCS)_2$ chains. Ortep plots of **3-Cd** and **4-Cd** can be found in Figure S11 (Supporting Information) (Cd: orange; S: yellow; N: blue; C: dark grey; O: red; H: light grey).

The bond lengths of the two different Cd coordination modes show only small differences but the octahedral coordination is more distorted for Cd2 (Tables S3 and S4, Supporting Information). Moreover, the sequence of the two crystallographically independent cations along the chain is different. In 3-Cd the two different coordination modes alternate (ABA-BAB...), whereas in 4-Cd two Cd^{II} cations coordinated by one N and one O atom (A), are followed by one Cd^{II} cation that is only coordinated by two pyridine N atoms (B) leading to a sequence of AABAAB... (Figure 4). The Cd^{II} cations are further linked into layers by bridging 3-HMPy ligands (Figure 4). Interestingly, only Cd2 ions are involved in the layer formation, whereas this is not the case for Cd1. This means that in 3-Cd any second and in 4-Cd any third Cd cation acts as node in the coordination network. It is noted, that in both compounds, O-H-O hydrogen bonding between the O-H hydrogen atom of the 3-HMPy ligand, which is coordinated to the central metal atoms, and the O atom of the terminally bonded ligand is observed (Figure 4 and Table 2). In 4-Cd the hydroxyl H atom of the terminal ligand is additionally hydrogen bonded to the thiocyanate N atom, which is not the case in 3-Cd, where the O-H hydrogen atom is linked to a thiocyanate N atom of a neighboring layer (Figure 4).

The structures of **3-Cd** and **4-Cd** are strongly related to that of several other thiocyanate coordination polymers. For most compounds with the composition $[M(NCS)_2(L1)_2]$ (M = Mn, Fe, Co, Ni, Cd; L1 = monodentate N-donor co-ligand), similar



Figure 4. Crystal structure of 3-Cd with view along the crystallographic c axis (left) and of 4-Cd along the a axis with intermolecular O-H···O and N-H···O hydrogen bonding shown as dashed lines (Cd: orange; S: yellow; N: blue; C: dark grey; O: red; H: light grey).

 $M(NCS)_2$ chains are observed, in which the metal cations are only coordinated by terminal N-donor co-ligands.

If bridging co-ligands (L2) are used, compounds with the composition $[M(NCS)_2(L2)]$ are frequently obtained, in which the metal cations are linked by pairs of anionic ligands into chains, that are further connected by the bridging co-ligands L2 into layers. In **3-Cd** alternating bridging and terminal co-ligands are observed, which leads to a ratio Cd(NCS)₂ to 3-hydroxymethylpyridine of 2:3. Within the chains in **4-Cd**, two cations are coordinated by bridging and one by a terminal co-

Table 2. Hydrogen bonding /Å,° for 3-Cd and 4-Cd

D–H•••A	$d(H \cdot \cdot \cdot A)$	$d(D \cdot \cdot \cdot A)$	< <i>D</i> –H••• <i>A</i>
3-Cd			
O(11)–H(11A)•••O(31)	2.20	2.760(5)	125.2
O(21)-H(21A)····N(4)	2.34	3.122(5)	159.3
O(31)-H(31A)····N(3)	2.24	3.048(5)	168.7
C(11)–H(11)•••S(3)	3.03	3.926(4)	163.3
C(26)-H(26C)···S(2)	2.80	3.731(5)	162.1
4-Cd			
O(21)–H(21A)•••O(11)	1.87	2.698(3)	169.1
O(11)-H(11A)····N(2)	2.11	2.891(3)	154.7
C(11)-H(11)-S(1)	3.00	3.919(2)	162.2
C(24)–H(24)•••S(2)	3.02	3.642(3)	124.3
C(26)–H(26A)•••S(3)	3.01	3.876(3)	147.2
C(24)–H(24)•••O(21)	2.66	3.538(3)	154.7

ligand, leading to a ratio of 3:4. This means that the two compounds represent structural intermediates between the usually observed structures with the composition $[M(NCS)_2(L1)_2]$ and $[M(NCS)_2(L2)]$.

 $Zn(NCS)_2(3-HMPY)_2$ monohydrate (**1-Zn-H₂O**) crystallizes in the monoclinic space group $P2_1/n$ with all atoms in general positions. All investigated crystals are non-merohedral twinned and therefore, a twin refinement was performed (see Experimental Section). The Zn^{II} cations are tetrahedral coordinated by two N-bonding thiocyanate anions and two N-bonding 3-HMPy ligands (Figure 5 top, Figure S12 and Table S5, Supporting Information).



Figure 5. Crystal structure of $1-Zn-H_2O$ with view along the crystallographic *b* axis with intermolecular O–H···O and O–H···S hydrogen bonding shown as dashed lines (Zn: dark orange; S: yellow; N: blue; C: dark grey; O: red; H: light grey). An ORTEP plot of 1-Zn can be found in Figure S12 (Supporting Information).

In the crystal structure the discrete complexes are connected by intermolecular O–H···O hydrogen bonding between the hydroxyl H atom and the hydroxyl O atom of neighboring 3-HMPy ligands into chains, that elongate along the *a* axis. By this arrangement channels are formed, that contain the hydrate water molecules, which are linked to the host structure by intermolecular O–H···O hydrogen bonding between one hydroxyl H atom of the co-ligands and the water O atom, one water H atom and one hydroxyl O atom as well as by O–H···S hydrogen bonding between one water H atom and the S atom of one of the thiocyanate anions (Figure 5 bottom and Table 3).

Table 3. Hydrogen bonding /Å,° for 1-Zn.

<i>D</i> –H•••A	<i>d</i> (H••• <i>A</i>)	$d(D \cdot \cdot \cdot A)$	< <i>D</i> –H••• <i>A</i>
C(11)–H(11)O(31A)	2.55	3.497(6)	171.8
O(11)-H(11A)O(21B)	1.95	2.768(6)	164.7
O(21)-H(21A)O(31)	1.95	2.760(6)	160.8
O(31)-H(31A)O(11)	2.04	2.827(6)	154.8
O(31)-H(31B)S(1C)	2.50	3.268(4)	151.6

The crystal structure of **1-Zn** was determined by XRPD analysis. **1-Zn** crystallizes in the orthorhombic space group *Pnma* with Z = 4. All Zn cations as well as both symmetry independent thiocyanate anions are located on a mirror plane. The Zn cations are coordinated by two terminal N-bonded anionic ligands and two symmetry equivalent HMPy co-ligands, which are coordinated by the pyridine N atoms to the central metal atom into discrete tetrahedrally coordinated complexes (Figure 6).



Figure 6. View of a discrete complex in the crystal structure of 1-Zn.

IR and Raman Investigations

To check if one can differ between the different coordination modes of the anionic ligands, IR and Raman spectroscopic investigations were performed. For terminal N-bonded anions the CN stretching vibration is usually observed above 2050 cm^{-1} , whereas for μ -1,3-bridging anionic ligands it is shifted to values of about 2100 cm^{-1} .^[10] However, the actual values depend strongly on the nature of the metal cation and the co-ligand and therefore, in several cases these regions overlap.

For **1-Cd** one band is observed in the IR spectra at 2046 cm⁻¹ and one in the Raman spectra at 2048 cm⁻¹, which is in perfect agreement with the structure results because only one crystal-lographically independent and terminal N-bonded thiocyanate anion is present (Figure S13, Supporting Information). In contrast, in **2-Cd** two different anionic ligands are observed of which one is only terminal N-bonded, whereas the second act as a μ -1,3-bridging ligand. In agreement with these findings two different bands are observed in the IR (2053 and 2104 cm⁻¹) and two bands in the Raman spectra (2053 and 2098 cm⁻¹), with the vibration at higher values corresponding to the μ -1,3-bridging mode (Figure S13, Supporting Information).

For **3-Cd** three or four CN stretching vibrations are observed in the range of 2073 to 2115 cm⁻¹, that can be traced back to the four crystallographically independent μ -1,3-bridging ligands (Figure S14, Supporting Information). **4-Cd** also shows several vibrations, which are observed between 2047 and 2122 cm⁻¹ (Figure S14). Because of the fact that in **3-Cd** and **4-Cd** only bridging thiocyanate anions are present it is obvious, that for the compounds reported herein one cannot clearly distinguish between a terminal and a bridging coordination of the anionic ligands, because some of these values are shifted to very low wave numbers.

For **1-Zn** only one band is observed for the CN stretch in the Raman respectively in the IR spectra at 2083 and 2074 cm⁻¹, which are in good agreement with values observed for other Zn(NCS)₂ complexes with a tetrahedral coordination (Figure S15, Supporting Information).

Thermoanalytical Investigations

To investigate the thermal properties of all compounds measurements using simultaneously differential thermoanalysis and thermogravimetry were performed (DTA-TG).

Upon heating 1-Cd only one step of 71.0% is observed in the TG curve that corresponds to the removal of all co-ligands $(\Delta m_{\text{calcd.}} = 67.1\%)$ and to a partial decomposition of Cd(NCS)₂ formed as product (Figure S16, Supporting Information). Surprisingly, there is one very sharp additional endothermic peak at 85 °C, where the sample mass does not change, indication for a possible phase transformation. To check the reversibility of this event measurements using differential scanning calorimetry (DSC) were performed. Upon heating, one endothermic event occurs at a peak temperature of 90.5 °C and upon cooling no exothermic signal is observed indicating the formation of an amorphous phase (Figure S17, Supporting Information). If this sample is heated again, the endothermic signal disappeared and there is no indication for a recrystallization of the sample. In one of the following heating cycles a small jump in the base line is observed, which might be traced back to a glass transition (Figure S17). Interestingly, if a sample is cooled down after the endothermic event was observed in the DSC measurements and investigated by XRPD, the powder pattern is identical to that of the pristine material 1-Cd (Figure S18, Supporting Information). These results are in agreement with the performed thermomicroscopy experiments (Figure

S19, Supporting Information). Upon heating to 94 °C the crystal faces disappeared, indicating the beginning of melting. However, no complete melting is observed and there are some indications for the formation of a crystalline powder, which points to a transition which proceeds via melting and crystallization of a new phase (Figure S20, Supporting Information).

Additional measurements using temperature dependent XRPD measurements reveal that starting from 85 °C the intensity of all reflections drop down dramatically and some additional reflections occur whose intensities increase with increasing temperature (Figures S20 and S21, Supporting Information). On cooling, a mixture of **1-Cd** and a new crystalline phase is obtained, which is somehow in disagreement with the results of the DSC and the thermomicroscopic investigations. However, these measurements were performed in nearly static nitrogen atmosphere, whereas the temperature dependent XRPD measurements were performed in an oxygen atmosphere and therefore, some decomposition cannot be excluded. In any case, the additional Bragg reflections do not correspond to that of one of the other Cd^{II} compounds.

DTA-TG measurements on **2-Cd**, **3-Cd**, and **4-Cd** show no well resolved thermogravimetric curves, in which always the complete 3-HMPy ligands are removed (Figure S22, Supporting Information). There is no hint for the formation of additional ligand-deficient phases as usually observed for this class of compounds.^[10] The DTA-TG curve for **1-Zn** is slightly better resolved and in the DTG curve two distinct maxima are observed, indicating for a further mass loss step, in which a new 3-HMPy deficient phase might form (Figure S23, Supporting Information). This measurement was stopped after the first mass loss step and investigated by XRPD, which shows that a new phase might have formed of very low crystal-linity. Therefore, no further investigations were performed.

Luminescence Properties

Figure 7 shows the emission spectra of the compounds 1-Cd, 2-Cd, 3-Cd, and 4-Cd in comparison to the emission spectrum of the ligand 3-HMPy, excited at 25000 cm⁻¹ (Fig-



Figure 7. Emission spectra of **1-Cd** (black curve), **2-Cd** (red curve), **3-Cd** (blue curve), **4-Cd** (pink curve), and the 3-HMPy ligand (green curve), excited at 25000 cm⁻¹.



ures S24–S28, Supporting Information). The respective emission spectrum of compound **1-Cd** (Figure 7, black curve) is composed of a broad band with a maximum at 21074 cm⁻¹ and full width at half maximum (FWHM) of 4898 cm⁻¹ (Table 4).

Table 4. Emission maximum, excitation energy and FWHM /cm⁻¹ ofcompounds 1-Cd, 2-Cd, 3-Cd, 4-Cd, and of the 3-HMPy ligand.

Compound	Emission maximum	Excitation energy	FWHM
1-Cd	21074	25000	4898
2-Cd	20000	25000	5673
3-Cd	20028	25000	6015
4-Cd	20020	25000	4996
3-HMPy	20807	25000	4780

In general, ligand-based luminescence is expected for hybrid organic-inorganic compounds, in which the metal ion does not show d-d or f-f electronic transitions, e.g., metal ions such as Cd²⁺ and Zn²⁺ with a d¹⁰ configuration, as previously reported in the literature.^[50,51] Therefore, since Cd²⁺ ions do not present radiative electronic transitions, the emission of the Cd²⁺ complexes originate from the $\pi^* \rightarrow \pi$ transitions of the aromatic units of the organic ligand.^[52,53] This fact agrees with the similar shape and position of the emission spectrum of 1-Cd and the 3-HMPy ligand. Similarly as for 1-Cd, the emission spectrum (Figure 7, green curve) of the 3-HMPy ligand comprises a broad band at the blue-green spectral range with maximum at 20807 cm⁻¹ with a FWHM of 4780 cm⁻¹. The emission spectrum (Figure 7, red curve) of 2-Cd, on the other hand, is red-shifted in comparison to the emission bands of 1-Cd and the ligand, distributed over the green spectral range (Figure 8), with a maximum at 20000 cm^{-1} and a FWHM of 5673 cm^{-1} . These optical properties are very similar to the ones of the other Cd²⁺ compounds, **3-Cd** and **4-Cd** (Figure 7, blue and pink curves). Hence, the emission maxima of the emission bands of 3-Cd and 4-Cd are located at, respectively, 20028 cm^{-1} and 20020 cm^{-1} with a FWHM of 6015 cm⁻¹ and 4996 cm⁻¹. This trend is also observed at the respective reflection spectra (Figure S29, Supporting Information), in which the spectra of 2-Cd, 3-Cd, and 4-Cd strongly overlap and are redshifted in comparison to the reflection spectrum of 1-Cd. Similar as for the emission spectra, the absorption spectral range of 1-Cd overlaps with the one of the pure ligand 3-HMPy (Figure S27, Supporting Information). From the reflection spectra, the bandgap of approximately 4.5 eV was estimated for compounds 2-Cd, 3-Cd, and 4-Cd and approximately 5.7 eV for 1-Cd.[54]

The similarity between the optical properties of **1-Cd** and the 3-HMPy as well as the difference to the optical properties of **2-Cd**, **3-Cd**, and **4-Cd** lie most probably on the nature of the interaction between the single complex units and therefore between the π electrons on these different structures. For instance, the structure of **1-Cd** is composed of discrete complexes, linked mainly by intermolecular O–H···O hydrogen bonding between the hydroxyl hydrogen atom of the ligand of one complex and the hydroxyl O atom of a neighbored complex, very similar to the expected interaction between single ligand molecules in pure 3-HMPy. In contrast, the Cd²⁺ complex units in **2-Cd**, **3-Cd**, and **4-Cd** are interconnected to



Figure 8. Photographs of compounds 1-Cd, 2-Cd, 3-Cd, and 4-Cd illuminated with visible (left) and near UV light at 400 nm (right), irradiated with an optical fiber.

chains and layers, forming extended coordination polymer networks, increasing the interaction between the ligand π electrons, shifting the emission bands to lower energies.^[51] The optical properties of the analogous Zn²⁺ compounds were not characterized because no large amount of pure phases were obtained due to their hygroscopic nature.

Conclusions

Several new Cd^{II} coordination compounds with a different ratio between the metal thiocyanate and the 3-HMPy ligand were synthesized. Surprisingly, two of the Cd compounds exhibit a M:L ratio of 2:3 and 3:4, which is rarely observed in this class of compounds and which leads to the fact that some of the 3-HMPy ligands are only terminal bonded, whereas some others act as bridging ligands. With Zn a hydrate and an anhydrate were obtained but the XRPD and TGA investigations indicate the presence of additional hydrates that possibly differ in the water content. Thermoanalytical investigations reveal no indication for the formation of additional 3-HMPy deficient crystalline phases as previously observed for similar coordination compounds. However, in these compounds the co-ligands are always coordinated only with the pyridine N atom to the central metal atoms, whereas with 3-HMPy as ligand an additional, presumably much stronger M-O bond is formed via the oxygen atom and this might prevent elimination of this ligand in different steps at lower temperatures. The Cd compounds present ligand-based luminescence in the blue-green spectral range. The optical properties

could be used to differentiate between the structure of the discrete complex and that of the coordination polymers.

Experimental Section

Synthesis: Ba(NCS)₂·3H₂O and 3-hydroxymethylpyridine were purchased from Alfa Aesar, Cd(SO₄)·8/3H₂O and Zn(SO₄)·H₂O were bought from Merck. All chemicals were used without further purification. Cd(NCS)₂ and Zn(NCS)₂ were prepared by the reaction of equimolar amounts of Zn(SO₄)·H₂O, Cd(SO₄)·8/3H₂O and Ba(NCS)₂· 3H₂O in water. The resulting white precipitate of BaSO₄ was filtered off and the filtrates were concentrated to complete dryness resulting in white residues of Cd(NCS)₂ and Zn(NCS)₂.

Synthesis of 1-Cd: Single crystals suitable for single-crystal X-ray structure determination were obtained by the reaction of Cd(NCS)2 (57.1 mg, 0.25 mmol) with 3-hydroxymethylpyridine (143.6 µL, 1.5 mmol) in a mixture of 1.0 mL ethanol, which was overlaid with 2 mL ethyl ether in a closed test tube at room temperature for several days. A crystalline powder was obtained by the reaction of Cd(NCS)₂ (228.6 mg, 1.0 mmol) with 3-hydroxymethylpyridine (579.5 µL, 6.0 mmol) in 3.0 mL methanol. Yield: 81.5%. C₂₆H₂₈CdN₆O₄S₂ (665.0781 g·mol⁻¹): calcd. C 46.95, H 4.24, N 12.64, S 9.64%; found: C 46.847, H 4.182, N 12.313, S 9.143 %. **IR** (ATR): $\tilde{v}_{max} = 3322$ (wb), 3215 (wb), 3037 (w), 2851 (w), 2045 (s), 1598 (w), 1579 (w), 1479 (w), 1430 (m), 1385 (w), 1229 (w), 1195 (w), 1128 (w), 1104 (w), 1059 (w), 1014 (s), 958 (m), 846 (w), 825 (w), 794 (s), 707 (s), 642 (s), 622 (m), 602 (m) cm⁻¹ (Figure S13, Supporting Information). Ra**man**: $\tilde{v}_{max} = 3067$ (m), 3040 (m), 2998 (w), 2915 (w), 2858 (w), 2048 (s), 1601 (w), 1495 (w), 1033 (s), 802 (w), 643 (w) cm⁻¹ (Figure S13).

Synthesis of 2-Cd: Single crystals suitable for single-crystal X-ray structure determination were obtained by the reaction of Cd(NCS)₂ (114.3 mg, 0.5 mmol) with 3-hydroxymethylpyridine (193.2 µL, 2.0 mmol) in 3.0 mL dest. H₂O in a closed test tube at room temperature. The white precipitate was filtered off after 30 s and the filtrate was left for standing in a closed test tube for several days. A microcrystalline powder was obtained by the reaction of Cd(NCS)2 (114.3 mg, 0.5 mmol) with 3-hydroxymethylpyridine (193.2 µL, 2.0 mmol) in 5.0 mL H₂O in a closed test tube at room temperature after 5 d. Yield: 75.1 %. $C_{14}H_{14}CdN_4O_2S_2$ (446.8228 g·mol⁻¹): calcd. C 37.63, H 3.16, N 12.54, S 14.35%; found: C 49.91, H 5.63, N 13.62, S 6.49%. **IR** (ATR): \tilde{v}_{max} = 3318 (wb), 3181 (wb), 2933 (w), 2104 (s), 2053 (s), 1603 (w), 1584 (w), 1480 (w), 1435 (m), 1401 (w), 1374 (w), 1330 (w), 1242 (w), 1223 (w), 1194 (m), 1131 (w), 1107 (w), 1055 (m), 1033 (s), 1005 (s), 932 (w), 839 (w), 828 (w), 795 (s), 795 (s), 754 (w), 702 (s), 647 (m) 603 (m) cm^{-1} (Figure S13). Raman: $\tilde{v}_{max} = 3074$ (w), 2938 (w), 2098 (s), 2052 (s), 1604 (m), 1585 (m), 1495 (m), 1438 (w), 1376 (w), 1243 (w), 1195 (m), 1056 (m), 1033 (s), 1007 (w), 828 (m), 781 (m), 766 (w), 648 (m) cm⁻¹ (Figure S13).

Synthesis of 3-Cd: Single crystals suitable for single-crystal X-ray structure determination were obtained by the reaction of Cd(NCS)₂ (269 mg, 1.17 mmol) with 3-hydroxymethylpyridine (28.14 μ L, 0.294 mmol) in 1 mL ethanol and 2 mL of ether in a closed test tube at 120 °C after 3 d. A crystalline powder was obtained by the reaction of Cd(NCS)₂ (114.3 mg, 0.5 mmol) with 3-hydroxymethylpyridine (96.6 μ L, 1.00 mmol) in 2.0 mL H₂O after 4 d. Yield: 78.6%. C₂₂H₂₁Cd₂N₇O₃S₄ (784.5178 g·mol⁻¹): calcd. C 33.68, H 2.70, N 12.50, S 16.35%; found: C 34.774, H 2.776, N 12.118, S 15.289%. **IR** (ATR): $\bar{v}_{max} = 3412$ (w), 3273 (w), 2122 (m), 2102 (s), 2092 (m), 2047 (s), 1601 (w), 1584 (w), 1481 (w), 1433 (m), 1369 (w), 1333 (w), 1206 (w), 1128 (w), 1105 (w), 1060 (m), 1040 (m), 1008 (m),

925 (w), 835 (w), 802 (m)789 (m), 758 (m), 705 (s), 649 (m), 622 (m) cm⁻¹ (Figure S14). **Raman**: $\tilde{v}_{max} = 3071(m)$, 3003 (w), 2939 (w), 2883 (w), 2880 (w), 2730 (w), 2116 (m), 2079 (s), 2077 (s), 1994 (w), 1605 (w), 1035 (m) cm⁻¹ (Figure S14).

Synthesis of 4-Cd: Single crystals suitable for single-crystal X-ray structure determination were obtained by the reaction of Cd(NCS)₂ (68.6 mg, 0.30 mmol) with 3-hydroxymethylpyridine (14.4 μ L, 0.15 mmol) in 1.5 mL of H₂O in a closed test tube at room temperature for 19 d. A crystalline powder was obtained by the reaction of Cd(NCS)₂ (274.3 mg, 1.2 mmol) with 3-hydroxymethylpyridine (58 µL, 0.6 mmol) in 3.0 mL H₂O. Yield: 74.3 %. C₃₀H₂₈Cd₃N₁₀O₄S₆ (1122.2129 g·mol⁻¹): calcd. C 32.11, H 2.51, N 12.48, S 17.14%; found: C 49.91, H 5.63, N 13.62, S 6.49%. IR (ATR): v_{max} = 3412 (w), 3273 (w), 2122 (m), 2102 (s), 2092 (m), 2047 (s), 1601 (w), 1584 (w), 1481 (w), 1433 (m), 1369 (w), 1333 (w), 1206 (w), 1128 (w), 1105 (w), 1060 (m), 1040 (m), 1008 (m), 925 (w), 835 (w), 802 (m), 789 (m), 758 (m), 705 (s), 649 (m), 622 (m) cm⁻¹ (Figure S14). Ra**man**: $\tilde{v}_{max} = 3048$ (mn), 2140 (s), 2127 (s), 2092 (s9, 2076 (m), 2052 (s), 1603 (m), 1582 (w), 1495 (m), 1228 (w), 1188 (w), 1054 (w), 1034 (s), 835 (w), 810 (w), 772 (w), 649 (w) cm⁻¹ (Figure S14).

Synthesis of 1-Zn-H₂O: Single crystals suitable for single-crystal Xray structure determination were obtained by the reaction of $Zn(NCS)_2$ (181.5 mg, 1.0 mmol) with 3-hydroxymethylpridine (96.6 μ L, 1.0 mmol) in 3.0 mL ethanol after letting the solvent evaporate for several days. No phase pure crystalline powder could be obtained.

Synthesis of 1-Zn: A crystalline powder was obtained by the reaction of Zn(NCS)₂ (90.8 mg, 0.5 mmol) with 3-hydroxymethylpyridine (94.1 μL, 1.0 mmol) in 2.5 mL dest. H₂O after stirring the reaction mixture for 1 h. Yield: 79.3 %. C₁₄H₁₄N₄O₂S₂Zn (399.8028 g·mol⁻¹): calcd. C 42.06, H 3.53, N 14.01, S 16.04 %; found: C 41.787, H 3.428, N 13.606, S 16.148 %. **IR** (ATR): \tilde{v}_{max} = 3441 (mb), 2930 (w), 2074 (s), 1720 (w), 1585 (w), 1486 (m), 1436 (m), 1379 (m), 1331 (w), 1253 (w), 1201 (m), 1128 (w), 1106 (w), 10411 (m), 981 (m), 947 (m), 835 (m), 798 (m), 700 (s), 659 (m), 622 (m) cm⁻¹. **Raman**: \tilde{v}_{max} = 3043 (mb), 2933 (m), 2973 (m), 2083 (s), 1616 (w), 1035 (s), 838 (m), 659 (w) cm⁻¹ (Figure S15)

XRPD Investigations and Rietveld Refinement: The XRPD measurements for phase analysis and temperature dependent XRPD measurements were performed with a Stoe Transmission Powder Diffraction System (STADI P) with Cu- $K_{\alpha 1}$ radiation ($\lambda = 1.540598$ Å) equipped with a MYTHEN 1 K detector (Dectris Ltd.) and a Ge(111) Johann monochromator. The temperature dependent measurements of **1-Cd** were performed with a X'PERT PRO from PANalytical in reflection mode and with a PIXcel detector using Cu- K_{α} radiation.

Because the anhydrate **1-Zn** is hygroscopic, samples of different batches were gently ground and filled into Ø 0.5 mm quartz capillaries (Hilgenberg). Afterwards temperature dependent XRPD patterns were recorded in the range of 5–60° 2θ within ca. 2 h. The samples were heated from 40–130 °C and 40–110 °C, respectively with 10 °C steps. The capillary from the latter experiment was cooled down to room temperature and the XRPD pattern of the formed **1-Zn** was measured from 5–80° 2θ within 10 hours.

A Pawley^[55] refinement was performed using the lattice parameters and space group of Zn(NCS)₂(3-methypyridine)₂ as starting parameters with TOPAS V5.^[56,57] The peak profile was described during the Pawley refinement using the fundamental parameter approach of TOPAS.^[58] The background was modeled by Chebychev polynomials. Zeitschrift für anorganische

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Table 5. Selected crystal data and details of the Rietveld refinement for 1-Zn.

	1-Zn		
Formula	$ZnC_{14}H_{14}N_4O_2S_2$		
MW /g·mol ⁻¹	399.83		
Crystal system	orthorhombic		
Space group	Pnma		
Wavelength /Å	1.540596		
a /Å	8.1895(2)		
b /Å	13.8581(3)		
c /Å	15.4183(4)		
a /°	90		
β /°	90		
γ /°	90		
V/Å ³	1749.85(7)		
<i>T /</i> K	295		
Z	4		
$D_{\rm calc}$ /g·cm ⁻³	1.518		
μ / mm^{-1}	4.286		
$\theta_{\rm max}$ /°	80.225		
$R_{\rm wp}/\%^{\rm a)}$	3.25		
$R_{\rm p}^{"'}/\%^{\rm a}$	2.05		
R_{exp}^{r} /% a)	0.69		
$R_{\rm Bragg} / \%^{\rm a)}$	3.01		

a) As defined in TOPAS.

The isostructural model of $Zn(NCS)_2(3$ -methypyridine)₂ was used for the Rietveld refinement of **1-Zn**. The position of the zinc atoms and both symmetry independent thiocyanates (described by rigid bodies in z-matrix notation) were refined with the symmetry constraints of the mirror plane.^[56] Additionally, one of the N_{thio}–Zn bond was restraint to a chemical sensible value (Zn1–N2, 2 Å). The position of the 3-HMPy ligand was refined by using a rigid body in the z-matrix notation and an angle restraint (the angle between Zn1 N11 and Zn1 N11

Table 6. Selected crystal data and details of the structure refinements.

C13 was restraint to be 180°). For the final Rietveld refinement all atomic positions, the peak profile, zero error, an overall thermal displacement parameter, background were refined with the con- and restraints mentioned above. Selected crystal data and details of the Rietveld refinement can be found in Table 55.

Single-crystal Structure Analysis: Data collections were performed with an imaging plate diffraction system (IPDS-2) from STOE & CIE using Mo- K_{α} radiation. Structure solution was performed with SHELXT and structure refinement was performed against F^2 using SHELXL-2014.^[59,60] A numerical absorption correction was applied using programs X-RED and X-SHAPE of the program package X-Area.^[61] All non-hydrogen atoms were refined with anisotropic displacement parameters. The C-H hydrogen atoms were positioned with idealized geometry and were refined isotropic with $U_{iso}(H) = -1.2$ $U_{eq}(C)$ using a riding model. The O-H hydrogen atoms were either positioned with idealized geometry allowed to rotate but not to tip or were located in the difference fourier map and their bond lengths were set to ideal values and afterwards they were refined isotropic with $U_{\rm iso}({\rm H}) = -1.5 \ U_{\rm eq}({\rm O})$ using a riding model. In **3-Cd** the hydroxyl group is disordered and was refined using a split model with restraints. The crystal of 1-Zn-H₂O was non-merohedral twinned. Both individuals were indexed separately and the twin law was determined. After merging symmetry equivalent reflections, data in HKLF-5 format were generated and a twin refinement was performed [BASF-parameter: 0.216(3)]. Selected crystal data and details of the structure refinements are summarized in Table 6.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1564925 (1-Cd), CCDC-1564927 (2-Cd), CCDC-1564926 (3-Cd), CCDC-1564928 (4-Cd), CCDC-1564924 (1-Zn-

	1-Cd	2-Cd	3-Cd	4-Cd	1-Zn-H ₂ O
Formula	C ₂₆ H ₂₈ CdN6O ₄ S ₂	$C_{14}H_{14}CdN_4O_2S_2$	C ₂₂ H ₂₁ Cd ₂ N ₇ O ₃ S ₄	C ₃₀ H ₂₈ Cd ₃ N ₁₀ O ₄ S ₆	C ₁₄ H ₁₄ N ₄ O ₃ S ₂ Zn
MW /g·mol ⁻¹	665.06	446.81	784.50	1122.18	415.78
Crystal system	orthorhombic	triclinic	monoclinic	triclinic	monoclinic
Space group	Pbcn	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a /Å	18.2233(6)	7.3446(3)	8.9598(2)	7.4429(6)	13.3907(3)
b /Å	9.0907 (2)	10.3415(5)	22.6232(5)	8.8283(8)	8.4346(2)
<i>c</i> /Å	17.4375(4)	11.0607(5)	14.3924(4)	16.662(2)	15.6471(4)
$a /^{\circ}$	90	95.025(4)	90	80.91(1)	90
β /°	90	93.999(4)	99.253(2)	85.08(1)	91.763(2)
γ /°	90	91.471(4)	90	65.55(1)	90
$V/Å^3$	2888.7(2)	834.41(7)	2879.4(3)	983.9(2)	1766.43(7)
T/K	293	170	293	200	170
Z	4	2	4	1	4
D _{calc} /mg·m ³	1.529	1.778	1.810	1.894	1.563
μ /mm ⁻¹	0.943	1.572	1.804	1.974	1.646
$\theta_{\rm max}$ /°	27.993	28.003	27.961	26.997	27.069
Min/max. trans.	0.6701/0.9181	0.6685/0.8371	0.5447/0.6921	0.7082/0.7638	_
Refl. collected	45980	12139	42073	13764	28129
Unique refl.	3459	4027	6884	4229	3890
R _{int}	0.0423	0.0406	0.0569	0.0247	0.0487 ^{a)}
Refl. $[F_{\rm o} > 4\sigma(F_{\rm o})]$	2970	3710	5853	3760	3252
Parameters	180	209	351	242	220
$R_1 [F_{\rm o} > 4\sigma(F_{\rm o})]$	0.0403	0.0277	0.0406	0.0268	0.0541
wR_2	0.0817	0.0761	0.0811	0.0721	0.1687
GOF	1.220	1.064	1.126	1.024	1.053
$\Delta ho_{ m max/min}$ /e·Å $^{-3}$	1.239/ -0.357	0.754/-0.994	0.600/ -0.848	1.068/ -0.983	1.036/-0.792

a) This $R_{\rm int}$ refers to the data set, where overlapping reflections are omitted.

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H₂O), and CCDC-1564923 (1-Zn) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Other Physical Methods: CHNS analysis was performed using a EURO EA elemental analyzer, fabricates by EURO VECTOR Instruments. All IR data were obtained with an ATI Mattson Genesis Series FTIR Spectrometer, control software: WINFIRST, from ATI Mattson. DTA-TG measurements were performed in a dynamic air atmosphere in Al_2O_3 crucibles using a STA PT 1600 thermobalance from Linseis. The DSC measurements were performed with a DSC 1 Star System with STARe Excellence Software from Mettler-Toledo AG. Thermomicroscopy was performed using a hot-stage from Linkam and a microscope from Olympus. All thermoanalytical instruments were calibrated using standard references materials. Luminescence spectra were measured with a HORIBA Jobin Yvon GmbH (Unterhaching, Germany) spectrometer (Fluorolog3) at room temperature, equipped with a iHR-320-FA Triple Grating spectrograph, R928P Photomultiplier and a 450 W xenon lamp.

Supporting Information (see footnote on the first page of this article): ORTEP plots. Lists with bond lengths and angles, experimental and calculated XRPD patter, IR and Raman spectra , DTA-TG curves as well as Excitation and emission spectra.

Acknowledgements

This project was supported by the Deutsche Forschungsgemeinschaft (Project No. NA 720/5–2 and TE 1147/1–1) and the State of Schleswig-Holstein. We thank *Prof. Dr. Wolfgang Bensch* for access to his experimental facilities. *LSG* thanks *Dr. Sebastian Bette* for all the help-ful discussions.

Keywords: Cd and Zn thiocyanate; Coordination compounds; Crystal structure; Luminescence; Thermal properties

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Received: July 27, 2017 Published Online: ■



T. Neumann, C. dos Santos Cunha, H. Terraschke, L. S. Germann, R. E. Dinnebier, I. Jess, C. Näther* 1–12

Synthesis, Structures, and Physical Properties of Thiocyanate Coordination Compounds with 3-Hydroxymethylpyridine

