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Structural diversity in Cd(NCS)$_2$-3-cyanopyridine coordination compounds: synthesis, crystal structures and thermal properties

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Abstract: Five new compounds with the compositions $[Cd(NCS)_2(3\text{-cyanopyridine})_2]_n \cdot$ 3-cyanopyridine (**1**), $[Cd(NCS)_2(3\text{-cyanopyridine})_2]_n \cdot 1/3$ 3-cyanopyridine (**2**), $[Cd(NCS)_2(3\text{-cyanopyridine})_2]_n$ (**3**), $\{[Cd(NCS)_2]_2(3\text{-cyanopyridine})_3\}_n$ (**4**), and $\{[Cd(NCS)_2]_3(3\text{-cyanopyridine})_4\}_n$ (**5**) have been obtained by the reaction of Cd(NCS)$_2$ with 3-cyanopyridine in different solvents. While large amounts of compounds **1–4** could be prepared as powders, only a few single crystals of **5** were accidently obtained. Thermoanalytical investigations have shown that **4** could also be obtained by annealing of **1** or **2** and that under slightly different conditions **5** could be obtained as part of a mixture with **4**. The crystal structures of all compounds can be divided in two sets of compounds. Compounds **1**, **2** and **3** consist of chains in which the Cd cations show three different coordination environments and in which the coligands are only terminally bonded. In the structures of **4** and **5** similar chains are observed, which are connected into layers via some of the 3-cyanopyridine coligands.

Keywords: 3-cyanopyridine; cadmium thiocyanate; chain compounds; crystal structures; thermal properties.

Dedicated to: Professor Arndt Simon on the occasion of his 80th birthday.

1 Introduction

The structural chemistry of transition metal thiocyanate coordination compounds is characterized by a large variability and a versatile coordination behavior. Most compounds with less chalcophilic metal cations like, e.g. Mn(II), Fe(II), Co(II), and Ni(II) contain N-terminally coordinated thiocyanate anions and are of interest because, e.g. several of them show spin crossover [1–4]. On the other hand, compounds with bridging thiocyanate anions are of importance because they can form dimers as well as 1D and 2D networks, in which significant magnetic exchange can be observed [5–14]. For the metal cations mentioned above the coordination to the sulfur atom of the anionic ligand is energetically unfavorable and therefore, such compounds are frequently difficult to synthesize from solution [15]. However, there is an alternative approach reported in the literature that is based on thermally induced ligand removal from precursor complexes with terminal thiocyanate anions [15–17].

All this is completely different for coordination compounds based on Cd(NCS)$_2$, because this cation prefers to coordinate to sulfur, which means that in this case compounds with terminally N-bonded anionic ligands are more difficult to synthesize [18–21]. Especially this chemical behavior is the reason why the structural chemistry of Cd(NCS)$_2$ coordination compounds is much richer than that of the paramagnetic late first row transition metals mentioned above and that compounds with more condensed thiocyanate networks can be easily synthesized from solution [22–24]. This includes a large number of compounds with different chain structures. In most of them the metal cations are linked by pairs of anionic ligands into chains, in which the cations show either an all-*trans* or a *cis-cis-trans* coordination [25–30]. Dependent on the actual metal coordination these chains can be linear or corrugated, and there are also examples where within such chains an alternating 5-fold and 6-fold Cd(II) coordination is present [31]. Moreover, two of such chains can be condensed into double chains with μ-1,1,3(S,N)-coordinating thiocyanate anions, a structure type that is reminiscent of spin ladders [32, 33]. Also 2D networks are observed, in which the Cd(II) cations are linked by pairs of anionic ligands into chains that are further linked into layers by single μ-1,3(N,S)-bridging thiocyanate anions [30, 34]. With Cd(NCS)$_2$ also a number of polymorphic or isomeric compounds have been reported that can be transformed into each other [33, 35]. Cd(NCS)$_2$ coordination compounds show structural motifs that have also

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been observed for the paramagnetic cations and in several cases they were found to be isotypic. Summarizing, $Cd(NCS)_2$ coordination compounds with condensed thiocyanate structures can be easily synthesized and allow conclusions, which compounds might be accessible with the paramagnetic analogs, which is the reason why we have been interested in the structural chemistry of this class of compounds for several years.

In the course of our investigations we introduced 3-cyanopyridine as coligand, that can also act as a bridging ligand *via* the cyano N atom which might lead to the formation of structures of enhanced dimensionality. With this ligand no $Cd(NCS)_2$ compounds had been reported in the literature, but several thiocyanate complexes containing cobalt(II), nickel(II), copper(II) or zinc(II) have been reported, most of which consist of ligand-rich discrete complexes and contain additional solvent or uncoordinated 3-cyanopyridine solvate molecules [36–39].

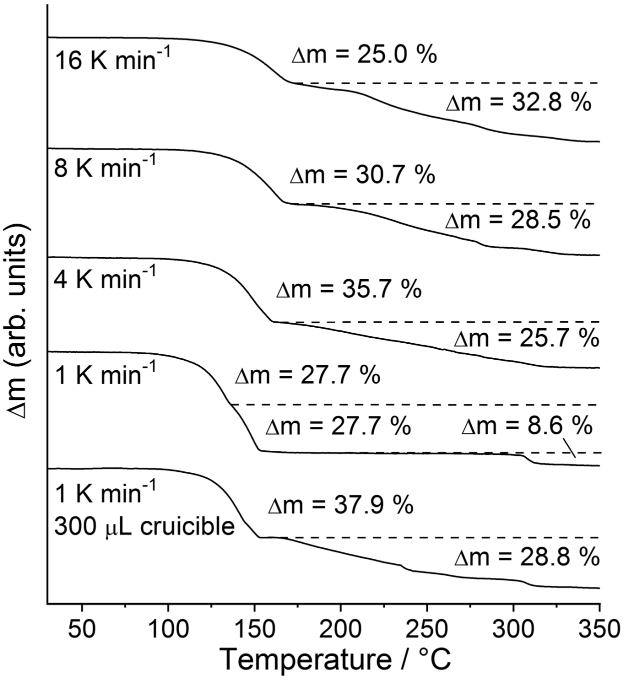

Fig. 1: TG curves for **1** measured with 16, 8, 4 and 1 K min^{-1} in a 300 μL and with 1 K min^{-1} in a 120 μL crucible under nitrogen atmosphere. The events at $T = 300$°C and above result from the decomposition of $Cd(NCS)_2$.

2 Results and discussion

2.1 Synthesis and thermoanalytical investigations

The reaction of $Cd(NCS)_2$ with 3-cyanopyridine in water, ethanol or methanol leads to the formation of two different 3-cyanopyridine-rich compounds with the compositions $[Cd(NCS)_2(3\text{-cyanopyridine})_2]_n \cdot$ 3-cyanopyridine (**1**) and $[Cd(NCS)_2(3\text{-cyanopyridine})_2]_n \cdot 1/3$ 3-cyanopyridine (**2**). While compound **1** can be obtained after one or two days from all three solvents if a ratio of $Cd(NCS)_2$ to 3-cyanopyridine ("M:L ratio") of 1:4 or higher is used, a lower M:L ratio of 1:2 is needed for the synthesis of **2**. However, **2** could not be obtained from methanol, even if a M:L ratio of 1:2 was used, because **1** was formed instead.

To check if more ligand-deficient compounds can be obtained, the thermal properties of both solvates were investigated. Thermogravimetric measurements of **1** have shown that its decomposition behavior depends on the heating rate as well as on the size of the crucible (Fig. 1), which is used for the measurement, while for **2** only a dependency on the heating rate was observed. Because for **2** similar TG curves were obtained, they are not shown here, but are discussed below.

If crucibles of 120 μL and heating rates between 4 and 16 K min^{-1} are used for **1**, a discrete step is observed in the beginning, but upon further heating a series of steps follows that cannot be fully resolved (Fig. 1). The mass loss in the first step depends on the heating rate and is always higher than that calculated for the removal of one of the 3-cyanopyridine ligands, indicating that a product of undefined stoichiometry or a mixture of compounds are formed. If the heating rate is lowered to 1 K min^{-1} two mass losses are observed, with each of them corresponding to the removal of 1.5 3-cyanopyridine ligands. Therefore, a compound with the composition $\{[Cd(NCS)_2]_2(3\text{-cyanopyridine})_3\}_n$ might have formed. Interestingly if a crucible of 300 μL is used, a mass loss of 37.9% is observed, that is in rough agreement with that calculated for the removal of about 1.8 coligands, which points to the formation of an additional 3-cyanopyridine deficient phase. The dependence on the size of the crucible can be explained by the fact that in larger crucibles the 3-cyanopyridine rich atmosphere that is generated in the first decomposition process is trapped for a longer period of time, which stabilizes intermediates of the pyrolysis.

The TG curves obtained for compound **2** are also very poorly resolved and depend strongly on the heating rate. The emission of the 3-cyanopyridine solvate molecules cannot be resolved. However, at higher heating rates a discrete step is also observed, in which more than 1/3 of the coligands are emitted, but powder X-ray diffraction (PXRD) investigations of the residues obtained after these steps revealed that only amorphous products were formed.

The products formed after the first mass loss of **1** at different heating rates were investigated by PXRD, which showed that at higher heating rates always amorphous products were obtained. In contrast, at the rate of 1 K min^{-1} compound **1** was transformed into a new phase of poor crystallinity if the 300 µL crucible was used. To increase the crystallinity, compounds **1** or **2** were annealed at $T = 120$°C for several hours. In both cases a much better crystalline residue was obtained within 2 h that shows reflections that are also observed in the pattern of the residue obtained by thermogravimetric measurements. If annealing is continued to 5 h, no 3-cyanopyridine could be detected by elemental analysis, which means that $Cd(NCS)_2$ was formed. Interestingly the powder pattern of this $Cd(NCS)_2$ phase is different from that of the known modification of $Cd(NCS)_2$, but similar to that of $Ni(NCS)_2$ (Fig. 2) [40].

To check if the crystalline phases obtained by thermal decomposition are also available from solution, additional experiments were conducted, in which relatively low amounts of 3-cyanopyridine compared to $Cd(NCS)_2$ were used. In the course of these experiments single crystals of additional compounds with the compositions $[Cd(NCS)_2(3\text{-cyanopyridine})_2]_n$ (**3**) and $\{[Cd(NCS)_2]_2(3\text{-cyanopyridine})_3\}_n$ (**4**) were obtained. Compound **3** could only be obtained from ethanol with M:L ratios of 1:1 and 2:1 and reaction times of 1–3 h. If the same M:L ratio is used while the reaction time is increased to one or more days, compound **4** is obtained. It is noted that **3** is often contaminated with compounds **1**, **2**, **4** or other unidentified phases. However, comparison of the calculated patterns with those measured for the residues obtained during the thermoanalytical investigations proves that pure compound **4** is formed by annealing of compound **1**. Moreover, the product obtained by thermogravimetry using a heating rate of 1 K min^{-1} in 300 µL crucibles could be identified as a mixture of **4** and an unknown phase as major product (Fig. 3). To identify the unknown phase, a large number of crystallization

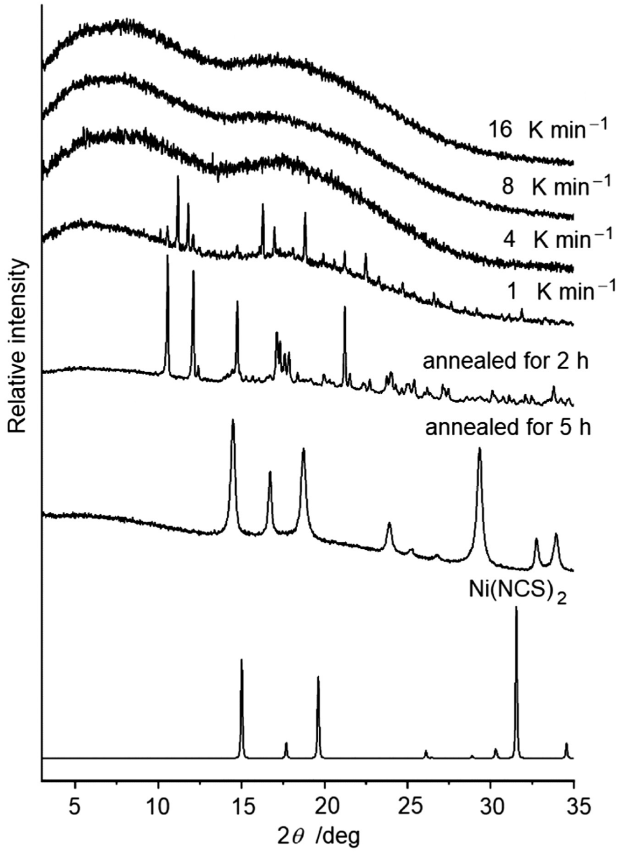

Fig. 2: Experimental PXRD patterns of the residues obtained after the first mass step of **1** using different heating rates and of those obtained by annealing **1** for 2 h and 5 h, together with the pattern calculated for $Ni(NCS)_2$.

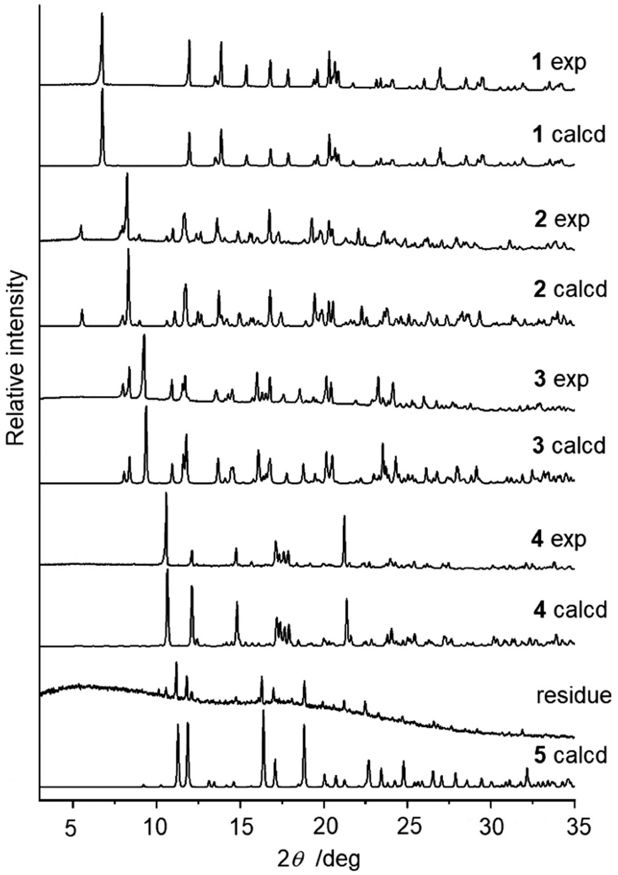

Fig. 3: Experimental and calculated PXRD patterns for **1–5** together with the experimental pattern of the residue obtained by thermogravimetric measurements of **1** at 1 K min^{-1} using the 300 µL crucible.

experiments were performed and accidently a few single crystals of this phase were obtained, which proved that a more 3-cyanopyridine deficient compound with the composition $\{[Cd(NCS)_2]_3(\text{3-cyanopyridine})_4\}_n$ (**5**) had formed. No access to larger amounts of this compound was found. The occurrence of mixtures of compound **4** and **5** that exhibit an unusual stoichiometry might explain why in most cases different mass losses are observed in the TG measurements.

2.2 Crystal structures

2.2.1 Crystal structures of the chain compound $[Cd(NCS)_2(\text{3-cyanopyridine})_2]_n$ (3) and its solvates (1 and 2)

All three compounds crystallize in the triclinic space group $P\bar{1}$ with $Z=2$ (**1**), $Z=6$ (**2**) or $Z=4$ (**3**). The asymmetric unit of compound **1** contains two crystallographically independent Cd cations that are located on centers of inversion, that of compound **2** of three unique Cd cations in general positions and that of compound **3** of three unique Cd cations, of which two are located on special positions. In all compounds the Cd cations are coordinated octahedrally and are linked into chains by pairs of thiocyanate anions. Compounds **1** and **2** represent solvates in which the chains are arranged in a way that channels are formed along the crystallographic *a* axis, in which the solvate 3-cyanopyridine molecules are located (Fig. 4).

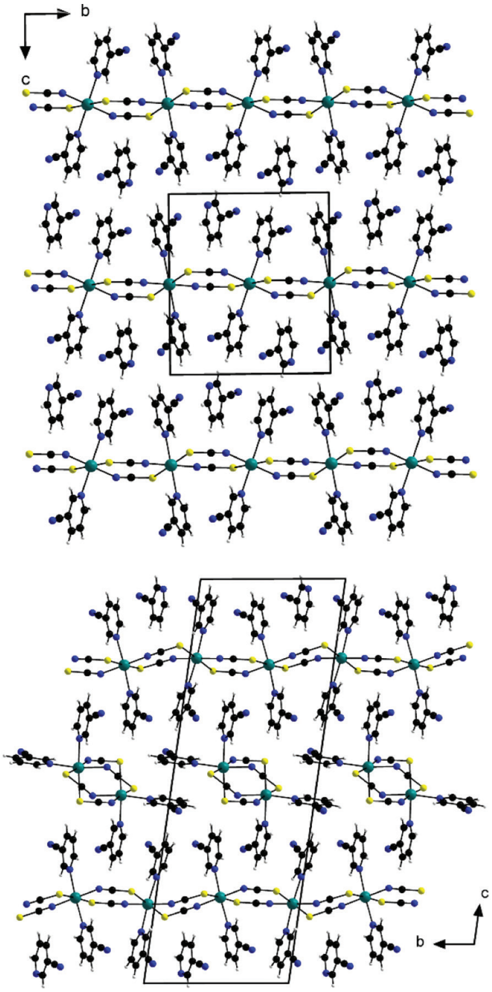

Fig. 4: View of the crystal structure of **1** (top) and of **2** (bottom) along the crystallographic *a* axis (Cd: turquoise, N: blue, C: black, S: yellow, H: gray).

Interestingly, in all three chain compounds different Cd coordination environments are observed. In compound **1** the two S- and the two N-coordinating thiocyanate anions as well as the two 3-cyanopyridine coligands are in *trans* positions. In compound **2** two different chains are present. One of them shows the usual all-*trans* coordination whereas in the second one an all-*cis* coordination of the thiocyanate anions and the 3-cyanopyridine molecules is observed, which to the best of our knowledge has never been observed before in such thiocyanate coordination polymers. In compound **3**, also an all-*cis* coordination is found, but because this compound shows disordering for some of the thiocyanate anions a *cis*-*cis*-*trans* coordination is also observed, in which the N-bonding thiocyanate anions are *trans*, while the S-bonding thiocyanate anions as well as the coligands are *cis* (Fig. 5).

In all cases the coordination environments are strongly distorted with values of the mean quadratic elongation of $\lambda_{oct}=1.016$ for Cd1 and $\lambda_{oct}=1.015$ for Cd2 in **1**, $\lambda_{oct}=1.018$ for Cd1 and $\lambda_{oct}=1.018$ for Cd2 in **2** as well as $\lambda_{oct}=1.020$ for Cd1 and $\lambda_{oct}=1.019$ for Cd2 in **3** for the all-*trans* coordination environments. The corresponding values for the octahedral angle variance amount to $\sigma_{\theta\langle oct\rangle}{}^2=14.7$ for Cd1 and $\sigma_{\theta\langle oct\rangle}{}^2=9.8$ for Cd2 in **1**, to $\sigma_{\theta\langle oct\rangle}{}^2=17.2$ for Cd1 and $\sigma_{\theta\langle oct\rangle}{}^2=16.5$ for Cd2 in **2** and to $\sigma_{\theta\langle oct\rangle}{}^2=20.3$ for Cd1 and $\sigma_{\theta\langle oct\rangle}{}^2=20.7$ for Cd2 in **3** [41]. This shows that the degree of longitudinal as well as of the angular distortions increases with decreasing amounts of the 3-cyanopyridine molecules, if only the all-*trans* coordination environments are considered. For the other coordination environments values of $\lambda_{oct}=1.011$ in **2**, $\lambda_{oct}=1.020$ for all-*cis* in **3** as well as $\lambda_{oct}=1.033$ for *cis*-*cis*-*trans* in **3** are found. The corresponding values for the octahedral angle variance amount to $\sigma_{\theta\langle oct\rangle}{}^2=18.1$ in **2**, $\sigma_{\theta\langle oct\rangle}{}^2=23.9$ for all-*cis* in **3** as well as $\sigma_{\theta\langle oct\rangle}{}^2=47.8$ for *cis*-*cis*-*trans* in **3**. Similarly to the values found for the all-*trans* coordination environments, the degree of distortion is higher in the solvate deficient compounds.

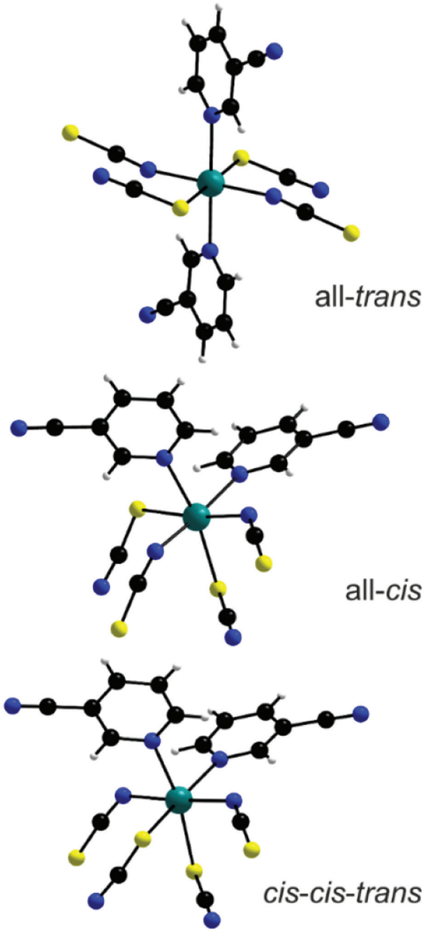

Fig. 5: Different coordination environments of the Cd cations as observed in **1**, **2** and **3** (Cd: turquoise, N: blue, C: black, S: yellow, H: gray).

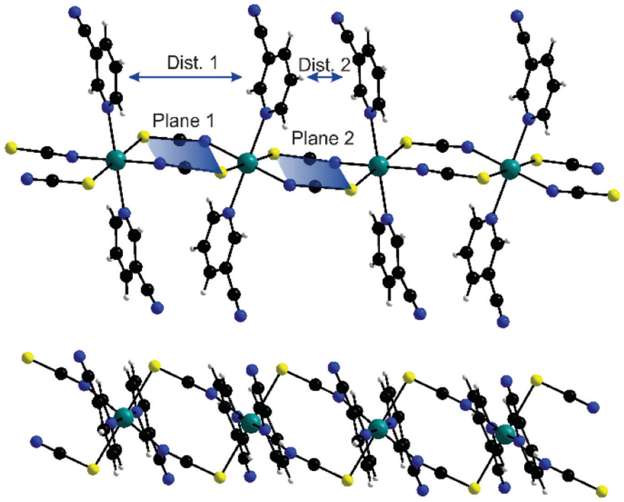

Fig. 6: Side view (top) and top-down view (bottom) of a linear chains in **3**, in which only all-*trans* coordination environments are present, as a representative for the linear chains found in **1**, **2** and **3** (Cd: turquoise, N: blue, C: black, S: yellow, H: gray).

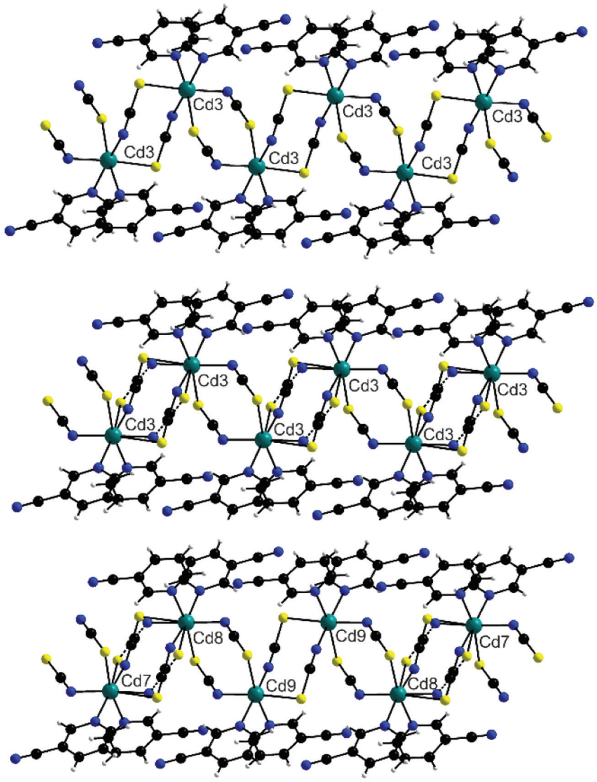

Fig. 7: Zig-zag chains found in the crystal structure of **2** (top) and in the substructure (middle) as well as the superstructure of **3** (bottom). Disordered thiocyanate anions are indicated by dotted bonds; Cd: turquoise, N: blue, C: black, S: yellow, H: gray.

The different Cd coordinations in the three chain compounds lead to different chain geometries. The occurrence of an all-*trans* coordination in compound **1** leads to the formation of linear chains (Fig. 6), while in compound **2** two different Cd environments are present with the all-*trans* coordination leading to the formation of linear chains, whereas the all-*cis* coordination results in corrugated chains (Figs. 6 and 7). Corrugated chains are also observed in compound **3**, because both, the all-*cis* and *cis-cis-trans* coordination, lead to this chain geometry (Fig. 7).

The crystal structures of the linear chains are similar in all three compounds. The 6-membered ring planes of the opposing 3-cyanopyridine coligands are parallel and oriented nearly perpendicular to the chain direction (Fig. 6).

Moreover, along the chains the distances between adjacent 3-cyanopyridine coligands alternate, which means that always a very long and a relatively short distance are observed, indicating π–π interactions for the latter (Fig. 6 and Table 1). This arrangement also leads to the deviation of the chains from linearity, which is especially the case in compound **2.** In contrast to compounds **1** and **3**, in compound **2** the dihedral angle between two

Table 1: Distances between adjacent coligand molecules and angles between neighboring (NCS)$_2$ planes in compounds **1**, **2** and **3**.

Compound	Dist. 1/Å	Dist. 2/Å	∠ plane 1 and 2/deg
1	7.5084(5)	4.0218(2)	0.00(8) 0.00(8)
2	7.2586(3) 7.4212(3)	3.9891(1) 4.0687(1)	24.35(11) 24.35(11)
3	7.3390(3)	3.9251(2)	0.00(10) 0.00(10)

neighbored (NCS)$_2$ planes amounts to 24.353° (Fig. 6 and Table 1).

The geometries of the corrugated chains in compounds **2** and **3** with an all-*cis* arrangement of the coordinating ligands are also similar (Fig. 7). What is special in these chains is the fact that the Cd–N–C angles in the all-*cis* coordination environments deviate very strongly from linearity with values between 151 and 131°, much smaller than the values for most other transition metal thiocyanates, especially those with an all-*trans* coordination. It is noted that in compound **3** disorder is observed, which means that in every second (NCS)$_2$ unit the direction of the thiocyanate anions is reversed (Fig. 7: middle). For this compound additional reflections are observed leading to a 4-fold larger unit cell, in which each fourth (NCS)$_2$ unit is disordered (Fig. 7: bottom), but we decided to refine this structure in the subcell for several reasons (see Section 4).

2.2.2 Crystal structures of the layered compounds {[Cd(NCS)$_2$]$_2$(3-cyanopyridine)$_3$}$_n$ (4) and {[Cd(NCS)$_2$]$_3$(3-cyanopyridine)$_4$}$_n$ (5)

Compounds **4** and **5** crystallize in the triclinic space group $P\bar{1}$ and the monoclinic space group $P2_1/c$ with $Z=4$ and $Z=2$ formula units in the unit cell, respectively. The asymmetric unit of compound **4** contains five crystallographically independent 3-cyanopyridine ligands, eight thiocyanate anions and three Cd(II) cations in general positions as well as two unique Cd(II) cations that are located on centers of inversion. In compound **5** the asymmetric unit consists of two crystallographically independent 3-cyanopyridine ligands and three thiocyanate anions in general positions as well as two unique Cd(II) cations, of which one is located on a center of inversion. Similarly to those in compounds **1**, **2** and **3** the Cd cations in both compounds are octahedrally coordinated by two 3-cyanopyridine ligands and two N-bonding and two S-bonding thiocyanate anions and are linked into linear chains by pairs of thiocyanate anions. In contrast to the former compounds some of the 3-cyanopyridine coligands connect adjacent chains into layers by coordinating *via* the 3-cyano group. This means that in compounds **4** and **5**, both, terminal and bridging coligands are present.

In contrast to **5**, compound **4** consists of three crystallographically independent chains, which contain either exclusively Cd1 (chain 1), Cd2 and Cd3 (chain 2) or Cd4 and Cd5 (chain 3). Furthermore, they differ in the way, in which the 3-cyanopyridine molecules are coordinated to the Cd cations. While in chains 1 and 2 each Cd cation is bonded to a bridging as well to a terminal 3-cyanopyridine molecule, the bridging ligands in chain 1 are always linked *via* the pyridine N atom, whereas in chain 2 they are always bound *via* the cyano N atom (Fig. 8). In chain 3 all 3-cyanopyridine ligands are coordinated *via* the pyridine N atom, but here the Cd cations are coordinated by either only bridging or only terminal 3-cyanopyridine ligands (Fig. 8). In chains 1 and 2 every Cd cation is linked to one neighboring chain, whereas in chain 3 each second Cd cation is connected to two neighboring chains leading to a ratio between bridging and terminal coligands of 1:2.

In contrast, for **5** only one crystallographically independent chain is found, in which the two Cd cations are coordinated differently. While both coligands connected to Cd2 are involved in bridging adjacent chains, only one of the 3-cyanopyridine molecules coordinated to Cd1 is bridging, while the other is bound terminally (Fig. 8). This leads to a ratio between bridging and terminal coligands of 1:1, which means that compound **5** shows a more condensed thiocyanate network as compared to that in compound **4**. Furthermore both of the coligands bound to Cd2 coordinate *via* the pyridine N atom, while the bridging coligand molecule bound to Cd1 is coordinated *via* the cyano N atom (Fig. 8). This is probably one of the reasons for the relatively high degree of angular distortion of the coordination octahedron of Cd1 compared to that of Cd2 ($\sigma_{\theta\langle\mathrm{oct}\rangle}{}^2=25.8$ and $\lambda_{\mathrm{oct}}=1.017$ for Cd1, and $\sigma_{\theta\langle\mathrm{oct}\rangle}{}^2=4.5$ and $\lambda_{\mathrm{oct}}=1.014$ for Cd2).

3 Conclusions

Several new compounds based on Cd(NCS)$_2$ and 3-cyanopyridine have been presented, in which the ratio between metal salt and coligand is always different. In compound **3** this ratio is 1:2 leading to the formation of chains in which the metal cations are linked by pairs of anionic ligands, while in **1** and **2** similar chains are accompanied

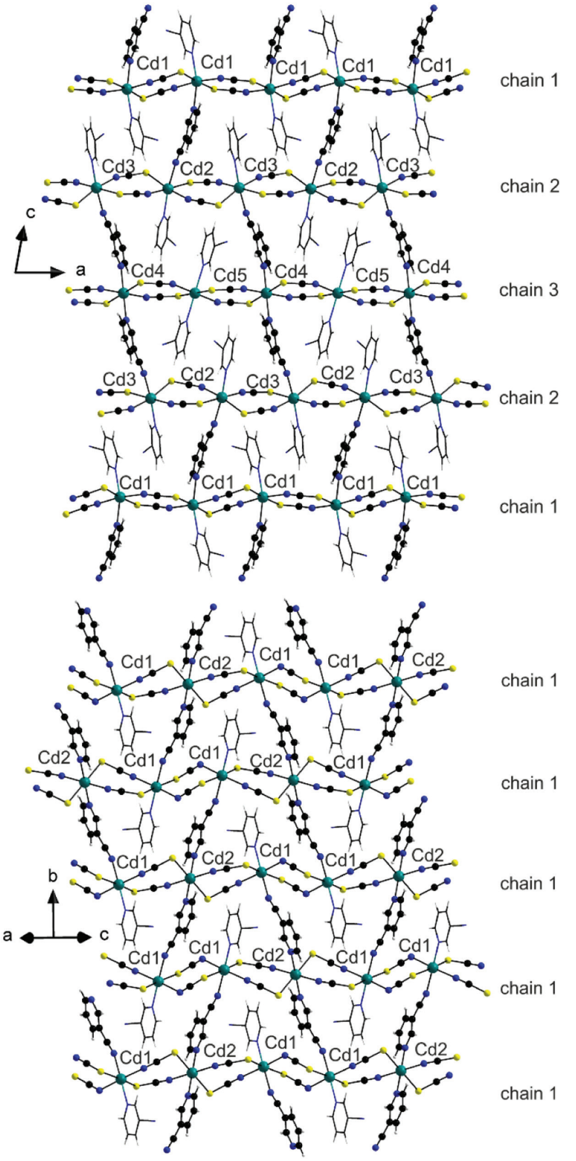

Fig. 8: View onto a layer as observed in the crystal structure of compounds **4** (top) and **5** (bottom). For clarity, the terminal 3-cyanopyridine coligands are shown using a wire stick model (Cd: turquoise, N: blue, C: black, S: yellow, H: gray).

by different amounts of additional 3-cyanopyridine solvate molecules. In these compounds three different Cd coordination environments are observed with the all-*trans* coordination leading to the formation of linear chains, whereas all-*cis* and the *cis-cis-trans* coordination result in the formation of corrugated chains. However, the 3-cyanopyridine molecules can also act as bridging ligands and therefore structures with more condensed networks are possible. This is realized in the crystal structures of **4** and **5**, in which the ratio between Cd(NCS)$_2$ and 3-cyanopyridine is 2:3 and 3:4, respectively. This means that in compound **4** where the same linear thiocyanate chains are present as in **1–3**, the ratio between bridging and terminal coligands is 1:2, but in compound **5** it is 1:1, leading to the formation of 2D instead of 1D networks. However, in the chain compound **3** only terminally coordinating coligands are present. If half of the coligands would be removed from compound **3**, a compound with an Cd(NCS)$_2$:3-cyanopyridine ratio of 1:1 would be obtained in which all terminal coligands would be transformed into bridging coligands. This would lead to the most condensed network in which each Cd cation is linked to a Cd cation of a neighboring chain. Compounds **4** and **5** thus represent structural intermediates between the chain and the "ideal" layered structures. Surprisingly from all of our investigations there is no hint that a 1:1 compound with a composition of [Cd(NCS)$_2$(3-cyanopyridine)]$_n$ exists, and such a compound could also not be prepared by ligand removal *via* thermal annealing of 3-cyanopyridine-rich precursors.

4 Experimental section

4.1 Synthesis

4.1.1 General

$CdSO_4 \cdot 8/3H_2O$ was obtained from Merck and $Ba(NCS)_2 \cdot 3H_2O$ as well as 3-cyanopyridine were obtained from Alfa Aesar. All chemicals were used without further purification. Cd(NCS)$_2$ was prepared by the reaction of equimolar amounts of $CdSO_4 \cdot 8/3H_2O$ and $Ba(NCS)_2 \cdot 3H_2O$ in water. The precipitated $BaSO_4$ was filtered off and the filtrate was concentrated to complete dryness resulting in a colorless residue of Cd(NCS)$_2$. If not noted otherwise the reactions were carried out in snap cap vials at ambient conditions. After the reaction the residue was filtered off and dried in air.

4.1.2 Synthesis of [Cd(NCS)$_2$(3-cyanopyridine)$_2$]$_n$ · 3-cyanopyridine (1)

A mixture of Cd(NCS)$_2$ (114.4 mg, 0.50 mmol) and 3-cyanopyridine (208.3 mg, 2.00 mmol) in 2 mL of water was stirred for one day. Single crystals were obtained in a similar way from a mixture of Cd(NCS)$_2$ (57.1 mg, 0.25 mmol) and 3-cyanopyridine (52.1 mg, 0.50 mmol) in 1 mL of methanol. – Elemental analysis for $C_{20}H_{12}CdN_8S_2$ (540.9009 g mol^{-1}): calcd. C 44.41, H 2.24, N 20.72, S 11.86; found C 42.26, H 2.05, N 20.17, S 11.06.

4.1.3 Synthesis of $[Cd(NCS)_2(3\text{-cyanopyridine})_2]_n \cdot 1/3$ 3-cyanopyridine (2)

$Cd(NCS)_2$ (114.4 mg, 0.50 mmol) and 3-cyanopyridine (52.1 mg, 0.50 mmol) were stirred in 2 mL of water for one day. Single crystals were synthesized by layering a mixture of $Cd(NCS)_2$ (34.3 mg, 0.15 mmol) in 1 mL of water with 2 mL of diethylether and carefully adding a solution of 3-cyanopyridine (3.9 mg, 0.04 mmol) in 1 mL diethylether. The diethylether was evaporated slowly and after one day colorless crystals were obtained. – Elemental analysis for $C_{16}H_{9.33}CdN_{6.67}S_2$ (471.4934 g mol^{-1}): calcd. C 40.76, H 2.00, N 19.80, S 13.60; found C 40.59, H 1.98, N 19.90, S 14.19.

4.1.4 Synthesis of $[Cd(NCS)_2(3\text{-cyanopyridine})_2]_n$ (3)

A powder was obtained by the reaction of $Cd(NCS)_2$ (114.4 mg, 0.50 mmol) with 3-cyanopyridine (52.1 mg, 0.50 mmol) in 2.0 mL ethanol. After 3 h the mixture was filtered and a colorless solid was obtained. Single crystals were synthesized using the same method as described in 4.1.3, but with different amounts of $Cd(NCS)_2$ (68.6 mg, 0.30 mmol) and 3-cyanopyridine (15.6 mg, 0.15 mmol) and without evaporation of the diethylether. Elemental analysis for $C_{14}H_8CdN_6S_2$ (436.7897 g mol^{-1}): calcd. C 38.50, H 1.85, N 19.24, S 14.68; found C 38.92, H 1.91, N 19.22, S 14.40.

4.1.5 Synthesis of $\{[Cd(NCS)_2]_2(3\text{-cyanopyridin})_3\}_n$ (4)

A mixture of $Cd(NCS)_2$ (228.8 mg, 1.00 mmol) and 3-cyanopyridine (52.1 mg, 0.50 mmol) was stirred in 2 mL ethanol. After one day a colorless powder was obtained. Single crystals were synthesized by layering a suspension of $Cd(NCS)_2$ (68.6 mg, 0.60 mmol) with 2 mL diethylether and carefully adding a solution of 3-cyanopyridine (7.8 mg, 75 μmol) in 1 mL diethylether. After one day very small needles precipitated. – Elemental analysis for $C_{22}H_{12}Cd_2N_{10}S_4$ (769.4683 g mol^{-1}): calcd. C 34.34, H 1.57, N 18.20, S 16.67; found C 34.62, H 1.40, N 18.63, S 16.78.

4.1.6 Synthesis of $\{[Cd(NCS)_2]_3(3\text{-Cyanopyridin})_4\}_n$ (5)

Single crystals could be obtained by layering a mixture of $Cd(NCS)_2$ (137.2 mg, 0.60 mmol) in 1 mL of water with 2 mL of diethylether with a solution of 3-cyanopyridine (15.6 mg, 0.15 mmol) in 1 mL diethylether. After one day colorless crystals had formed, which were suitable for the structure determination. No phase pure powder of **5** could be synthesized, but mixtures containing **5** could be obtained by thermal degradation of **1** in nitrogen atmosphere using a heating rate of 1 K min^{-1} in a crucible with a volume of 300 μL.

4.2 Elemental analysis

CHNS analyses was performed using an EURO EA elemental analyzer, fabricated by EURO VECTOR Instruments.

4.3 Single-crystal structure analyses

Data collections were performed with an imaging plate diffraction system IPDS-2 from STOE & Cie using Mo*Kα* radiation. Structure solutions were performed with SHELXT [42] (compound **3**) or SHELXS-97 [43] (compounds **1**, **2**, **4** and **5**) and structure refinements performed against F^2 using SHELXL-2018 [44]. A numerical absorption correction was applied using the programs X-RED and X-SHAPE of the program package X-AREA [45–47]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and were refined isotropically with $U_{iso}(H) = 1.2\ U_{eq}(C)$ using a riding model.

In compound **3** one of the thiocyanate anions is disordered leading to a centrosymmetric Cd-$(NCS)_2$-Cd pair, in which each Cd cation is coordinated by the S or N atom of this ligand. For this structure super structure reflections are observed that lead to a 4-fold larger triclinic unit cell with $a = 13.8420(8)$, $b = 22.1948(15)$, $c = 23.5542(14)$ Å, $\alpha = 112.178(5)$, $\beta = 93.435(5)$, $\gamma = 97.248(5)°$ and $V = 6601.7(8)$ Å^3 with $Z = 16$ and 9 crystallographically independent Cd cations. In this unit cell the disorder is reduced but still one Cd-$(NCS)_2$-Cd pair is disordered. The refinement led to much poorer reliability factors than that in the subcell and the displacement parameters of some of the thiocyanate anion were enlarged. For this unit cell the ADDSYM option in PLATON [48] suggests a pseudo-translation, which is valid for 97% of the structure. The super cell can be transformed into the subcell using the matrix 0.25 −0.25 −0.25; −0.75 −0.25 −0.25; 0.25 0.75 −0.25 (1 −1 −2; −1 0 −1; 0 1 −1 is the matrix for the transformation of the atomic coordinates) and therefore structure refinement was performed in the subcell.

The crystals of compound **4** are of very poor quality, which is obvious from a view of its diffraction pattern that is far from that expected for a single crystal (Fig. 9). However, indexing leads to a reasonable triclinic unit cell, for which the structure could not be solved, obviously

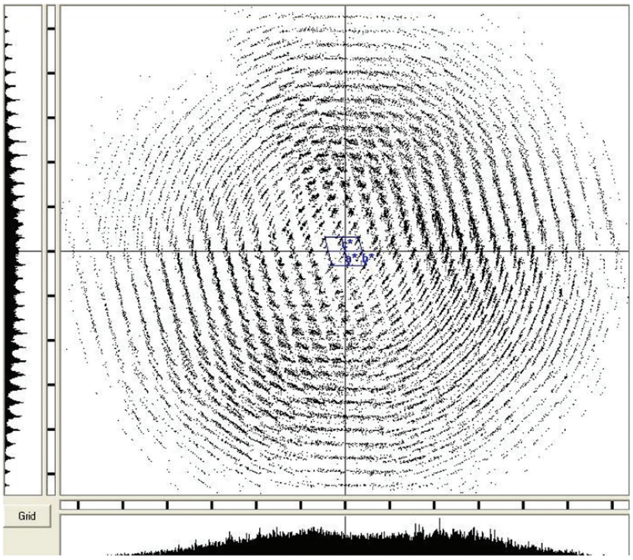

Fig. 9: Reciprocal space plot of compound **4** along [100].

because inaccurate intensities were extracted. Therefore, the mosaic spread and the integration box was varied systematically until the structure was solved and refined to reasonable *R* values. Selected crystal data and details of the structure refinements can be found in Table 2.

CCDC 1963757 (**1**), 19637578 (**2**), 1963759 (**3**), 1963760 (**4**) and 1963761 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

4.4 X-ray powder diffraction (XRPD)

The measurements were performed using a STOE Transmission Powder Diffraction System (STADI P) with Cu$K\alpha_1$ radiation ($\lambda = 1.540598$ Å) equipped with a MYTHEN 1K detector from Dectris and a Ge(111) monochromator from STOE & Cie.

4.5 Thermogravimetry and differential scanning calorimetry (TG-DSC)

TG-DSC measurements were performed in a dynamic nitrogen atmosphere in Al_2O_3 crucibles using a STA-PT1600

Table 2: Selected crystal data and details of the structure determinations for **1**, **2**, **3**, **4** and **5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{14}H_8CdN_6S_2 \cdot C_6H_4N_2$	$C_{14}H_8CdN_6S_2 \cdot 1/3\ C_6H_4N_2$	$C_{14}H_8CdN_6S_2$	$C_{22}H_{12}Cd_2N_{10}S_4$	$C_{30}H_{16}Cd_3N_{14}S_6$
MW/g mol^{-1}	540.90	471.49	436.78	769.46	1102.13
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	7.4045(5)	7.6199(2)	7.7426(3)	11.4395(7)	10.3722(3)
b/Å	11.5175(7)	11.3461(4)	11.2597(5)	14.7433(10)	15.6932(5)
c/Å	13.1054(9)	32.3632(10)	19.6070(8)	17.5518(12)	12.2003(3)
α/deg	90.050(5)	97.976(2)	102.283(3)	74.555(5)	90
β/deg	91.259(5)	94.854(2)	98.893(3)	79.720(5)	96.259(2)
γ/deg	90.609(5)	90.805(3)	91.599(3)	89.278(5)	90
V/Å^3	1117.31(13)	2760.05(15)	1646.84(12)	2805.6(3)	1974.04(10)
T/K	298(2)	200(2)	200(2)	200(2)	200(2)
Z	2	6	4	4	2
D_{calcd}/g cm^{-3}	1.61	1.70	1.76	1.82	1.85
μ/mm^{-1}	1.2	1.4	1.6	1.9	2.0
θ_{max}/deg	28.067	25.000	26.005	25.100	26.999
Refl. collected	19 118	32 813	14 394	20 148	22 704
Refl. unique	5338	9698	6432	9840	4307
R_{int}	0.0410	0.0547	0.0219	0.1139	0.0466
Transm. min; max	0.634; 0.855	0.610; 0.805	0.672; 0.790	0.641; 0.836	0.570; 0.740
Refl. [$F_0 > 4\,\sigma(F_0)$]	3976	8295	5271	6841	3862
Parameters	283	695	446	688	241
R_1 [$F_0 > 4\,\sigma(F_0)$]	0.0368	0.0455	0.0337	0.0959	0.0353
wR_2 (all unique data)	0.0775	0.1294	0.0814	0.2911	0.0937
GOF	1.036	1.064	1.063	1.053	1.067
$\Delta\rho_{max;\,min}$/e Å^{-3}	0.68; −0.56	1.05; −1.17	0.95; −2.11	3.18; −2.88	0.57; −0.74

thermobalance from Linseis. The instrument was calibrated using standard reference materials. For the experiments using large crucibles the thermobalance STA-PT1000 from Linseis was used. All measurements were performed with a flow rate of 75 mL · min^{-1} and were corrected for buoyancy.

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Graphical synopsis

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