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Special
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Synthesis and crystal structure of structurally different cadmium selenocyanate and thiocyanate coordination compounds containing 3-chloropyridine as ligand

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Dedicated to Prof. Dr. Michael Ruck on the occasion of his 60th birthday.

Four compounds with the composition $\text{Cd}(\text{NCSe})_2(3\text{-ClPy})_4$ (1), $[\text{Cd}(\text{NCSe})_2(3\text{-ClPy})_2] \cdot 3\text{-ClPy}$ (2), $\text{Cd}(\text{NCSe})_2(3\text{-ClPy})_2$ (3) and $\text{Cd}(\text{NCS})_2(3\text{-ClPy})$ (4) with 3-ClPy = 3-chloropyridine were synthesized. In the structure of 1 discrete complexes are observed, whereas in 2 the Cd cations are linked by pairs of selenocyanato anions into chains and between the chains 3-chloropyridine solvate molecules are embedded. In compound 3 each two Cd cations are linked by pairs of anionic ligands into dinuclear units, that are further connected into layers by μ -1,3 single bridging selenocyanate anions. In compound 4, both, octahedrally and tetrahedrally coordinated Cd cations are present, that are linked by μ -1,3-bridging anionic ligands into a three-dimensional network.

Thermoanalytical investigations prove that compound 1 loses the 3-chloropyridine ligands stepwise upon heating and transforms into compound 4 *via* compound 3 as an intermediate. Further investigations show that the thiocyanate analogue $\text{Cd}(\text{NCS})_2(3\text{-ClPy})$ 5 that is not reported in the literature can also be prepared. Since no single crystals were available, the structure was solved from PXRD data and refined using the Rietveld method, which revealed that this compound is an isomer of 4. In its crystal structure the Cd cations are linked by μ -1,3(N,S) and μ -1,3,3(N,S,S)-bridging anionic ligands into chains that are further connected *via* Cd_2S_2 rings into double chains.

Introduction

Coordination compounds based on thiocyanate anions have attracted much of interest in recent years. Our interest predominantly focuses on the magnetic properties of such compounds, because this anionic ligand is able to mediate reasonable magnetic exchange,^[1–3] and therefore, compounds that shows a variety of magnetic properties can be observed. For the synthesis of such compounds the metal cations must be linked by the thiocyanate anion. Depending on the neutral coligands and the ratio between metal thiocyanate and the coligand networks of different dimensionality can be observed. For compounds with mono coordinating coligands and cations

that prefer an octahedral coordination, discrete complexes with a ratio between $\text{M}(\text{NCS})_2$ and coligand of 1:4 are observed and such compounds are of interest, e.g. in the field of spin crossover (SCO).^[4–7] If the ratio amounts to 1:3, usually dinuclear complexes are observed^[3,8] and if this ratio is further reduced to 1:2, compounds with 1D or 2D metal thiocyanate networks are obtained. Depending on the actual metal coordination (all-*trans* or *cis-cis-trans*) the chains can be linear or corrugated.^[9–10] In this context, compounds based on Co(II) are of special interest, because they can show 3D magnetic ordering or single chain magnet behaviour.^[11–18] Compared to chains, layered compounds are rare but with, e.g. Co(II) or Ni(II) they show ferromagnetic ordering.^[19–20] Finally, paramagnetic compounds with a $\text{M}(\text{NCS})_2$:coligand ratio of 1:1 are rare and only sparsely investigated.^[21]

The main problem in the synthesis of such compounds is the fact that cations like, e.g. Mn(II), Fe(II), Co(II) or Ni(II) are less chalcophilic, and therefore prefer a terminal coordination of the thiocyanate anions, which means that compounds with bridging anionic ligands are difficult to prepare, especially if they should exhibit a very low ratio between $\text{M}(\text{NCS})_2$ and coligand.

This is completely different for compounds based on $\text{Cd}(\text{NCS})_2$, because this cation is much more chalcophilic than the paramagnetic cations. In this case the reactivity is practically reversed, and discrete complexes with terminally N-bonded thiocyanate anions are more difficult to prepare, whereas compounds with a bridging coordination are much easier available. Moreover, with $\text{Cd}(\text{NCS})_2$ the structural variability is much larger and many compounds with unusual stoichiometry, unusual metal thiocyanate networks and different metal

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coordinations are reported in the literature.^[22–29] This versatile structural behaviour is one of the reasons why we are also interested in the synthesis and crystal structure of coordination compounds based on $\text{Cd}(\text{NCS})_2$. Moreover, in several cases such compounds are isotypic to its paramagnetic analogues and therefore, can be used as structural models, e.g. for a Rietveld refinement, when no single crystals of the paramagnetic compounds are available.^[30] Finally, if one compound with a rare or new topology of the $\text{Cd}(\text{NCS})_2$ network was obtained, one can try to prepare such a compound with paramagnetic metal cations. Compared to thiocyanate coordination polymers much less compounds with selenocyanate anions are reported in the CCDC database.^[31] In this regard, the question arose whether selenocyanate compounds show crystal structures similar to that with thiocyanate and if they will form isotypic compounds. It is also of interest if the chemical reactivity is similar, which means that compounds with a very low $\text{Cd}(\text{NCSe})_2$:coligand ratio can more easily be crystallized. Therefore, in the course of our systematic project we tried to prepare compounds based on $\text{Cd}(\text{NCSe})_2$ and in this work we used 3-chloropyridine (3-CIPy) as coligand. With thiocyanate some compounds are already reported, which include $\text{Cd}(\text{NCS})_2(3\text{-CIPy})_4$, that consists of discrete complexes and $\text{Cd}(\text{NCS})_2(3\text{-CIPy})_2$, that consist of linear chains.^[32]

Results and Discussion

Synthetic aspects

Reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ and KNCS with different amounts of 3-chloropyridine in water, respectively ethanol leads to the formation of two colorless compounds with the composition $\text{Cd}(\text{NCSe})_2(3\text{-CIPy})_2$ (**3**) and $\text{Cd}(\text{NCSe})_2(3\text{-CIPy})$ (**4**). The CN stretching vibrations of the selenocyanate anions are observed at 2092 and 2115 cm^{-1} for **3** and at 2129 cm^{-1} for **4**, indicating that the Cd cations are linked by bridging selenocyanate anions (Figure S1 and S2). Even if a 10-fold excess of 3-chloropyridine is used no compound with the composition $\text{Cd}(\text{NCSe})_2(3\text{-CIPy})_4$ is observed, for which the thiocyanate analogue is reported.^[32] This compound (**1**), however, is available if $\text{Cd}(\text{NCSe})_2$ is reacted with pure 3-chloropyridine without any solvent. For this compound, the CN-stretching vibration of the anionic ligands is observed at 2057 cm^{-1} , in agreement with the presence of only terminally bonded anionic ligands (Figure S3). In this context it is noted that in one of these batches we accidentally found a crystal of a further colorless compound, for which we determined a composition of $[\text{Cd}(\text{NCSe})_2(3\text{-CIPy})_2] \cdot 3\text{-CIPy}$ (**2**) by single crystal X-ray analysis (see below). All attempts to prepare pure samples of **2** failed, because in nearly all cases pure colorless powders of **1** were obtained and **2** seems to decompose into **3** and thus, might be formed under kinetic control.

Powder X-ray diffraction (PXRD) investigations indicate that compound **1** might be isotypic to its thiocyanate analogs, which should not be the case for compound **3** (Figure S4).^[32] For compound **2** and **4**, no thiocyanate analog is reported in

the literature. In further experiments colorless single crystals of **1**, **3** and **4** were prepared and together with **2** investigated by single crystal X-ray diffraction.

Crystal Structures

Compound **1** crystallizes in the monoclinic space group $C2/c$ with $Z=4$ and is isotypic to its thiocyanate analog reported in the literature (Table S1).^[32] Its asymmetric unit consists of one Cd cation that is located on a center of inversion as well as one selenocyanate anion and two crystallographically independent 3-chloropyridine ligands that occupy general positions (Figure S5). The Cd cations are octahedrally coordinated by two terminal N-bonded selenocyanate anions as well as four 3-chloropyridine ligands (Figure 1). Bond lengths and angles shows that the octahedra are slightly distorted (Table S2). In the crystal structure, the discrete complexes are linked by weak intermolecular $\text{C}\cdots\text{H}\cdots\text{Se}$ hydrogen bonding (Table S3).

In compound **2** the ratio between $\text{Cd}(\text{NCSe})_2$ and 3-chloropyridine amount to 1:3. This compound crystallizes in the monoclinic space group $P2_1/c$ with $Z=8$ formula units in the unit cell (Table S1). The asymmetric units consists of two crystallographically independent Cd cations, four selenocyanate anions as well as six crystallographically independent 3-chloropyridine ligands, all of them located in general positions (Figure S6).

Each Cd cation is octahedrally coordinated by two μ -1,3-bridging selenocyanate anions and two 3-chloropyridine ligands (Figure 2). The Cd coordination of both independent cations is comparable and shows that both octahedra are slightly distorted (Table S4).

The Cd cations are linked by pairs of μ -1,3-bridging selenocyanate anions into chains, that are linear because of the all-*trans* coordination (Figure 2). Between the chains additional 3-chloropyridine guest molecules are located (Figure S7). In the crystal structure a number of $\text{C}\cdots\text{H}\cdots\text{Se}$ and $\text{C}\cdots\text{H}\cdots\text{N}$ contacts are observed of which only two $\text{C}\cdots\text{H}\cdots\text{Se}$ angles and one $\text{C}\cdots\text{H}\cdots\text{N}$ angle show values close to linearity and might correspond to a significant interaction (Table S5). It is noted that this type of

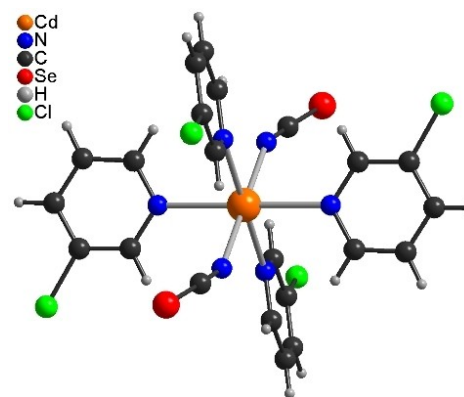


Figure 1. Crystal structure of **1**, showing the Cd coordination. An Ortep plot of **1** can be found in Figure S5.

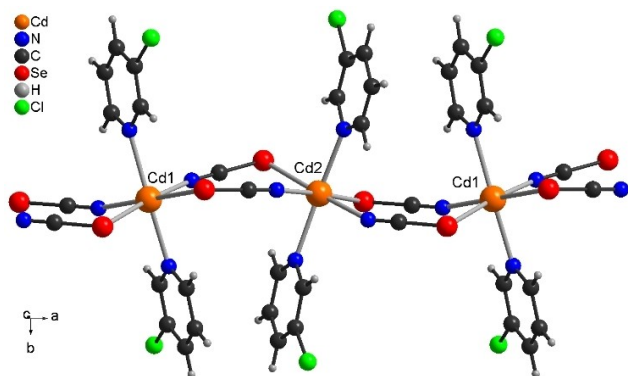


Figure 2. Crystal structure of **2**, showing a part of a chain. An Ortep plot of **2** can be found in Figure S6. The 3-chloropyridine solvate molecules are omitted for clarity.

chain is very common for thio- and selenocyanate coordination polymers, even if for the latter much less examples are reported in the literature.^[27,30,33]

Compound **3** crystallizes in the orthorhombic space group *Pbca* with *Z*=8 formula units in the unit cell and is not isotopic to its thiocyanate analog $\text{Cd}(\text{NCS})_2(3\text{-ClPy})_2$ reported in the literature (Table S1).^[32] The asymmetric unit of **3** consists of one crystallographically independent Cd cation as well as of two independent selenocyanate anions and two independent 3-chloropyridine ligands, all of them located in general positions (Figure S8).

In the crystal structure, the Cd cations are octahedrally coordinated by two N- and two Se-bonded thiocyanate anions as well as two 3-chloropyridine ligands in an all-*trans* coordination (Figure 3 and S8). Bond lengths and angles around the Cd centers agree with values reported in the literature (Table S6).

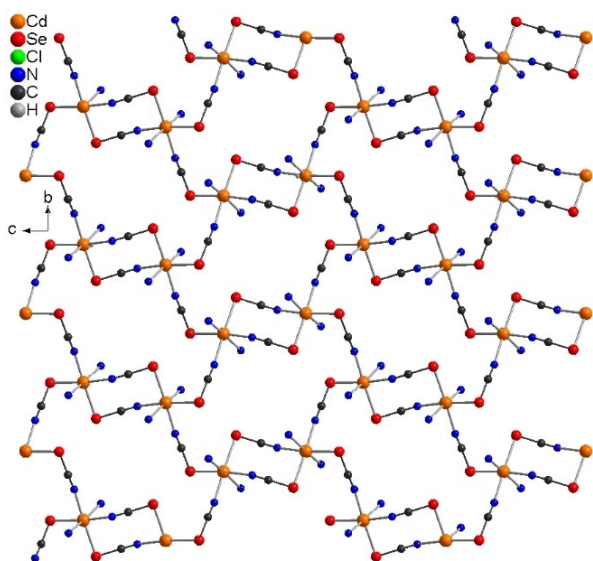


Figure 3. Crystal structure of **3** with view onto a part of a layer. An Ortep plot of **3** can be found in Figure S8.

The Cd cations are linked by pairs of anionic ligands into dimeric units, that are further connected into layers parallel to the *bc*-plane by single μ -1,3-bridging selenocyanate anions (Figure 3). These layers are further connected by very weak intermolecular C—H...Se hydrogen bonding (Table S7).

It is noted that this structure is completely different from its thiocyanate analog $\text{Cd}(\text{NCS})_2(3\text{-chloropyridine})$, in which the Cd cations are connected into linear chains by pairs of μ -1,3-bridging thiocyanate anions.^[32] In this context it is also mentioned that chains are frequently observed in thio- and selenocyanate chemistry, whereas layers are rarer.^[19–20,34]

The most 3-chloropyridine-deficient compound **4** crystallizes in the monoclinic space group *C2/c* with *Z*=8 formula units in the unit cell (Table S1). For this composition, the thiocyanate analog is unknown but one compound with the composition $\text{Co}(\text{NCS})_2(2,6\text{-dimethylpyrazine})_2$ is found that is isotopic to **4** and that was determined from PXRD data.^[21] The asymmetric unit of **4** consists of two crystallographically independent Cd cations of which one is located on a center of inversion and the second on a 2-fold rotation axis, one distinct 3-chloropyridine ligand and two independent selenocyanate anions, that occupy general positions (Figure S9).

In the crystal structure of **4** two different Cd coordinations are observed. Cd1 is octahedrally coordinated by two 3-chloropyridine ligands as well as four bridging selenocyanate anions that are only coordinated with their N-atoms to the Cd centers (Figure 4, S9 and Table S8). The second Cd cation is in a tetrahedral coordination of four Se-bonding selenocyanate anions (Figure 4 and S9).

Each of the octahedrally coordinated Cd cations is linked to four tetrahedrally coordinated Cd cations *via* single μ -1,3-bridging selenocyanate anions (Figure 4) forming an unusual three-dimensional network. Within this network the tetrahedrally and octahedrally coordinated Cd cations as well as the 3-

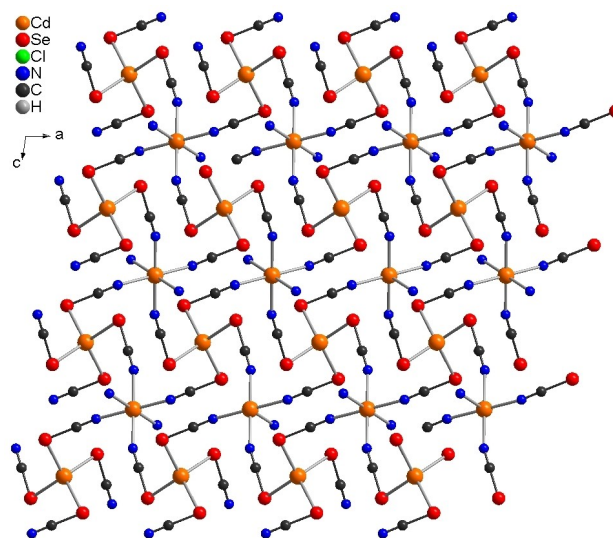


Figure 4. Crystal structure of **4** with view along the crystallographic *b*-axis. Please note, that only the N atom of the 3-chloropyridine ligands is shown. An Ortep plot of **4** can be found in Figure S9.

chloropyridine ligands are arranged in separate columns (Figure 5).

In these columns the 6-membered pyridine rings are parallel oriented and the distance between the centroids of the neighbored pyridine rings amount to 4.175 Å, indicating weak π - π interactions (Figure 5).

Finally it is noted that to the best of our knowledge only one compound with cobalt(II)thiocyanate and such a network is reported, whereas such compounds with selenocyanate anions are unknown.^[21]

Thermoanalytical investigations

To prove if compound 2, 3 or 4 or a different isomer of one of these compounds can be obtained by thermal ligand removal, the most 3-chloropyridine-rich compound 1 was investigated by simultaneously differential thermoanalysis and thermogravimetry (DTA-TG). Upon heating compound 1 to 250 °C, three mass losses are observed, that are each accompanied with endothermic events in the DTA curve (Figure 6). From the derivative of the thermogravimetric curve (DTG), it is obvious that the second mass loss is poorly and the third mass loss reasonably resolved (Figure 6). The experimental mass loss in each step is in rough agreement with that calculated for the removal of two 3-chloropyridine ligands in the first and each one 3-chloropyridine ligand in the second and third mass loss ($\Delta m_{\text{calc.}}(-3 \text{ 3-chloropyridine}) = 14.6\%$). There is no hint for the formation of a compound with the same composition as compound 2. To increase the resolution a second measurement with 1 °C/min was performed, which shows that even the first step can successfully be resolved (Figure S13).

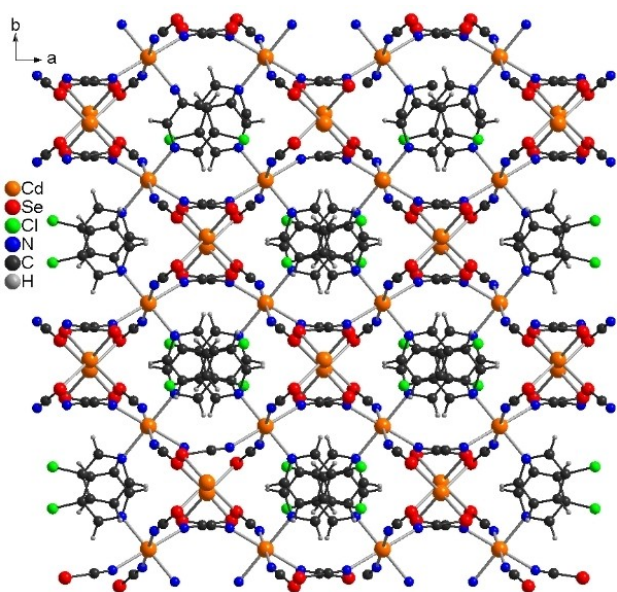


Figure 5. Crystal structure of 4 with view along the crystallographic *c*-axis.

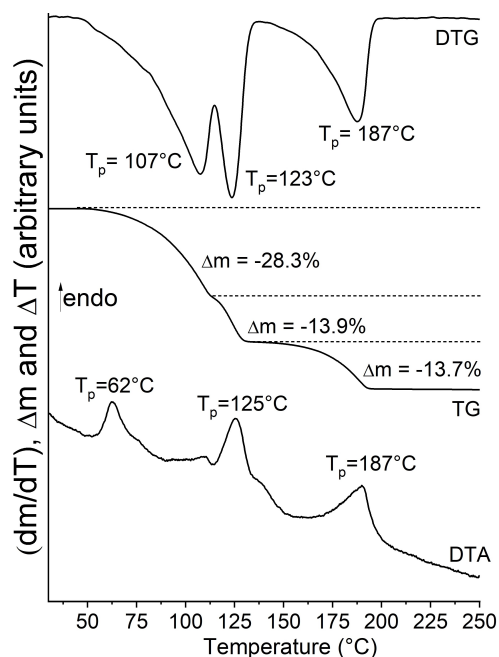


Figure 6. DTG, TG and DTA curve for compound 1 measured with 8 °C/min in nitrogen.

To identify the compounds formed after each mass loss the corresponding residues were isolated and investigated by IR spectroscopy. The IR spectra of the residue formed after the first mass loss is identical to that of 3 and that after the second mass loss corresponds to that of compound 4 (Figure S14 and S15). Moreover, PXRD investigations prove that compound 1 transforms into 4 *via* compound 3 as intermediate (Figure 7).

Finally it is noted that the thermal reactivity is very similar to that of the corresponding $\text{Co}(\text{NCS})_2$ compounds with 2,6-

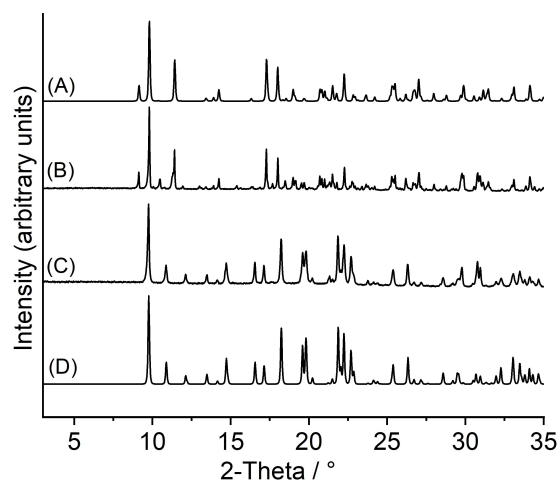


Figure 7. Experimental PXRD pattern of the residue obtained after the first (B) and second (C) mass loss in a thermogravimetric measurement of compound 1, together with the powder pattern calculated for compound 3 (A) and 4 (D).

dimethylpyrazine as ligand.^[21] With this ligand a discrete complex with the composition $\text{Co}(\text{NCS})_2(2,6\text{-dimethylpyrazine})_4$ is reported that loses half of the coligands upon heating and transforms into $\text{Co}(\text{NCS})_2(2,6\text{-dimethylpyrazine})_2$ that shows the same layered structure as compound **3**. Upon further heating one additional coligand is removed leading to the formation of $\text{Co}(\text{NCS})_2(2,6\text{-dimethylpyrazine})$, that is isotypic to compound **4**.

Synthesis and crystal structure of $\text{Cd}(\text{NCS})_2(3\text{-Clpy})$

As mentioned above, the thiocyanate analogue to $\text{Cd}(\text{NCSe})_2(3\text{-Clpy})$ (**4**) is unknown, but our investigations indicate that it might be available. Therefore, $\text{Cd}(\text{NCS})_2$ was reacted in different ratios with 3-chloropyridine and the colorless residues were investigated by PXRD. It was found that in those cases, where the reactants were used in ratio 1:1 predominantly the known compound $\text{Cd}(\text{NCS})_2(3\text{-Clpy})_2$ was obtained but if a large excess of $\text{Cd}(\text{NCS})_2$ was used in the synthesis, a compound was obtained that shows a powder pattern that is different from that of $\text{Cd}(\text{NCS})_2(3\text{-Clpy})_2$ and $\text{Cd}(\text{NCSe})_2(3\text{-Clpy})$ (**4**). In its IR spectrum the CN stretching vibration of the thiocyanate anions is observed at 2119 cm^{-1} , indicating that the bridging thiocyanate anions are present (Figure S16). All attempts to prepare single crystals failed and therefore, its crystal structure was determined from PXRD data by scratch.

The new compound $\text{Cd}(\text{NCS})_2(3\text{-Clpy})$ **5** crystallizes in the triclinic space group $P\bar{1}$ with $Z=2$ formula units in the unit cell and all atoms in general positions (Table S9). The asymmetric unit consist of one crystallographically independent Cd cation, one 3-chloropyridine ligand as well as two independent thiocyanate anions. The Cd cations are octahedrally coordinated by two N- and three S-bonding thiocyanate anions and one 3-chloropyridine ligand (Figure 8). The cations are linked by pairs of anionic ligands into linear chains. These two chains condense into double chains by the sulfur atoms of the $\mu\text{-}1,3,3(\text{N,S,S})$ bonding thiocyanate anions forming four-membered Cd_2S_2 rings (Figure 8).

It is noted, that even this structural motif is rarely observed and only a few examples are reported in the literature.^[35–37]

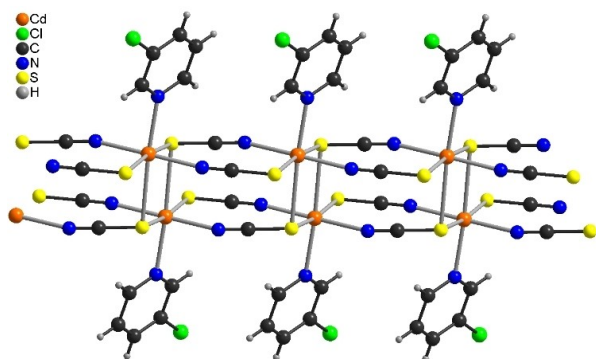


Figure 8. Crystal structure of $\text{Cd}(\text{NCS})_2(3\text{-Clpy})$ with view of a part of a chain.

Conclusions

In the present contribution new $\text{Cd}(\text{NCSe})_2$ coordination compounds with 3-chloropyridine as coligand were presented. These compounds exhibit different ratios between $\text{Cd}(\text{NCSe})_2$ and 3-chloropyridine, which directly influence the dimensionality of the $\text{Cd}(\text{NCSe})_2$ substructure. Discrete complexes were observed for ratio 1:4, whereas a 1D structure was found for ratio 1:3. The observation of a chain structure for this ratio is surprising, because in practically all cases such structures consist of dinuclear units, in which two cations are linked by pairs of anion ligands and where the coordination sphere is completed by two additional coligands and one only terminally N-bonded anionic ligand. In this case the formation of a chain is only possible if 1/3 of the coligands act as solvate molecules, which might be responsible for the fact, that this compound is unstable and loses the solvate coligands. This reaction leads to a ratio between $\text{Cd}(\text{NCSe})_2$ and coligand of 1:2 and one would expect that the chain structure is retained. Surprisingly a different isomer was obtained that consists of layers (2D). If one more coligand is removed a compound with a ratio of 1:1 formed, that consists of a very rare structure with 4-fold and 6-fold coordinated Cd cations that are linked into a 3D network. Starting from the discrete precursors, the 2D and 3D compound can also be prepared by thermal ligand removal, where the 1D compound does not occur. All this shows that prediction of structure and reactivity of such compounds is difficult, because of their enormous structural variability. That the situation is even more complex is obvious if these structures are compared with those of the thiocyanate analogues, where the corresponding compounds are frequently isotypic. The discrete complexes with ratio 1:4 are isotypic and the solvate with ratio 1:3 does not exist. The 1:2 compound with thiocyanate forms a chain structure instead of the layered isomer. Because the 1:1 compound is not reported in the literature, we prepared this compound and determined its structure from PXRD data. We found that instead of the 3D network with selenocyanate, the thiocyanate compound shows a condensed chain structure, which again shows that the structure prediction even for anions that frequently behave structurally similar and very often forms isotypic compounds is sometimes difficult to achieve. Both structural motifs are very rare and such compounds can usually only be prepared from solution if chalcophilic metal cations are used in the synthesis. Concerning the reactivity of thio- and selenocyanate compounds our results indicate that condensed structures with selenocyanate might be more easily available with chalcophilic Cd cations, because compound **4** is easily available by the reaction of stoichiometric ratios, whereas for the thiocyanate analogue an excess of $\text{Cd}(\text{NCS})_2$ is needed, because otherwise $\text{Cd}(\text{NCS})_2(3\text{-Clpy})_2$ is obtained.

Experimental Section

General

$\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$ and was obtained from Merck and $\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$ (98%) was obtained from Alfa Aesar. $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ (98%), KNCSe (98.5%) and 3-chloropyridine (99%) was obtained from Sigma-Aldrich. $\text{CdSO}_4 \cdot 8 \text{H}_2\text{O}$ was obtained from Carl Roth. All chemicals were used without further purification.

$\text{Cd}(\text{NCS})_2$ was prepared by the reaction of equimolar amounts of $\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$ and $\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$ in water. The precipitated BaSO_4 was filtered off and the filtrate was concentrated to complete dryness resulting in a colourless residue of $\text{Cd}(\text{NCS})_2$.

Synthesis of $\text{Cd}(\text{NCSe})_2(3\text{-ClPy})_4$ (1)

To a mixture of 38.6 mg (0.125 mmol) $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ and of 36.0 mg (0.25 mmol) KNCSe , 1890 μL (20 mmol) of 3-chloropyridine was added. Within 2 d single crystals of compound **4** were obtained, that were dried on a filter paper. Yield: 77%. If a solvent is used in the synthesis, always compound **3** is obtained.

Synthesis of $[\text{Cd}(\text{NCSe})_2(3\text{-ClPy})_2]_2 \cdot 3\text{-ClPy}$ (2)

A few crystals of **2** were accidentally obtained in a batch of compound **1**. This compound cannot be prepared pure, because in nearly all cases compound **1** is obtained and if the reaction is performed in solvent, compound **3** will form.

Synthesis of $\text{Cd}(\text{NCSe})_2(3\text{-ClPy})_2$ (3)

154 mg (0.5 mmol) $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, 144 mg (1 mmol) KNCSe , 20 mmol (1890 μL) and 94.5 μL (1 mmol) 3-chloropyridine were stirred in 2 mL of H_2O at room-temperature for 2 d. The precipitate of **3** was filtered off, washed with a very small amount of water and dried on air. Yield: 81%. If the reaction is performed without stirring single crystals were obtained within a few days.

Synthesis of $\text{Cd}(\text{NCSe})_2(3\text{-ClPy})$ (4)

77 mg (0.25 mmol) $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, 72 mg (0.5 mmol) KNCSe and 23.6 μL (0.25 mmol) 3-chloropyridine were stirred in 2 mL ethanol at room-temperature for 2 d. The precipitate of **4** was filtered off, washed with a very small amount of ethanol and dried on air. Yield: 71%. If the reaction is performed without stirring single crystals were obtained within a few days

Synthesis of $\text{Cd}(\text{NCS})_2(3\text{-ClPy})$ (5)

114.3 mg (0.5 mmol) $\text{Cd}(\text{NCS})_2$ and 23.6 μL (0.25 mmol) of 3-chloropyridine were stirred in 2 mL water at room-temperature for 3 d. The precipitate was filtered off, washed with a very small amount of water and dried on air. Yield: 67%. The large excess of $\text{Cd}(\text{NCS})_2$ is needed, because otherwise the known compound $\text{Cd}(\text{NCS})_2(3\text{-ClPy})_2$ will form.^[32]

Single crystal structure analysis

Data collections were performed with an XtaLAB Synergy-S diffraction system equipped with micro-focus source (PhotonJet-S) and a HyPix-6000HE Hybrid Photon Counting (HPC) detector using $\text{CuK}\alpha$ radiation. Structure solution was performed with SHELXT^[38] and structure refinements were performed against F^2 using SHELXL-

2018.^[39] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located in the difference map but positioned with idealized geometry and refined isotropically with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ using a riding model.

CCDC-2265216 (1), CCDC-2265218 (2), CCDC-2265219 (3) and CCDC-2265217 (4), contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

PXRD structure analysis

Data for *ab-initio* structure determination were measured on a Panalytical Empyrean diffractometer equipped with $\text{Cu-K}\alpha$ radiation, a focussing X-ray mirror and a PIXcel 1D detector. The sample was loaded in a glass capillary (Spezialglas Nr. 10, Hilgenberg, Germany) and spun during the measurement to avoid effects of preferred orientation. All steps of the structure determination were carried out using TOPAS Academic Version 6.0.^[40] In a first attempt all observed reflections were included for indexing, which lead only to poor figures of merit for the proposed unit cells. Inspection of PXRD data of two different batches indicated that – by lower intensities of a few weak reflections – an impurity phase might be present. Omission of those reflections lead to several triclinic cell metrics with volumes of 545 \AA^3 , which is in agreement with $Z=2$ for the sum formula of **5**. The cell with space group $P\bar{1}$ and $a=5.893 \text{ \AA}$, $b=8.335 \text{ \AA}$, $c=11.246 \text{ \AA}$, $\alpha=94.381^\circ$, $\beta=91.210^\circ$, $\gamma=96.764^\circ$ was used for a Pawley fit to determine precise lattice parameters, zero point error and the background, which was modelled by a Chebyshev polynomial. The instrumental line broadening was described using the fundamental parameter approach^[41] and sample dependent line broadening was modelled using the double Voigt approach.^[42] Structure solution was carried out in real space using simulated annealing^[43] as means for global optimisation of the structural building blocks. Two distinct thiocyanate anions and one 3-chloropyridine were modelled as rigid bodies and their positional and rotational degrees of freedom were optimized together with the position of one Cd^{2+} cation. Bond lengths for the rigid bodies were taken from published crystal structures of similar compounds. After an extended run of several 10000 cycles a decent minimum could repeatedly be reached, which was subject to further Rietveld refinement. In surplus to the aforementioned parameters the isotropic displacement parameters were refined, with one joint parameter for all C, N and S atoms. The final refinement lead to a stable minimum with satisfying fit parameters as well as a convincing visual agreement of observed and calculated patterns. The corresponding plot can be found in Figure S17 and Table S9 summarises the crystal structure data and details of the structure refinement.

CCDC-2265203 ($\text{Cd}(\text{NCS})_2(3\text{-ClPy})_2$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Other physical measurements

The XRPD measurements for the characterization of all samples were performed with a STOE Transmission Powder Diffraction System (STADI P) with $\text{Cu-K}\alpha_1$ radiation and a Dectris Mythen 1 K detector with a Johann-type-Ge(111) monochromator from STOE & CIE. IR spectra were recorded at RT on a Bruker Vertex70 FT-IR ATR spectrometer using a broadband spectral range extension VERTEX FM for full mid and far IR. For the TG-DTA measurements, a STA-PT1000 thermobalance from Linseis was used. Measurements were

performed in Al₂O₃ crucibles and under a dynamic nitrogen atmosphere.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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