

Cite this: *CrystEngComm*, 2012, **14**, 5412–5420

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PAPER

# Synthesis of new stable and metastable thiocyanato coordination polymers by thermal decomposition and by solution reactions†

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Received 20th March 2012, Accepted 15th May 2012

DOI: 10.1039/c2ce25389e

Investigations on the thermal behavior of the 1 : 4 (ratio between metal and neutral co-ligand) compound  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_4]_n$  (**1-Cd**) show that the pyridine ligands can be removed in three separate steps. In the first TG step a pyridine-deficient 1 : 2 compound of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$  (**2-Cd/III**) is obtained, which transforms into an 1 : 1 compound of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})]_n$  (**3-Cd**) on further heating. Rietveld refinement of **2-Cd/III** proves that this compound represents a new form, which is different from that of the 1 : 2 compounds **2-Cd/I** and **2-Cd/II** reported recently. In further experiments a fourth 1 : 2 compound of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$  (**2-Cd/IV**) was crystallized and characterized by single crystal X-ray diffraction. In the crystal structures of **2-Cd/II**, **2-Cd/III** and **2-Cd/IV** the metal cations are linked by the anionic ligands into chains, in which the Cd cations are coordinated by two *trans*-oriented pyridine ligands and four thiocyanato anions within slightly distorted octahedra. For the literature known compound **2-Cd/I** no atomic coordinates are given, but for **2-Cd/II** an all-*cis*, for **2-Cd/III** an all-*trans* and for **2-Cd/IV** an alternating *cis-cis-trans* arrangement of the thiocyanato anions is observed. Solvent mediated conversion experiments prove that **2-Cd/III** transforms into **2-Cd/IV** via **2-Cd/II** as intermediate and therefore, the *cis-cis-trans* coordinated compound **2-Cd/IV** represents the thermodynamic stable form at room-temperature. The 1 : 1 compound **3-Cd** can also be prepared from solution. In its crystal structure the Cd cations are coordinated by one pyridine ligand as well as two *N*-bonded and three *S*-bonded thiocyanato anions. Two neighboring octahedra are connected by two  $\mu$ -1,1,3(*S,S,N*)-coordinating anions into double octahedra, which are further linked into chains by  $\mu$ -1,1,3(*S,S,N*)- and  $\mu$ -1,3-coordinating thiocyanato anions. IR investigations of the 1 : 4, 1 : 2 and 1 : 1 compounds reveal that the different coordination modes of the anionic ligands can be rationalized by analyzing the changes in the values of their asymmetric  $\nu_{\text{as}}(\text{CN})$  stretching vibration. Additional investigations on **2-Cd/II**, **2-Cd/III** and **2-Cd/IV** using differential scanning calorimetry and X-ray powder diffraction reveal that on heating additional crystalline 1 : 2 compounds are formed in reversible and irreversible phase transitions.

## Introduction

Since several years the development of strategies for a more rational design of coordination architectures in order to prepare compounds with well defined physical properties is an active field of chemical research.<sup>1–11</sup> This approach, called “Crystal Engineering” includes investigations on the interactions in

crystals and on structure–property relationships in solids.<sup>3,12–19</sup> In this context one has to be aware of the phenomenon of polymorphism or isomerism, which is frequently encountered in such compounds and which makes any considerations on the rational design of one special compound much more difficult.<sup>20–27</sup> In this context not only the structural aspects of these phenomena are of interest but also investigations on the thermodynamic and kinetic properties should be performed.<sup>28–30</sup>

Currently, we are particularly interested in the synthesis and structure–property relationships of coordination compounds that show cooperative magnetic phenomena. For the preparation of such compounds paramagnetic transition metals must be connected by small-sized ligands and several of such compounds were reported in literature.<sup>2,10,31–42</sup> In this context we are interested in the synthesis, structures, thermal and magnetic properties of new thio- and selenocyanato coordination polymers. Unfortunately compounds with terminal *N*-bonded anions

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† Electronic supplementary information (ESI) available: Rietveld difference plot of **2-Cd/III** as well as IR spectra of **1-Cd**, **2-Cd/II**, **2-Cd/III**, **2-Cd/IV** and X-ray powder pattern of the residue formed after the second TG step in the thermal decomposition reaction of **1-Cd**, X-ray powder pattern of  $\text{Cd}(\text{NCS})_2$  and powder pattern for **3-Cd** calculated from single crystal data. CCDC reference numbers 872124–872126. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce25389e

can easily be prepared, whereas the synthesis of the bridging analogues is sometimes difficult to achieve if the synthesis is performed in the liquid state. However, recently we have shown that such compounds can easily be prepared in quantitative amounts by thermal decomposition of ligand-rich precursor compounds (ligand-rich = rich on neutral *N*-donor co-ligands) in which the transition metal cations are octahedrally coordinated by four *N*-donor ligands and two terminal *N*-bonded thio- or selenocyanato anions.<sup>43–54</sup>

Unfortunately, on thermal decomposition these intermediates are frequently obtained as microcrystalline powders of partly low crystallinity and therefore, structure determination is difficult to achieve. In some cases the bridging mode of the anions can be determined by IR-spectroscopy and therefore, such investigations are of special importance for our project.<sup>55–58</sup> However, in those cases in which detailed structural information is required the corresponding compounds with cadmium can be investigated because they are easy to obtain and they exhibit similar thermal reactivity as their paramagnetic analogues.<sup>59–62</sup> In several cases they are isotypic to their paramagnetic counterparts and thus, the structures of the latter compounds can be determined by Rietveld refinement. Moreover, with cadmium frequently different compounds with new topologies and more condensed networks can be prepared and this is the reason why we are also interested in their chemistry.<sup>62</sup>

In recent work we also investigated paramagnetic and diamagnetic coordination polymers with pyridine as a co-ligand.<sup>52,54</sup> With cadmium a ligand-rich 1 : 4 compound of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_4]$  (**1-Cd**) was already reported, which is isotypic to their paramagnetic counterparts.<sup>53,54</sup> Its crystal structure consists of discrete complexes in which the metal centers are octahedrally coordinated by two terminal *N*-bonded thiocyanato anions and four pyridine ligands. In 1987 Taniguchi *et al.* reported a 1 : 2 compound of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$  (**2-Cd/I**) crystallizing in space group  $P\bar{1}$  with  $a = 9.512(2) \text{ \AA}$ ,  $b = 27.357(10) \text{ \AA}$ ,  $c = 9.515(2) \text{ \AA}$ ,  $\alpha = 107.00(3)^\circ$ ,  $\beta = 112.47(2)^\circ$ ,  $\gamma = 79.19(3)^\circ$  but no atomic coordinates were given.<sup>63</sup> Based on the unit cell parameters Marsh *et al.* suggest a transformation in the monoclinic *C*-centered space group  $C2/c$  with  $a = 10.575 \text{ \AA}$ ,  $b = 15.818 \text{ \AA}$ ,  $c = 26.206 \text{ \AA}$ ,  $\beta = 95.93^\circ$  but no new investigations were performed.<sup>64</sup> In further work we obtained single crystals of a second 1 : 2 compound that crystallizes in the triclinic space group  $P\bar{1}$  (**2-Cd/II**) which exhibits unit cell parameters different from that of **2-Cd/I**.<sup>65</sup> Surprisingly, none of these 1 : 2 compounds is isotypic to their paramagnetic counterparts. Therefore we decided to reinvestigate the cadmium thiocyanato pyridine compounds in more detail, which also includes the exploration of new compounds. Within this project two new 1 : 2 and one new 1 : 1 compound were found by thermal decomposition and by solution reactions and investigated for their structural, thermal and spectroscopic properties and their thermodynamic stability. Here we report on these investigations.

## Results and discussion

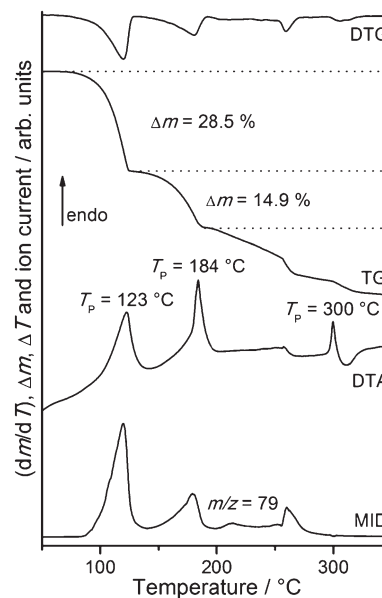
### Thermoanalytical investigations

On heating of the ligand-rich precursor  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_4]$  (**1-Cd**) in a thermobalance to 350 °C, three mass steps are

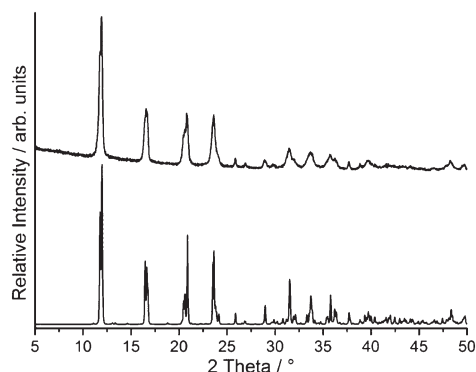
observed in the TG curve that are accompanied with endothermic events in the DTA curve (Fig. 1). From the DTG curve it is obvious that the first mass step is well and the second and third step poorly resolved and from the MS trend scan curve it is proven that only pyridine ( $m/z = 79$ ) is emitted in these steps. The experimental mass loss in the first TG step is in good agreement with that calculated for the loss of two pyridine ligands [ $\Delta m_{\text{(exp)}} = 28.5\%$ ;  $\Delta m_{\text{(calc)}} = 29.0\%$ ] and the mass loss in the second TG step corresponds to the removal of one pyridine ligand [ $\Delta m_{\text{(exp)}} = 14.9\%$ ;  $\Delta m_{\text{(calc)}} = 14.5\%$ ] (Fig. 1). On further heating the remaining pyridine is emitted forming cadmium thiocyanate, which decomposes at higher temperature.

Based on these investigations it can be assumed that in the first TG step a ligand-deficient 1 : 2 compound of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]$  is formed that on further heating transforms into a 1 : 1 compound of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})]$ . To verify this assumption the isolated intermediates were investigated by CHNS analysis, which supports the formation of a ligand-deficient intermediate of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]$  (**2-Cd/III**) in the first TG step, whereas the CHNS analysis result of the residue obtained after the second TG step is not in good agreement with that expected for  $[\text{Cd}(\text{NCS})_2(\text{pyridine})]$ .

However, investigations using X-ray powder diffraction reveal that the compound formed in the first TG step does not correspond to **2-Cd/I** or **2-Cd/II** known from literature.<sup>63–65</sup> Interestingly, a very good agreement is obtained if the experimental pattern of **2-Cd/III** is compared with that calculated for the corresponding compound  $[\text{Mn}(\text{NCS})_2(\text{pyridine})_2]_n$  reported recently.<sup>53</sup> Therefore, a Rietveld refinement was performed using the crystallographic data of  $[\text{Mn}(\text{NCS})_2(\text{pyridine})_2]_n$ , which clearly proved that they are isotypic (see Experimental Section and Fig. S1 in the ESI†). If the experimental X-ray powder pattern of **2-Cd/III** is compared with that calculated, it is obvious that a phase pure crystalline material has formed (Fig. 2).



**Fig. 1** DTG, TG, DTA, and MS trend scan curves for  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_4]$  (**1-Cd**). Heating rate  $4^\circ\text{C min}^{-1}$ ;  $\text{N}_2$  atmosphere; crucible:  $\text{Al}_2\text{O}_3$ ;  $\Delta m$  = mass loss (%);  $T_p$  = peak  $T/^\circ\text{C}$ .



**Fig. 2** Experimental X-ray powder pattern of the residue formed in the first TG step in the thermal decomposition reaction of **1-Cd** (top) together with X-ray powder pattern for **2-Cd/III** calculated from the results of the Rietveld refinement (bottom).

To characterize the intermediate obtained in the second TG step additional XRPD investigations were performed. These investigations clearly showed that the residue consists of a mixture of cadmium(II) thiocyanate and of a new ligand-deficient crystalline phase that might correspond to a compound of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})]$  (Fig. S2 in the ESI†).

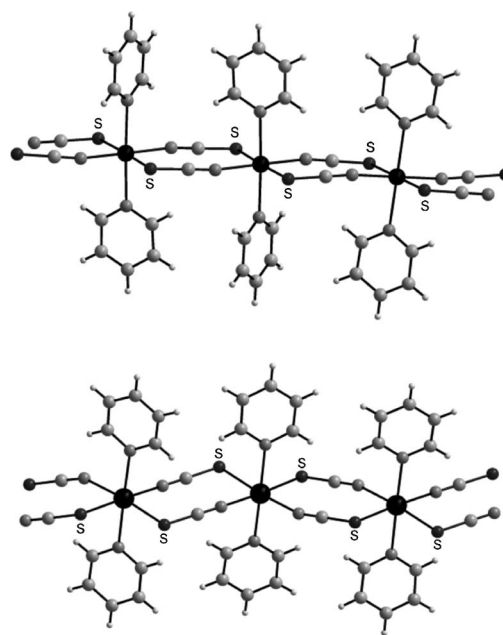
#### Crystal structure of $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$ (**2-Cd/III**)

The 1 : 2 compound **2-Cd/III** crystallizes in the triclinic space group  $P\bar{1}$  with  $Z = 3$  formula units in the unit cell (Table 1). The asymmetric unit consists of two crystallographically independent Cd cations, three thiocyanato anions and three pyridine ligands. One of the Cd cations is located on a center of inversion, whereas all other components occupy a general position. The Cd cations are coordinated by two *N*-bonded and two *S*-bonded thiocyanato anions within slightly distorted octahedra. The metal cations are linked *via*  $\mu$ -1,3-bridging anions into chains, in which all thiocyanato ligands are *trans* coordinated (Fig. 3: top).

Interestingly, this structure is significantly different from that of the 1 : 2 compound **2-Cd/II** reported recently (Fig. 3: bottom).<sup>65</sup>

**Table 1** Selected crystal data and details on the structure refinement from powder data for compound **2-Cd/III**

Formula	$\text{C}_{12}\text{H}_{10}\text{CdN}_4\text{S}_2$
MW $\text{g}\cdot\text{mol}^{-1}$	386.77
Crystal system	Triclinic
Space group	$P\bar{1}$
$a/\text{\AA}$	8.7915(9)
$b/\text{\AA}$	8.7921(7)
$c/\text{\AA}$	16.1275(18)
$\alpha$ ( $^\circ$ )	92.773(6)
$\beta$ ( $^\circ$ )	95.879(6)
$\gamma$ ( $^\circ$ )	114.341(7)
$V$	1124.14(19)
$D_{\text{calc}}$	1.669
$Z$	3
$2\theta$ range/ $^\circ$	5–50
no. reflections	661
no. parameters	41
$R_p, R_{wp}$	0.148, 0.149
$\text{GO}/\chi^2$	0.0527
$R_{\text{Bragg}}$	0.0278

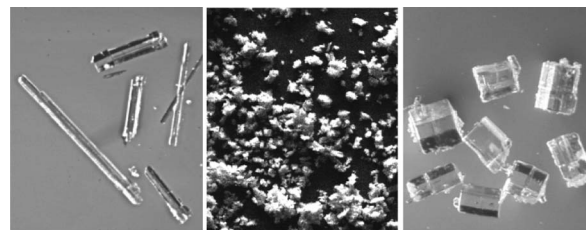


**Fig. 3** Crystal structure of **2-Cd/III** (top) and **2-Cd/II** (bottom) (black = cadmium(II), dark grey = sulfur, grey = nitrogen, light-grey = carbon, white = hydrogen).<sup>65</sup>

In this crystal structure the Cd cations are also linked by pairs of  $\mu$ -1,3-bridging thiocyanato anions into chains, and the thiocyanato anions are all-*cis* coordinated (Fig. 3: bottom).

#### Crystallization experiments on the 1 : 2 compounds

A search in the CCDC database revealed that an all-*trans* arrangement is usually observed in  $\mu$ -1,3-bridging thiocyanato coordination polymers and thus, the formation of the all-*cis* coordinated compound **2-Cd/II** from solution is somehow surprising.<sup>53,54,59,60,66–68</sup> Therefore, in order to prove if **2-Cd/III** can also be prepared in solution crystallization experiments under different reaction conditions were performed. In the course of these investigations an inhomogeneous product was obtained which consists of a large amount of needle-like crystals which were identified as **2-Cd/II** together with a small amount of colorless blocks (Fig. 4). Surprisingly, single crystal X-ray analysis of these blocks showed that a fourth 1 : 2 compound of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$  (**2-Cd/IV**) has formed.



**Fig. 4** Microscopic images of **2-Cd/II** (left), **2-Cd/III** (middle) and **2-Cd/IV** (right). The image of **2-Cd/III** was captured using scanning electron microscopy, whereas for **2-Cd/II** and **2-Cd/IV** a conventional lighting microscope was used.

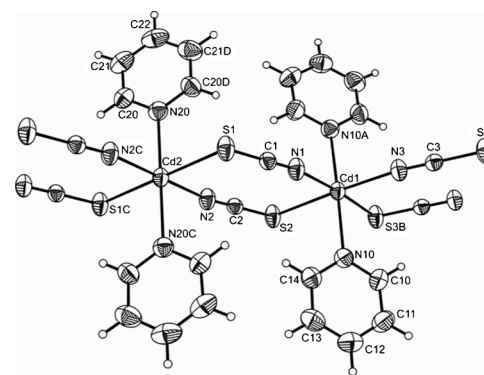
### Crystal structure of $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$ (**2-Cd/IV**)

The 1 : 2 compound **2-Cd/IV** crystallizes in the monoclinic space group  $C2/m$  with  $Z = 6$  formula units in the unit cell (Table 2). The asymmetric unit consists of two independent Cd cations, three thiocyanato anions and one and a half pyridine ligands.

The Cd cations are coordinated by two *N*-bonded and two *S*-bonded thiocyanato anions as well as two pyridine co-ligands in a slightly distorted octahedral geometry (Fig. 5 and Table 3). In the crystal structure the thiocyanato anions bridge the cadmium cations into chains with a topology of the coordination network that is very similar to that in **2-Cd/II** and **2-Cd/III** (Fig. 6). In contrast to the latter structures, in which either an all-*trans* or an all-*cis* coordination for the anionic ligands are found, in the new compound **2-Cd/IV** an alternating *cis-cis-trans* arrangement is observed (compare Fig. 3 and Fig. 6).

It must be noted that the arrangement of the chains in all three 1 : 2 compounds is very similar in order that the chains are parallel with the  $\text{Cd}(\text{NCS})_2$  units coplanar oriented (Fig. S3–S5 in the ESI†). The pyridine rings of neighboring chains in the all-*cis* and *cis-cis-trans* compounds are exactly eclipsed oriented maximizing  $\pi$ – $\pi$  interactions, whereas in the all-*trans* compound they are shifted relative to each other.

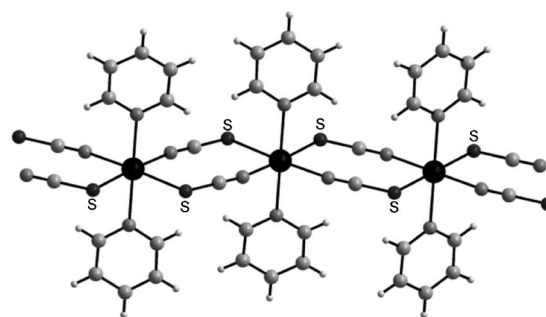
Based on the results of the single crystal structure determination a X-ray powder pattern was calculated and compared with those calculated for the 1 : 2 compound **2-Cd/II** and that measured for the crystalline mixture of **2-Cd/II** and **2-Cd/IV** (Fig. S6 in the ESI†). Interestingly, the powder patterns of **2-Cd/II** and **2-Cd/IV** are very similar and therefore, these compounds are difficult to distinguish in a routine measurement. This comparison also shows that the crystalline mixture, where the single crystal of **2-Cd/IV** was selected consists predominantly of **2-Cd/II**, whereas the existence of **2-Cd/IV** is difficult to prove. Surprisingly, if this crystalline batch is investigated one day later



**Fig. 5** ORTEP plot of **2-Cd/IV** with view of the coordination sphere of the cadmium(II) cations with labeling and displacement ellipsoids drawn at 50% probability level. Symmetry codes:  $A = x, -y + 1, z$ ;  $B = -x + 1, -y + 1, -z + 2$ ;  $C = -x + 1, -y + 1, -z + 1$ ;  $D = -x + 1, y, -z + 1$ .

**Table 3** Selected bond lengths (Å) and angles (°) for **2-Cd/IV**. Symmetry codes:  $B = -x + 1, -y + 1, -z + 2$ ;  $C = -x + 1, -y + 1, -z + 1$

Cd(1)–N(1)	2.316(6)	N(1)–Cd(1)–N(10)	91.00(12)
Cd(1)–N(3)	2.295(6)	N(3)–Cd(1)–N(1)	93.20(2)
Cd(1)–N(10)	2.360(5)	N(10)–Cd(1)–S(2)	88.51(11)
Cd(1)–S(2)	2.737(1)	S(2)–Cd(1)–S(3B)	82.96(5)
Cd(1)–S(3B)	2.749(1)	N(10)–Cd(1)–S(3B)	88.87(11)
Cd(2)–N(2)	2.314(6)	N(2)–Cd(2)–S(1)	92.20(15)
Cd(2)–N(20)	2.389(7)	N(20)–Cd(2)–S(1C)	90.00(1)
Cd(2)–S(1)	2.715(1)	S(1)–Cd(2)–S(1C)	180.0



**Fig. 6** Crystal structure of **2-Cd/IV** (black = cadmium(II), dark grey = sulfur, grey = nitrogen, light-grey = carbon, white = hydrogen).

the amount of **2-Cd/IV** increases indicating that the block-like crystals of **2-Cd/IV** grow on the cost of the needles of **2-Cd/II**.

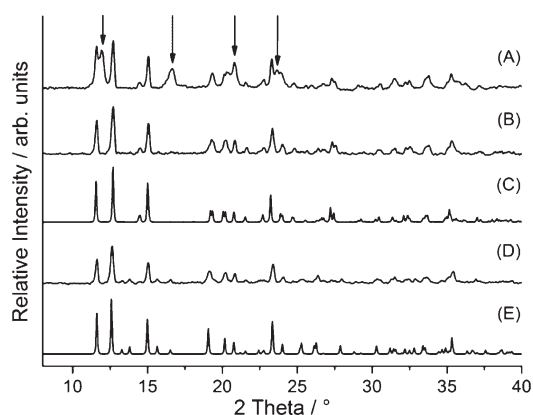
### Solvent mediated conversion experiments

In order to prove which of the different 1 : 2 compounds represents the thermodynamic most stable form at room-temperature a solvent mediated conversion experiment was performed. In this experiment a mixture of the all-*cis* **2-Cd/II** and the all-*trans* product **2-Cd/III** was stirred in a saturated solution in water at room-temperature and the solid residue was investigated by X-ray powder diffraction (Fig. 7). These investigations clearly show that all of the crystals of **2-Cd/III** disappeared within 1 day and therefore, clearly prove that the all-*trans* product **2-Cd/III** is the thermodynamically metastable form at room-temperature. However, if this batch is stirred for another three days it is proven that all of the crystals of **2-Cd/III**

**Table 2** Selected crystal data and details on the structure determinations from single crystal data for compounds **2-Cd/IV** and **3-Cd**

Compound	<b>2-Cd/IV</b>	<b>3-Cd</b>
Formula	$\text{C}_{12}\text{H}_{10}\text{CdN}_4\text{S}_2$	$\text{C}_7\text{H}_5\text{CdN}_3\text{S}_2$
MW $\text{g}\cdot\text{mol}^{-1}$	386.76	307.66
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$P2_1/n$
$a/\text{\AA}$	7.9395(7)	5.9496(3)
$b/\text{\AA}$	15.2318(8)	12.2417(8)
$c/\text{\AA}$	17.7558(13)	13.8473(7)
$\beta$ (°)	93.632(6)	102.234(4)
$V/\text{\AA}^3$	2142.9(3)	683.34(15)
$T/\text{K}$	293(2)	293(2)
$Z$	6	4
$D_c/\text{g cm}^{-3}$	1.798	2.073
$\mu/\text{mm}^{-1}$	1.811	2.592
Min, max transmission	0.755/0.862	0.6105/0.8281
$\theta_{\text{max}}$ (°)	27.00	26.99
Measured reflections	7448	15 155
Unique reflections	2409	2159
Reflections $[F_0 > 4\sigma(F_0)]$	1888	2026
Parameter	147	119
$R_{\text{int}}$	0.0277	0.0404
$R_1 [F_0 > 4\sigma(F_0)]$	0.0466	0.0218
$wR_2$ [all data]	0.0959	0.0465
GOF	1.128	1.147
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}/\text{e \AA}^{-3}$	0.46, –0.84	0.32, –0.37



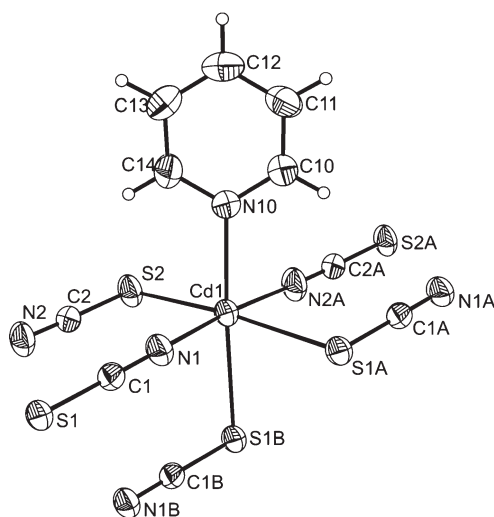


**Fig. 7** Experimental X-ray powder pattern of a mixture of **2-Cd/II** and **2-Cd/III** (A), of this mixture stirred for 1 d (B) and for 3 d in water (D) and powder pattern for **2-Cd/II** (C) and **2-Cd/IV** (E) calculated from single crystal data (the reflections of the all-*trans* product **2-Cd/III** are indicated by arrows).

transformed into **2-Cd/IV** and therefore, this form represents the thermodynamic most stable compound at room-temperature, whereas **2-Cd/II** and **2-Cd/III** are metastable (Fig. 7).

### Crystal structure of $[\text{Cd}(\text{NCS})_2(\text{pyridine})]_n$ (**3-Cd**)

The ligand-deficient 1 : 1 compound  $[\text{Cd}(\text{NCS})_2(\text{pyridine})]_n$  (**3-Cd**) crystallizes in the centrosymmetric space group  $P2_1/n$  with four formula units in the unit cell (Table 2). The asymmetric unit consists of one cadmium(II) cation, two crystallographically independent thiocyanato anions and one pyridine ligand, all of them located in general positions. In the crystal structure the Cd cations are 6-fold coordinated by three *S*- and two *N*-bonded thiocyanato anions and one pyridine ligand (Fig. 8). The Cd–N distances of the thiocyanato anions are comparable but for the Cd–S distances of the two



**Fig. 8** ORTEP plot of **3-Cd** with view of the coordination sphere of the cadmium(II) cation with labeling and displacement ellipsoids drawn at 50% probability level. Symmetry codes:  $A = x + 1, y, z$ ;  $B = -x, -y + 2, -z + 1$ .

**Table 4** Selected bond lengths (Å) and angles (°) for the ligand-deficient 1 : 1 compound **3-Cd**. Symmetry codes:  $A = x + 1, y, z$ ;  $B = -x, -y + 2, -z + 1$

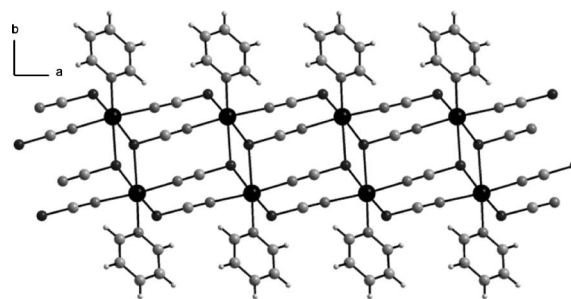
Cd(1)–N(1)	2.306(2)	N(1)–Cd(1)–S(2)	95.40(5)
Cd(1)–N(2A)	2.277(2)	N(2A)–Cd(1)–S(1B)	88.67(6)
Cd(1)–N(10)	2.327(2)	N(10)–Cd(1)–S(1A)	91.99(5)
Cd(1)–S(2)	2.671(1)	S(2)–Cd(1)–S(1B)	90.42(2)
Cd(1)–S(1A)	2.810(1)	S(1B)–Cd(1)–S(1A)	84.24(2)
Cd(1)–S(1B)	2.802(1)	N(10)–Cd(1)–S(1B)	176.22(5)

thiocyanato anions significant differences are observed (Table 4). These distinctions can be traced back to the different coordination modes of the two thiocyanato anions of which one is  $\mu$ -1,3-coordinating, whereas for the other a  $\mu$ -1,1,3-(*S,S,N*)-coordination is observed. Therefore, the Cd–S distances to the latter anion are elongated (Table 4). The angles around the Cd cations are significantly different from the ideal values and the coordination polyhedron can be described as slightly distorted octahedra.

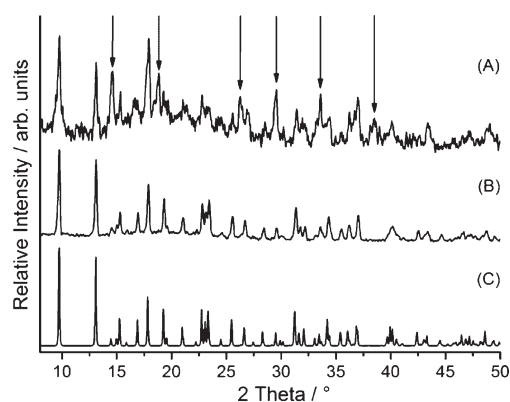
In the crystal structure two neighboring octahedra are connected by two  $\mu$ -1,1-(*S*)-coordinating thiocyanato anions *via* common corners into double octahedra which are located on centers of inversion with a Cd···Cd distance of 4.1626(3) Å (Fig. 9).

These double octahedra are connected *via*  $\mu$ -1,3- and  $\mu$ -1,1,3-(*S,S,N*)-bridging thiocyanato anions into double chains that elongate in the direction of the crystallographic *a*-axis (Fig. 9). The topology of this coordination network is without any precedence in literature. There is only one compound reported in which the metal cation is coordinated by three *S*- and two *N*-bonded thiocyanato anions and one water co-ligand but the coordination mode of the anions is completely different.<sup>69</sup>

Based on the single crystal X-ray data a powder pattern of **3-Cd** was calculated and compared with that obtained for the microcrystalline powder prepared in solution, which proves that the 1 : 1 compound was obtained phase pure (Fig. 10). Moreover, it can also be shown that the residue obtained in the second TG step in thermal decomposition reaction of **1-Cd** consists of **3-Cd** even if it is contaminated with cadmium thiocyanate and this explains why the results of the elemental analysis of this residue is not in good agreement with that calculated (Fig. 10).



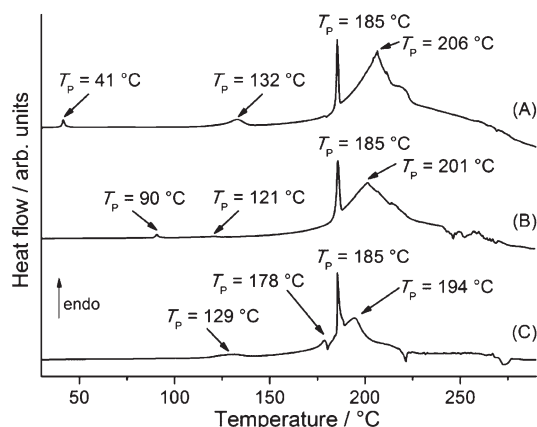
**Fig. 9** Crystal structure of **3-Cd** with view along the crystallographic *c*-axis (black = cadmium(II), dark grey = sulfur, grey = nitrogen, light-grey = carbon, white = hydrogen).



**Fig. 10** X-Ray powder pattern of the residue formed after the second TG step in the thermal decomposition reaction of **1-Cd** (A), experimental X-ray powder pattern of **3-Cd** obtained from solution (B) and powder pattern for **3-Cd** calculated from single crystal data (C). The reflections of  $\text{Cd}(\text{NCS})_2$  present in A are indicated by arrows.

### Investigations using differential scanning calorimetry and temperature dependent X-ray powder diffraction

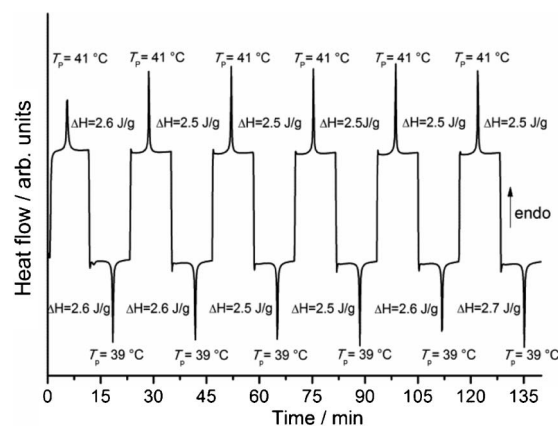
The investigations mentioned above clearly show that the *cis-cis-trans* compound **2-Cd/IV** is the thermodynamic stable form at room-temperature, whereas the all-*cis* and all-*trans* products are metastable and that **2-Cd/III** can only be obtained at high temperatures. To prove if one of the three forms can be transformed into each other on heating, measurements using differential scanning calorimetry (DSC) were performed. If the 1 : 4 compound **1-Cd** is investigated there are no hints for the formation of any further intermediates before this compound transforms into **2-Cd/III** (Fig. S7 in the ESI†). In contrast, on heating the metastable all-*cis* compound **2-Cd/II** two endothermic peaks of very low intensity at 41 °C and 132 °C are observed before decomposition into a mixture of the 1 : 1 compound **3-Cd** and  $\text{Cd}(\text{NCS})_2$  is observed at 185 °C (Fig. 11:A). In further investigations the reversibility of these thermic events were checked by consecutive heating and cooling cycles, which shows that both events are partly reversible (Fig. S8 in the ESI†). DSC measurements on the metastable all-*trans* product **2-Cd/III** also



**Fig. 11** Differential scanning calorimetry (DSC) measurements for **2-Cd/II** (A), **2-Cd/III** (B) and **2-Cd/IV** (C). Heating rate 3 °C min<sup>-1</sup>; N<sub>2</sub> atmosphere; T<sub>p</sub> = peak T/°C.

show two endothermic transformations at 90 °C and 121 °C before decomposition is observed and similar measurements on the reversibility of these events also reveal that they are nearly reversible with a small hysteresis (Fig. 11:B and Fig. S9 in the ESI†). Finally, for the thermodynamic most stable form **2-Cd/IV** one endothermic signal at 129 °C is observed before decomposition that is quasi-reversible, indicating the transformation into a new form (Fig. 11:C and Fig. S10 in the ESI†).

In additional DSC measurements all intermediates formed in the different reactions were isolated and investigated by X-ray powder diffraction. These investigations clearly prove that some of the reactions are fully reversible whereas in some other experiments residues are obtained that exhibit powder patterns significantly different to that of the pristine material (Fig. S11, Fig. S12 and Fig. S13 in the ESI†). Unfortunately these powder patterns are of low quality and therefore, cannot be indexed. In any case these thermal investigations strongly indicate that additional crystalline phases of composition  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$  will exist. Finally, as mentioned above the crystalline residue obtained after heating **2-Cd/II** to 50 °C shows a powder pattern that is identical to that of the pristine material indicating that this reaction is fully reversible (Fig. S11 in the ESI†). Moreover, because this reaction is accompanied with an exchange of heat a transition of second order can be excluded and this reaction might proceed by first order *via* nucleation and growth of a new phase. To investigate this reaction in more detail, successive heating and cooling cycles were measured which clearly prove that no hysteresis is observed and that the heat flow remains unchanged within 5 cycles (Fig. 12). This is surprising because for a first order transition one would expect at least some kind of exhausting transition, which is clearly not observed. Moreover, in most polymorphic transitions no full reversibility is observed and selected single crystals transform into a crystalline powder even if the crystal habit is unchanged. To investigate this transformation in more detail a full data set was measured for a single crystal of **2-Cd/II** at room-temperature and at 70 °C. Inspection of the reciprocal space shows that distinct reflections are present in addition to a large amount of diffuse scattering. Moreover, during heating the scattering power of the crystal dramatically decreases. Dependent on the



**Fig. 12** Differential scanning calorimetry (DSC) measurement: reversibility of compound **2-Cd/II**. Heating rate 3 °C min<sup>-1</sup>; N<sub>2</sub> atmosphere; T<sub>p</sub> = peak T/°C.

reflections used for indexing different unit cells were obtained but in none of them the structure can be solved.

### Infrared spectroscopic investigations

To check if the coordination mode of the thiocyanato anions can also be verified by IR spectroscopy additional investigations were performed. In compounds where the thiocyanato anions are terminal *N*-bonded the asymmetric  $\nu_{\text{as}}(\text{CN})$  vibration is expected to be at about  $2050\text{ cm}^{-1}$ , whereas for  $\mu$ -1,3-bridging thiocyanato anions the asymmetric  $\nu_{\text{as}}(\text{CN})$  vibration is shifted to higher values of about  $\geq 2100\text{ cm}^{-1}$ .<sup>58</sup> For the ligand-rich precursor  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_4]$  (**1-Cd**) only one band is observed at  $2054\text{ cm}^{-1}$ , which is in very good agreement with that expected for terminal *N*-bonded thiocyanato anions (Table 5). In the crystal structure of the ligand-deficient 1 : 2 compounds where only  $\mu$ -1,3-bridging thiocyanato anions are present the asymmetric stretching vibrations are observed between  $2089\text{ cm}^{-1}$  and  $2107\text{ cm}^{-1}$ . For the ligand-deficient 1 : 1 compound  $[\text{Cd}(\text{NCS})_2(\text{pyridine})]_n$  (**3-Cd**) both  $\mu$ -1,3- and  $\mu$ -1,1,3-(*S,S,N*)-bridging thiocyanato anions are present, which is indicated by two different values for  $\nu_{\text{as}}(\text{CN})$  at  $2105\text{ cm}^{-1}$  and  $2120\text{ cm}^{-1}$ , of which the latter should correspond to those anions that are  $\mu$ -1,1,3-(*S,S,N*)-coordinated (Table 5 and Fig. S14–S18 in the ESI†). Unfortunately these investigations clearly show that one cannot differ between the all-*cis*, all-*trans* and *cis-cis-trans* coordination.

However, if the values of the 1 : 4 compound **1-Cd** are compared with that of the isostructural compounds with paramagnetic metal cations it is obvious that manganese behaves similar to cadmium and that a continuous increase is observed from Mn to Ni. The same trend is observed for the 1 : 2 compounds in which a shift of about  $20\text{ cm}^{-1}$  is observed from Cd to Ni (Table 5). Surprisingly, the value for the Ni compound with only  $\mu$ -1,3-bridging anions is shifted to a range observed for the 1 : 1 compound **3-Cd** in which in addition  $\mu$ -1,1,3-(*S,S,N*) coordination is observed. These results clearly show that the values reported in literature for the coordination modes of the thiocyanato anions are not generally valid and the results of IR spectroscopic measurements should always carefully be analyzed.

**Table 5** Values of the  $\nu_{\text{as}}(\text{CN})$  stretching vibration in **1-Cd**, **2-Cd/II**, **2-Cd/III**, **2-Cd/IV**, **3-Cd** and related compounds of composition  $[\text{M}(\text{NCS})_2(\text{pyridine})_4]$  and  $[\text{M}(\text{NCS})_2(\text{pyridine})_2]_n$  ( $\text{M} = \text{Mn}, \text{Fe}, \text{Co}$  and  $\text{Ni}$ ) retrieved from literature but reinvestigated for comparison.<sup>53,54</sup> Please note that the coordination topology of the paramagnetic 1 : 2 compounds is the same as in **2-Cd/III**

Compound	$\nu_{\text{as}}(\text{CN})/\text{cm}^{-1}$
$[\text{Cd}(\text{NCS})_2(\text{pyridine})_4]$ ( <b>1-Cd</b> )	2054
$[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$ ( <b>2-Cd/II</b> )	2089 and 2107
$[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$ ( <b>2-Cd/III</b> )	2093
$[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$ ( <b>2-Cd/IV</b> )	2089
$[\text{Cd}(\text{NCS})_2(\text{pyridine})]_n$ ( <b>3-Cd</b> )	2105 and 2120
$[\text{Mn}(\text{NCS})_2(\text{pyridine})_4]$	2060
$[\text{Fe}(\text{NCS})_2(\text{pyridine})_4]$	2066
$[\text{Co}(\text{NCS})_2(\text{pyridine})_4]$	2073
$[\text{Ni}(\text{NCS})_2(\text{pyridine})_4]$	2082
$[\text{Mn}(\text{NCS})_2(\text{pyridine})_2]_n$	2090
$[\text{Fe}(\text{NCS})_2(\text{pyridine})_2]_n$	2093
$[\text{Co}(\text{NCS})_2(\text{pyridine})_2]_n$	2099
$[\text{Ni}(\text{NCS})_2(\text{pyridine})_2]_n$	2110

### Conclusions

In the present work we have shown that the thermal decomposition is an elegant route for the discovery and preparation of new ligand-deficient compounds, in which the metal cations are bridged by thiocyanato anions. In the present case a compound is obtained, in which an all-*trans* orientation of the anionic ligands is observed. Interestingly, this kind of coordination is usually observed in bridging thiocyanato coordination polymers, but in this case it is clearly metastable at room-temperature. In solution **2-Cd/III** transforms into **2-Cd/II** in which an all-*cis* coordination is observed but even this form is thermodynamic metastable at room-temperature because a transformation in **2-Cd/IV** is observed, in which an alternating *cis-cis-trans* arrangement is found. It is noted that the coordination mode of the anions in **2-Cd/I** reported recently is unknown because no atomic coordinates are given. However, in all of our investigations we never observed this crystalline phase.

We also have shown that by thermal decomposition reactions a most ligand-deficient 1 : 1 compound **3-Cd** was explored, which in this case cannot be obtained as phase pure material. However, this compound can simply be obtained from solution. In compound **3-Cd** an unusual 1D coordination topology is observed, which is without any precedence in literature. Based on our results we investigated if a similar compound can be obtained by thermal decomposition or by conventional solution reactions with the paramagnetic metals Mn, Fe, Co and Ni, which in this case is not possible. Obviously, a  $\mu$ -1,1,3-(*S,S,N*)-coordination with these hard metals is energetically less favored. Nevertheless, in previous work we have reported several examples, where corresponding ligand-deficient paramagnetic thio- and selenocyanato coordination polymers prepared by thermal decomposition were identified by crystallizing their cadmium thiocyanato analogues in solution.

### Experimental section

$\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ , pyridine and  $\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$  were obtained from Alfa Aesar and Merck, respectively. All chemicals were used without further purification.  $\text{Cd}(\text{NCS})_2$  was prepared by a 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 resulting precipitate of  $\text{BaSO}_4$  was filtered off and the filtrate was concentrated to complete dryness resulting in a white residue of  $\text{Cd}(\text{NCS})_2$ . The purity was checked by XRPD and CHNS analysis. All crystalline powders were prepared by stirring the reactants in solution at room temperature. The residues were filtered off and washed with water and diethyl ether and dried in air.

**Synthesis of  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_4]$  (**1-Cd**).** A white crystalline powder was obtained by the reaction of  $\text{Cd}(\text{NCS})_2$  (342 mg, 1.5 mmol) and pyridine (484  $\mu\text{L}$ , 6.0 mmol) in 3 mL water. Yield based on  $\text{Cd}(\text{NCS})_2$ : 802 mg (98.2%). CHNS analysis for  $\text{C}_{22}\text{H}_{20}\text{CdN}_6\text{S}_2$  (544.97): calcd. C 48.49, H 3.70, N 15.42, S 11.77; found C 48.18, H 3.81, N 15.82, S 11.33. IR (ATR):  $\nu_{\text{max}} = 3058$  (w), 2098 (m), 2054 (s), 1597 (s), 1571 (w), 1485 (m), 1443 (s), 1213 (m), 1149 (w), 1069 (m), 1035 (m), 1006 (m), 764 (m), 711 (m), 699 (s), 624 (m)  $\text{cm}^{-1}$  (Fig. S14 in the ESI†).



**Synthesis of  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$  (2-Cd/II).** White needle-shaped single-crystals suitable for X-ray structure determination were obtained by a reaction of  $\text{Cd}(\text{NCS})_2$  (11.4 mg, 0.05 mmol) and pyridine (2  $\mu\text{L}$ , 0.025 mmol) and 1.5 mL water and 1.5 mL diethylether in a snap-cap vial after one day.

A white crystalline powder was obtained by the reaction of  $\text{Cd}(\text{NCS})_2$  (114 mg, 0.5 mmol) and pyridine (20  $\mu\text{L}$ , 0.25 mmol) in 3 mL water after 1 d at room temperature. Yield based on  $\text{Cd}(\text{NCS})_2$ : 92.73 mg (95.9%). CHNS analysis for  $\text{C}_{12}\text{H}_{10}\text{CdN}_4\text{S}_2$  (386.77): calcd. C 37.27, H 2.61, N 14.49, S 16.58; found C 37.47, H 2.50, N 14.48, S 16.57. IR (ATR):  $\nu_{\text{max}}$  = 2107 (s), 2089 (s), 1597 (m), 1485 (m), 1440 (s), 1217 (m), 1149 (m), 1071 (m), 1034 (m), 1007 (m), 928 (w), 749 (m), 690 (s), 625 (m), 463 (m), 415 (m)  $\text{cm}^{-1}$  (Fig. S15 in the ESI†).

**Synthesis of  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$  (2-Cd/III).** This compound cannot be prepared in solution. However, a white crystalline powder was obtained as a residue in the first TG step of the thermal decomposition reaction of **1-Cd**. CHNS analysis for  $\text{C}_{12}\text{H}_{10}\text{CdN}_4\text{S}_2$  (386.77): calcd. C 37.27, H 2.61, N 14.49, S 16.58; found C 37.50, H 2.42, N 14.37, S 16.91. IR (ATR):  $\nu_{\text{max}}$  = 2093 (s), 1597 (m), 1484 (m), 1441 (s), 1241 (m), 1149 (m), 1068 (m), 1034 (m), 1007 (m), 932 (w), 752 (m), 693 (s), 625 (m), 462 (m), 415 (m)  $\text{cm}^{-1}$  (Fig. S16 in the ESI†).

**Synthesis of  $[\text{Cd}(\text{NCS})_2(\text{pyridine})_2]_n$  (2-Cd/IV).** White block-shaped single-crystals suitable for X-ray structure determination were obtained by a reaction of  $\text{Cd}(\text{NCS})_2$  (11.4 mg, 0.05 mmol) and pyridine (2  $\mu\text{L}$ , 0.025 mmol) and 1.5 mL water and 1.5 mL diethylether in a snap-cap vial after one week.

A white crystalline powder was obtained by the reaction of  $\text{Cd}(\text{NCS})_2$  (114 mg, 0.5 mmol) and pyridine (20  $\mu\text{L}$ , 0.25 mmol) in 3 mL water after 3 d at room temperature. Yield based on  $\text{Cd}(\text{NCS})_2$ : 92.73 mg (95.9%). CHNS analysis for  $\text{C}_{12}\text{H}_{10}\text{CdN}_4\text{S}_2$  (386.77): calcd. C 37.27, H 2.61, N 14.49, S 16.58; found C 37.28, H 2.46, N 14.41, S 16.86. IR (ATR):  $\nu_{\text{max}}$  = 2089 (s), 1597 (m), 1484 (w), 1440 (m), 1217 (m), 1148 (m), 1071 (m), 1035 (m), 1007 (m), 748 (m), 688 (s), 623 (m), 462 (m), 415 (m)  $\text{cm}^{-1}$  (Fig. S17 in the ESI†).

**Synthesis of  $[\text{Cd}(\text{NCS})_2(\text{pyridine})]_n$  (3-Cd).** White block-shaped single-crystals suitable for X-ray structure determination were obtained by the reaction of  $\text{Cd}(\text{NCS})_2$  (22.8 mg, 0.10 mmol) and pyridine (12  $\mu\text{L}$ , 0.15 mmol) and 1 mL water in a snap-cap vial after a few days.

A white crystalline powder was obtained by the reaction of  $\text{Cd}(\text{NCS})_2$  (228 mg, 1.0 mmol) and pyridine (120  $\mu\text{L}$ , 1.5 mmol) in 3 mL water. Yield based on  $\text{Cd}(\text{NCS})_2$ : 289 mg (94.1%). CHNS analysis for  $\text{C}_7\text{H}_5\text{CdN}_3\text{S}_2$  (307.66): calcd. C 27.33, H 1.64, N 13.66, S 20.84; found C 26.91, H 1.45, N 13.16, S 20.83. IR (ATR):  $\nu_{\text{max}}$  = 2120 (s), 2105 (s), 1600 (m), 1487 (w), 1441 (m), 1217 (m), 1152 (w), 1073 (m), 1037 (m), 1012 (m), 748 (m), 691 (s), 628 (m), 452 (m)  $\text{cm}^{-1}$  (Fig. S18 in the ESI†).

**Differential thermal analysis, thermogravimetry, and mass spectroscopy (DTA-TG-MS).** The heating-rate dependent DTA-TG measurements were performed in a nitrogen atmosphere (purity: 5.0) in  $\text{Al}_2\text{O}_3$  crucibles using a STA-409CD instrument from Netzsch. The DTA-TG-MS measurements were performed

with the same instrument, which is connected to a quadrupole mass spectrometer from Balzers *via* Skimmer coupling from Netzsch. The MS measurements were performed in analogue and trend scan mode in  $\text{Al}_2\text{O}_3$  crucibles in a dynamic helium atmosphere (purity: 5.0) using heating rates of 4  $^\circ\text{C min}^{-1}$ . All measurements were performed with a flow rate of 75  $\text{mL min}^{-1}$  and were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

**Single-crystal structure analysis.** The single-crystal structure investigations were performed with an imaging plate diffraction system (IPDS-2 for **3-Cd** and **2-Cd/IV**) with Mo-K $\alpha$ -radiation from STOE & CIE. The structure refinements were performed against  $|F|^2$  using SHELXL-97.<sup>70</sup> A numerical absorption correction was performed using X-Red Version 1.31 and X-Shape Version 2.11 of the program package X-Area.<sup>71,72</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = -1.2 \cdot U_{\text{eq}}(\text{C})$ ] using a riding model. Details of the structure determination are given in Table 2.

CCDC-872125 (**2-Cd/III**), CCDC-872124 (**2-Cd/IV**) and CCDC-872126 (**3-Cd**) contain 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/>.

**Rietveld refinement.** The structure model for compound **2-Cd/III** was obtained from the isotypic compound  $[\text{Mn}(\text{NCS})_2(\text{pyridine})_2]_n$ .<sup>53</sup> The Rietveld refinement was performed using Fullprof2k with the Winplotr software package.<sup>73,74</sup> After the initial refinements of the scale factors, zero-point, unit cell parameters, and profile parameters, the atomic positions were refined with soft constraints for the anionic ligand. All atoms were refined isotropically, and the hydrogen atoms were not considered. Details of the structure refinements are given in Table 1. For difference plots of the Rietveld refinement see Fig. S1 in the ESI†.

**Differential scanning calorimetry.** The DSC experiments were performed using a DSC 1 Star System with STARe Excellence Software from Mettler-Toledo AG.

**X-Ray powder diffraction (XRPD).** XRPD experiments were performed using 1) a PANalytical X'Pert Pro MPD Reflection Powder Diffraction System with Cu-K $\alpha$ -radiation ( $\lambda = 1.5406 \text{ \AA}$ ) that is equipped with a PIXcel semiconductor detector from PANalytical and 2) a Stoe Transmission Powder Diffraction System with Cu-K $\alpha$ -radiation ( $\lambda = 1.5406 \text{ \AA}$ ) from STOE & CIE, which is equipped with a linear position-sensitive detector (Delta 2 $\theta = 6.5\text{--}7^\circ$ ) from STOE & CIE and an Image Plate Detector (scan range overall: 0–127 $^\circ$ ).

**CHNS analysis.** CHNS analyses were performed using an EURO EA elemental analyzer, fabricated by EURO VECTOR Instruments and Software.

**Spectroscopy.** IR spectra were recorded on an Alpha IR spectrometer from Bruker equipped with a Platinum ATR QuickSnap<sup>TM</sup> sampling module between 4000–375  $\text{cm}^{-1}$ .



## Acknowledgements

This project was supported by the *Deutsche Forschungsgemeinschaft* (project: NA 720/3-1) and the *State of Schleswig-Holstein*. Special thanks to Inke Jess for her support in the single crystal measurements, and Professor Dr Wolfgang Bensch for the opportunity to use his experimental facility.

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