

# Synthesis, Crystal Structures and Polymorphism of New Cadmium and Zinc Thio- and Selenocyanato Coordination Compounds with 4-Acetylpyridine as *N*-Donor Ligand

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*Dedicated to Professor Heinrich Nöth on the occasion of his 85<sup>th</sup> birthday*

Reactions of cadmium(II) thio- and selenocyanate with 4-acetylpyridine in different molar ratios and in different solvents always lead to the formation of compounds of composition  $\text{Cd}(\text{NCS})_2(4\text{-acetylpyridine})_2$  (**Cd1-I**) and  $\text{Cd}(\text{NCSe})_2(4\text{-acetylpyridine})_2$  (**Cd2**). Both compounds are isotypic and crystallize in the monoclinic space group  $C2/c$ . In their crystal structures the Cd cations are coordinated by two *N*-bonded 4-acetylpyridine ligands as well as two *N*- and two *S/Se*-bonded thio- or selenocyanato anions within a slightly distorted octahedral geometry. The Cd cations are linked into chains by pairwise  $\mu$ -1,3-coordinating thio- or selenocyanato anions. In one reaction single crystals of a second polymorphic modification of composition  $\text{Cd}(\text{NCS})_2(4\text{-acetylpyridine})_2$  (**Cd1-II**) were obtained by accident. This modification crystallizes monoclinically in space group  $P2_1/c$ , exhibits the same topology of the coordination network as in **Cd1-I** and **Cd2** but a different arrangement of the chains in the crystal. Similar investigations with Zn(II) have revealed that only one compound of composition  $\text{Zn}(\text{NCS})_2(4\text{-acetylpyridine})_2$  can be prepared that crystallizes in the triclinic space group  $P\bar{1}$ . Its structure consists of discrete complexes in which the Zn(II) cations are tetrahedrally coordinated. A corresponding selenocyanato coordination compound could not be prepared.

**Key words:** Synthesis, Thio- and Selenocyanato Coordination Compounds, Crystal Structures, Thermoanalytical Measurements

## Introduction

Investigations on the synthesis, structures and properties of new coordination polymers are still an active field of chemical research [1 – 7]. In this context compounds that show cooperative magnetic properties are of importance, which can be prepared if paramagnetic transition metal cations are linked by, *e.g.*, small-sized anionic ligands that can mediate magnetic exchange interactions [8 – 12]. Consequently, a large number of such compounds were prepared in recent years based on oxalates, azides, formates and other ligands, and some selected examples are given in the reference list [13 – 19]. In contrast, transition metal thio- and selenocyanates in which the metal cations are linked by the anionic ligands are less well known, and most of the reported compounds have structures in which the anions are only terminally *N*-bonded [20 – 28]. This might be traced back to the fact that hard metal cations

like *e.g.* Mn, Fe, Co and Ni are less chalcophilic and therefore, the synthesis of compounds with  $\mu$ -1,3-bridging thio- or selenocyanato anions is sometimes difficult to achieve.

To overcome this problem we have established an alternative procedure in which coordination compounds with *N*-terminally bonded thio- and selenocyanato anions and additional neutral *N*-donor co-ligands are thermally decomposed leading to the formation of new coordination polymers in which the cations are octahedrally coordinated and linked by  $\mu$ -1,3-bridging anions [29 – 31]. Within this project we have prepared several compounds that show different magnetic properties including single-chain magnetic behavior [32 – 39]. Unfortunately, on thermal decomposition only microcrystalline compounds are obtained that are not suitable for single-crystal structure determination. However, in some cases this problem can be solved if similar compounds based on the more chal-

cophilic cadmium(II) are prepared, which can easily be crystallized, and for which several compounds are reported in which the Cd cations are linked into different coordination networks by the thio- and selenocyanato anions [40–44]. In several cases these compounds are isotopic to the paramagnetic analogs and therefore, the latter can be identified by powder X-ray diffraction. In this context it should be noted that on thermal decomposition of Co compounds sometimes tetrahedrally coordinated intermediates are observed that can be identified with a similar procedure using the corresponding Zn(II) compounds as structural analogs because this diamagnetic metal cation frequently favors a tetrahedral coordination [45–49]. This is the reason why we have started systematic investigations on the synthesis, the structures and the properties of thio- and selenocyanato coordination compounds based on Cd(II) and Zn(II) [43, 50–52].

In the course of our project we also tried to prepare paramagnetic coordination polymers based on the monodentate ligand 4-acetylpyridine. Unfortunately, on thermal decomposition of compounds of composition  $M(NCS)_2(4\text{-acetylpyridine})_4$  ( $M = \text{Mn, Fe, Co, Ni}$ ) several different crystalline phases of composition  $M(NCS)_2(4\text{-acetylpyridine})_2$  are obtained that so far could not be identified. These investigations have also shown that different polymorphic modifications or isomers might be formed on thermal decomposition, as also reported in the literature [53–60]. In order to check if compounds can be obtained that might be isotopic to the paramagnetic analogs we prepared coordination compounds based on  $\text{Cd}(\text{NCS})_2$  and  $\text{Zn}(\text{NCS})_2$  using 4-acetylpyridine as a co-ligand. Here we report on our investigations.

## Results and Discussion

### Synthetic investigations

To provide a broader basis for our study,  $\text{Cd}(\text{NCS})_2$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{KNCSe}$  were reacted in different molar ratios with 4-acetylpyridine in water, ethanol, methanol and acetonitrile, and the resulting precipitates were investigated by XRPD measurements. These investigations have shown that always one crystalline phase is found with  $\text{Cd}(\text{NCS})_2$  and  $\text{Cd}(\text{NCSe})_2$  that might be isotopic. Elemental analyses suggested that the composition of these compounds is  $\text{Cd}(\text{NCS})_2(4\text{-acetylpyridine})_2$  (**Cd1**)

and  $\text{Cd}(\text{NCSe})_2(4\text{-acetylpyridine})_2$  (**Cd2**) and IR-spectroscopic investigations showed the asymmetric CN stretching vibration for **Cd1** at  $2091\text{ cm}^{-1}$  and for **Cd2** at  $2098\text{ cm}^{-1}$  indicating that  $\mu$ -1,3-bridging thio-cyanato anions are present [61–64].

Similar investigations have revealed that the reaction of  $\text{Zn}(\text{NCS})_2$  with 4-acetylpyridine always leads to the formation of a compound of composition  $\text{Zn}(\text{NCS})_2(4\text{-acetylpyridine})_2$  (**Zn1**). The asymmetric CN stretching vibration band appears at  $2063\text{ cm}^{-1}$  indicating that in contrast to the Cd compounds **Cd1-I** and **Cd2** only terminally *N*-bonded thiocyanato anions are present [61–64]. Therefore, it is highly likely that this compound consists of discrete complexes in which the Zn cations are tetrahedrally coordinated by two *N*-bonded thiocyanato anions and two 4-acetylpyridine ligands. In contrast, coordination compounds based on zinc selenocyanate could not be prepared. All precipitates obtained were unstable and decomposed immediately into elemental selenium and some crystalline phases that could not be identified.

To investigate the Cd compounds in more detail, single crystals were grown and investigated by X-ray diffraction. In the course of these investigations a few single crystals of a second modification of  $\text{Cd}(\text{NCS})_2(4\text{-acetylpyridine})_2$  (**Cd1-II**) were obtained by accident.

### Crystal structures of the Cd(II) compounds

$[\text{Cd}(\text{NCS})_2(4\text{-acetylpyridine})_2]_n$  (**Cd1-I**) and  $[\text{Cd}(\text{NCSe})_2(4\text{-acetylpyridine})_2]_n$  (**Cd2**) are isotopic and crystallize in the monoclinic centrosymmetric space group  $C2/c$  with four formula units in the unit cell. The asymmetric units consist of one Cd(II) cation that is located on a center of inversion as well as of one 4-acetylpyridine ligand and one thiocyanato anion in general positions. The cadmium cations are each coordinated by two N atoms of two symmetry-related 4-acetylpyridine ligands as well as by two *N*- and two *S*- respectively *Se*- bonded anionic ligands in a slightly distorted octahedral geometry (Fig. 1: left and Table 1). As expected, the Cd–N and Cd–S/Se bond lengths to the anionic ligands are longer in the selenium compound, but surprisingly the Cd–N bond lengths to the 4-acetylpyridine ligand is not affected (Table 1). Bond lengths and angles are in good agreement with values reported in the literature [43, 44, 51, 52].

Table 1. Selected bond lengths (Å) and angles (deg) for **Cd1-I**, **Cd1-II** and **Cd2**. For symmetry codes see caption to Fig. 1.

	<b>Cd1-I</b>	<b>Cd1-II</b>	<b>Cd2</b>
Cd(1)–N(1)	2.301(4)	2.274(3)	2.328(4)
Cd(1)–N(11)	2.362(5)	2.396(3)	2.362(5)
Cd(1)–S(1B)	2.7424(16)	2.7472(10)	2.8129(6)
N(1)–Cd(1)–N(11)	89.81(16)	87.68(12)	N(1)–Cd(1)–N(11)
N(1)–Cd(1)–N(11A)	90.19(16)	92.32(12)	N(1)–Cd(1)–N(11A)
N(1)–Cd(1)–S(1B)	86.24(12)	87.20(8)	N(1)–Cd(1)–Se(1B)
N(1)–Cd(1)–S(1C)	93.76(12)	92.80(8)	N(1)–Cd(1)–Se(1C)
N(11)–Cd(1)–S(1C)	90.74(12)	91.29(8)	N(11)–Cd(1)–Se(1C)
N(11A)–Cd(1)–S(1C)	89.26(12)	88.71(8)	N(11A)–Cd(1)–Se(1C)

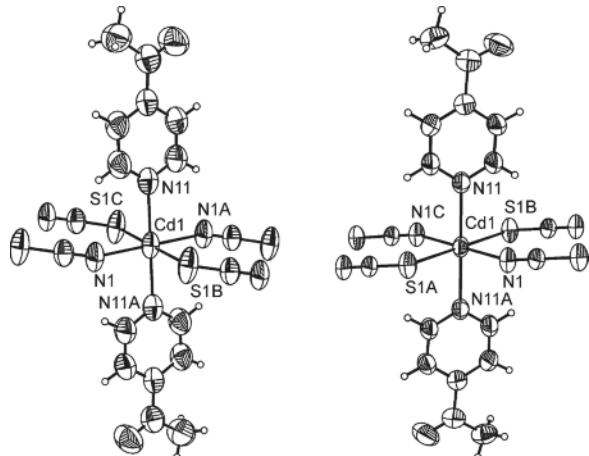


Fig. 1. Crystal structures of **Cd1-I** (left) and **Cd1-II** (right) with labeling and displacement ellipsoids drawn at the 50 % probability level. Symmetry codes: A:  $-x, -y, -z$ ; B:  $x, y + 1, z$ ; C:  $-x, y - 1, -z$  (**Cd1-I**) and A:  $-x + 1, -y + 1, -z$ ; B:  $x + 1, y, z$ ; C:  $-x, -y + 1, -z$  (**Cd1-II**).

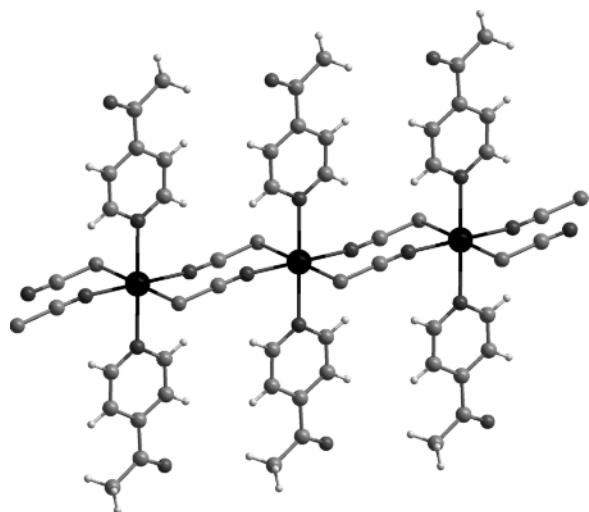


Fig. 2. Crystal structure of compound **Cd1-I**. View of the chains running in the direction of the crystallographic *b* axis.

The second modification of  $[\text{Cd}(\text{NCS})_2(4\text{-acetylpyridine})_2]_n$  (**Cd1-II**) crystallizes in the monoclinic centrosymmetric space group  $P2_1/c$  with two formula units per cell. The asymmetric unit consists of a Cd(II) cation that is located on a center of inversion as well as one 4-acetylpyridine ligand and one thiocyanato anion in general positions. The Cd coordination is identical to that in **Cd1-I** in that the cations are coordinated by two *trans*-oriented 4-acetylpyridine ligands and two S as well as two N atoms of  $\mu$ -1,3-bridging thiocyanato anions. Bond lengths and angles in both modifications are similar, but the Cd–N bond lengths to the anion are shortened, whereas that to the co-ligand are slightly elongated (Table 1).

The Cd cations are linked into chains by pairs of centrosymmetric  $\mu$ -1,3-bridging anionic ligands (Fig. 2). Within these chains all ligands are *trans*-oriented. This is a well known structural motif for thio- or selenocyanato coordination compounds with monodentate ligands and has been observed in a number of related compounds [43, 44, 51, 52].

Structural differences between the modifications **Cd1-I** and **Cd1-II** are found predominantly in the coordination environment of the Cd cations, which is

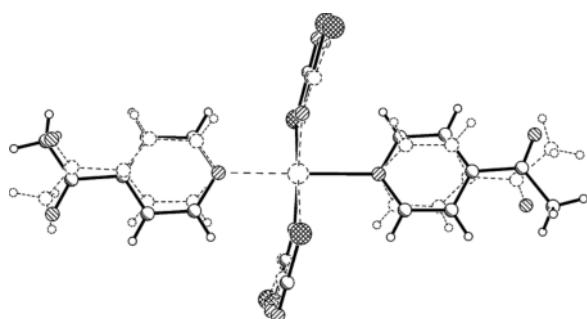


Fig. 3. Structural overlay plot for **Cd1-I** and **Cd1-II**.

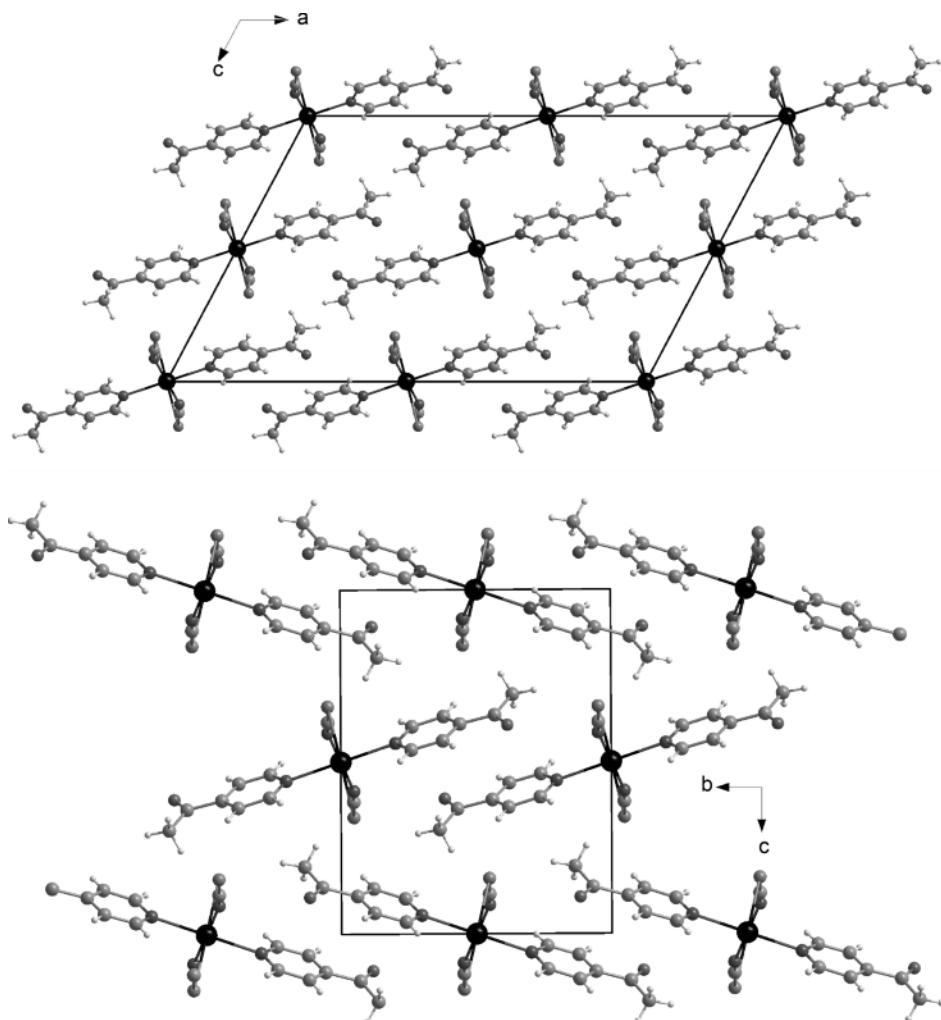


Fig. 4. Crystal structure of **Cd1-I**, viewed along the crystallographic *b* axis (top), and of **Cd1-II** as viewed along the crystallographic *a* axis (bottom).

obvious if their structures are fitted onto each other (Fig. 3). In each polymorph the 4-acetylpyridine oxygen atoms point in opposite directions as required by symmetry.

Structural differences are also found in the packing of the cadmium thiocyanato chains. In **Cd1-I** the thiocyanato chains extend in the direction of the crystallographic *b* axis (Fig. 4, top), whereas in form **Cd1-II** the chains point in the direction of the crystallographic *a* axis (Fig. 4, bottom). Moreover, in form **Cd1-I** the  $\text{Cd}(4\text{-acetylpyridine})_2$  units are parallel to each other, whereas in form **Cd1-II** they show a herringbone-like arrangement (Fig. 4).

Based on the results of the single-crystal structure determinations, powder X-ray patterns for the thiocyanato compound **Cd1-I** and the selenocyanato compound **Cd2** were calculated and compared with those measured. The results prove that both compounds are obtained as single-crystalline phases (Fig. 5).

#### *Thermoanalytical investigations and crystallization experiments on Cd1-I*

In order to check if form **I** of **Cd1** transforms into form **II** on heating, experiments using simultaneous differential thermoanalysis and thermogravime-

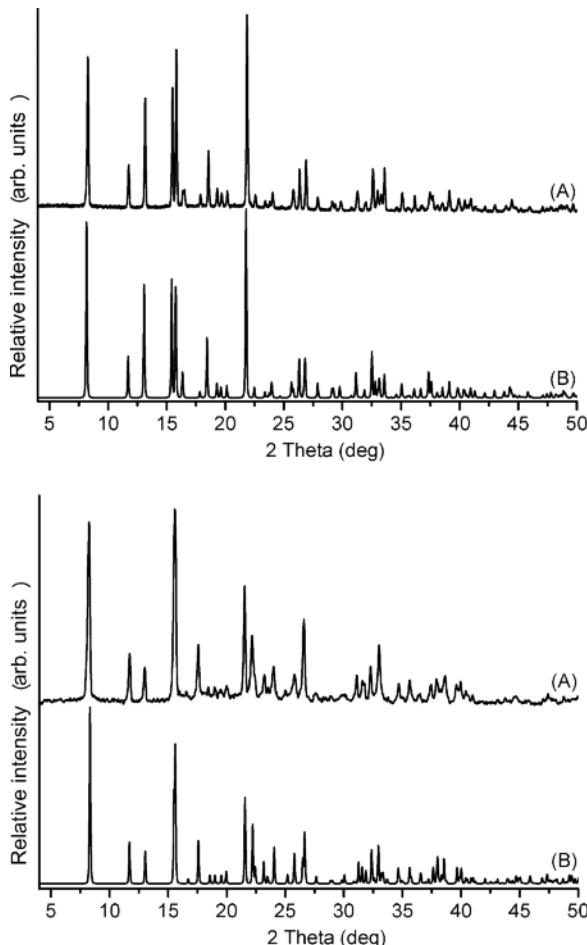


Fig. 5. Experimental powder X-ray patterns of **Cd1-I** (top: A) and of **Cd-2** (bottom: A) together with the powder patterns calculated from single-crystal data (bottom: B).

try (DTA-TG) were performed. On heating compound **Cd1-I** in a thermobalance a continuous mass loss is observed, which is accompanied by an endothermic event at about 200 °C observed in the DTA curve. This mass step is not completely finished up to 450 °C (Fig. 6). If the experimental mass loss is compared with that calculated for the removal of all 4-acetylpyridine ligands it is obvious that the removal of all ligands ( $\Delta m_{\text{calcd.}} = -51.4\%$ ) and the decomposition of Cd(NCS)<sub>2</sub> occur simultaneously. There is no hint for a polymorphic transformation prior to decomposition.

However, because the energies of polymorphic transformations are usually low, additional measure-

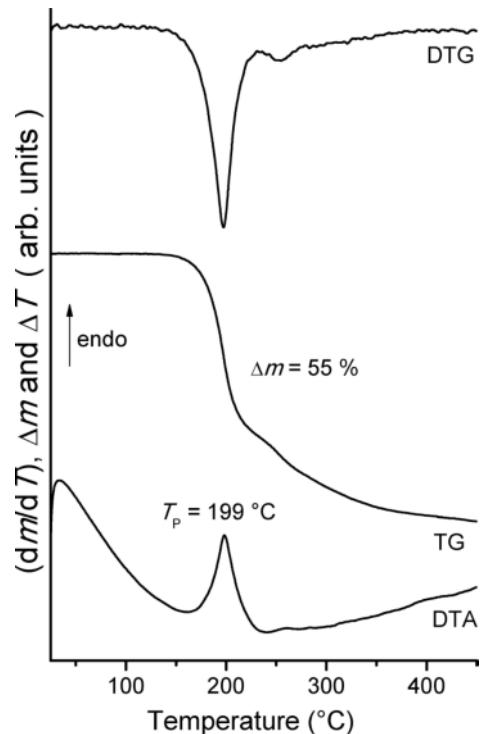


Fig. 6. DTG, TG and DTA curves for **Cd1-I** (heating rate = 4 °C min<sup>-1</sup>; given are the mass changes (%) and the peak temperature  $T_p$  in °C).

ments using differential scanning calorimetry were performed on **Cd-1** (Fig. 7). On heating decomposition starts at an onset temperature of about 203 °C, which is in good agreement with the result of the DTA-TG measurements but even here, no indications for a transition from form **I** into form **II** were observed.

To investigate if form **II** of **Cd1** can be obtained by kinetic control, Cd(NCS)<sub>2</sub> and 4-acetylpyridine were mixed in water, ethanol, methanol, and acetonitrile, and the product was immediately filtered off after formation of a precipitate. When the experimental pattern was compared with those calculated for both forms, it was obvious that **Cd1-I** had formed as a pure crystalline phase. Therefore, we have found no access to form **II**, and it can be assumed that it is metastable at room temperature. Based on the crystallographic density of both forms, which is higher for form **II**, it might be possible that this modification is more stable at lower temperatures, but several exceptions are known from the so-called density rule [65, 66].

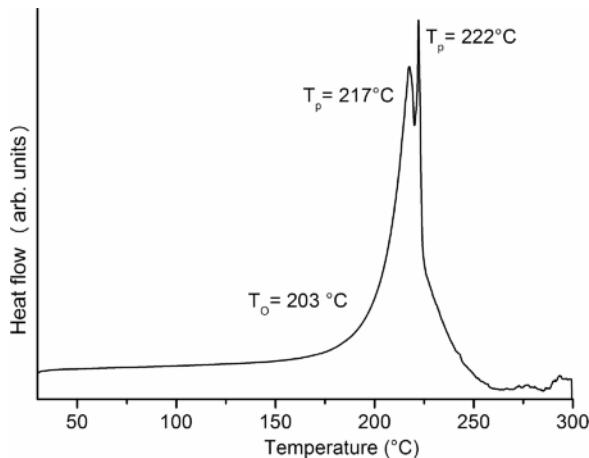


Fig. 7. DSC curve for **Cd1-I** (heating rate =  $10\text{ }^{\circ}\text{C min}^{-1}$ ; given is the peak temperature in  $^{\circ}\text{C}$ ).

### Crystal structure of **Zn1**

The 1 : 2 compound  $[\text{Zn}(\text{NCS})_2(4\text{-acetylpyridine})_2]$  (**Zn1**) crystallizes in the centrosymmetric triclinic

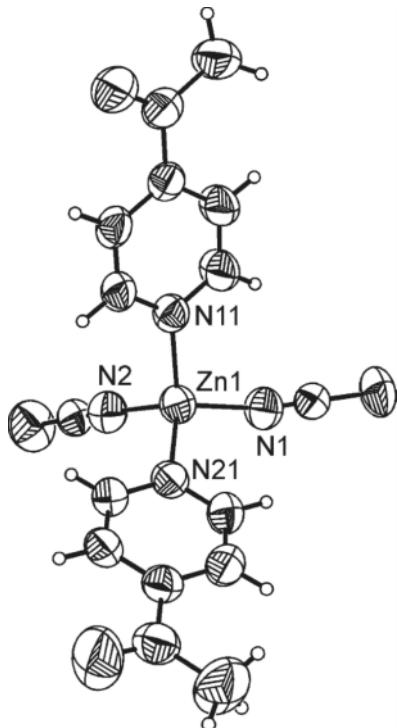


Fig. 8. Crystal structure of compound **Zn1** with atom labeling and displacement ellipsoids drawn at the 50 % probability level.

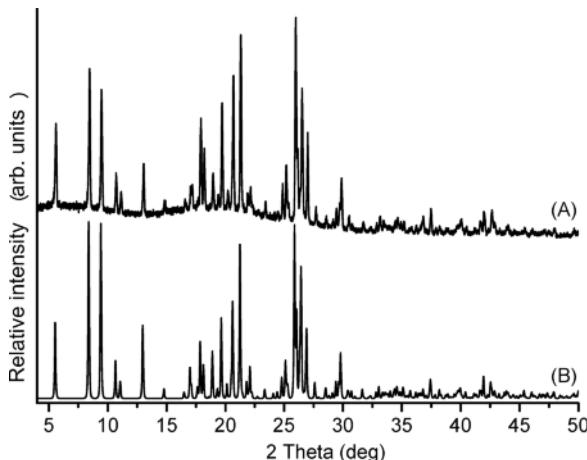


Fig. 9. Experimental powder X-ray pattern of **Zn1** (A) together with the powder pattern calculated from single-crystal data (B).

space group  $P\bar{1}$  with two formula units in the unit cell and all atoms in general positions. The zinc(II) cations are coordinated by four nitrogen atoms of two terminally *N*-bonded thiocyanato anions and two *N*-bonded 4-acetylpyridine co-ligands in a slightly distorted tetrahedral coordination geometry. The  $\text{Zn(II)}-\text{N}$  distances are  $1.929(3)$  and  $2.031(2)$  Å, while the angles around the  $\text{Zn(II)}$  cations are between  $105.37(9)$  and  $116.40(12)$ ° (Fig. 8, Table 2). These values are in agreement with those retrieved from the literature [46, 47, 49].

Comparison of the experimental powder X-ray pattern for **Zn1** with that calculated from single-crystal data proves that the compound is obtained as a single-crystalline phase (Fig. 9).

### Conclusion

In this contribution investigations on the synthesis and structures of new Cd(II) and Zn(II) thio- and selenocyanato coordination compounds are described. In the course of these investigations two compounds of composition  $\text{Cd}(\text{NCX})_2(4\text{-acetylpyridine})_2$  ( $\text{X} = \text{S, Se}$ ) were prepared, with the thiocyanato compound crystallizing in two different modifications. Form **II** was obtained by accident, whereas form **I** can be prepared as a phase-pure material and does not transform into form **II** on heating. Additionally, one compound of composition  $\text{Zn}(\text{NCS})_2(4\text{-acetylpyridine})_2$  was obtained that in contrast to the Cd compounds forms discrete tetrahedral complexes.

Table 2. Selected bond lengths (Å) and angles (deg) for **Zn1**.

Zn(1)–N(1)	1.939(2)	Zn(1)–N(11)	1.929(3)
Zn(1)–N(2)	2.031(2)	Zn(1)–N(21)	2.024(2)
N(1)–Zn(1)–N(2)	116.40(12)	N(2)–Zn(1)–N(11)	107.32(10)
N(1)–Zn(1)–N(11)	105.37(9)	N(2)–Zn(1)–N(21)	108.17(10)
N(1)–Zn(1)–N(21)	107.33(10)	N(11)–Zn(1)–N(21)	112.36(9)

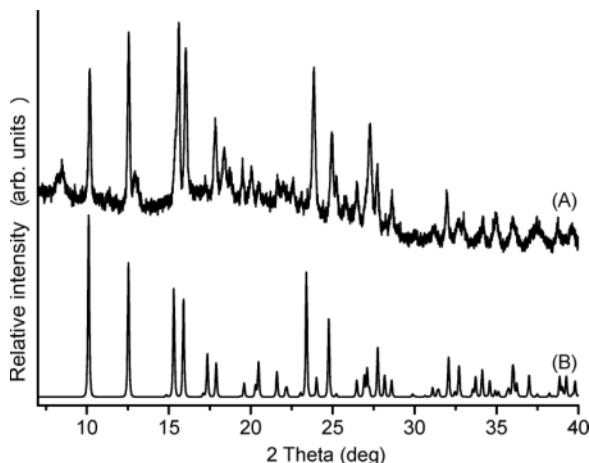


Fig. 10. Experimental powder X-ray pattern of the residue of the composition  $Mn(NCS)_2(4\text{-acetylpyridine})_2(H_2O)_2$  together with the powder pattern calculated from single-crystal data of **Cd1-I** (B).

These investigations are part of our current work on the corresponding compounds of composition  $M(NCS)_2(4\text{-acetylpyridine})_2$  with  $M = Mn(\text{II}), Fe(\text{II}), Co(\text{II})$  and  $Ni(\text{II})$  for which different polymorphic modifications or isomers may be obtained. We have already obtained one compound of composition  $Mn(NCS)_2(4\text{-acetylpyridine})_2$  by thermal decomposition of  $Mn(NCS)_2(4\text{-acetylpyridine})_2(H_2O)_2$ , but this product could not be structurally identified. When the experimental powder X-ray pattern of the Mn compound was compared with that calculated for **Cd1-I**, it became obvious that this modification had been formed with manganese but was contaminated with a second crystalline phase of the same composition, which is different from **Cd1-II** (Fig. 10). This clearly shows that the preparation of corresponding diamagnetic compounds can help in the identification of the paramagnetic counterparts. The preparation of the paramagnetic compounds as single-crystalline phases will be the subject of further investigations.

## Experimental Section

### Materials

$Cd(NO_3)_2 \cdot 4H_2O$ ,  $KNCSe$ ,  $ZnSO_4 \cdot H_2O$ , and  $CdSO_4 \cdot 8/3H_2O$  were obtained from Merck,  $Ba(NCS)_2 \cdot 3H_2O$  and 4-acetylpyridine were obtained from Alfa Aesar. The chemicals were used without further purification.

### Synthesis of $Cd(NCS)_2$

$Ba(NCS)_2 \cdot 3H_2O$  (3.076 g, 10 mmol) and  $CdSO_4 \cdot 8/3H_2O$  (2.566 g, 10 mmol) were stirred in water (100 mL). The colorless precipitate of  $BaSO_4$  was filtered off, and the water was removed from the filtrate by heating. The final product was dried at 80 °C. The homogeneity of the product was investigated by powder X-ray diffraction and elemental analysis.

### Synthesis of $Zn(NCS)_2$

$Ba(NCS)_2 \cdot 3H_2O$  (3.076 g, 10 mmol) and  $ZnSO_4 \cdot H_2O$  (1.795 g, 10 mmol) were stirred in water (100 mL). The colorless precipitate of  $BaSO_4$  was filtered off, and the water was removed from the filtrate by heating. The final product was dried at 80 °C. The homogeneity of the product was investigated by powder X-ray diffraction and elemental analysis.

### Synthesis of $[Cd(NCS)_2(4\text{-acetylpyridine})_2]_n$ (**Cd1-I**)

57.1 mg  $Cd(NCS)_2$  (1.50 mmol) and 55.1  $\mu L$  4-acetylpyridine (0.25 mmol) were stirred in 1.5 mL of methanol. The colorless precipitate was filtered off and dried. After slow evaporation of the solvent from the filtrate colorless single crystals suitable for X-ray diffraction were obtained. –  $C_{16}H_{14}CdN_4O_2S_2$  (470.84 g mol<sup>-1</sup>): calcd. C 40.8, H 3.0, N 11.9, S 13.6; found C 41.0, H 2.9, N 11.9, S 13.6. – IR (ATR):  $\nu_{max} = 2089$  (s), 1695 (s), 1413 (m), 1361 (m), 1263 (s), 1216 (w), 1060 (w), 1014 (w), 963 (w), 822 (s), 594 (s)  $\text{cm}^{-1}$ .

### Synthesis of $[Cd(NCS)_2(4\text{-acetylpyridine})_2]_n$ (**Cd1-II**)

Single crystals were accidentally obtained by the reaction of 342.9 mg  $Cd(NCS)_2$  (1.50 mmol) and 27.5  $\mu L$  4-acetylpyridine (0.25 mmol) in 1.5 mL  $H_2O$ . The precipitate obtained was filtered off and after slow evaporation of the

filtrate colorless single crystals suitable for X-ray diffraction were obtained.

*Synthesis of  $[Cd(NCSe)_2(4\text{-acetylpyridine})_2]_n$  (Cd2)*

154.2 mg  $Cd(NO_3)_2 \cdot 4H_2O$  (0.50 mmol), 136.9 mg  $KNCS$  (0.95 mmol) and  $27.5 \mu L$  4-acetylpyridine (0.25 mmol) were stirred in 1.5 mL of  $H_2O$ . Single crystals suitable for X-ray diffraction were prepared under identical reaction conditions without stirring. After 5 d colorless single crystals were obtained. – IR (ATR):  $\nu_{max} = 2098$  (s), 1697 (s), 1609 (w), 1575 (w), 1413 (m), 1361 (m), 1323 (w), 1266 (s), 1216 (m), 1059 (m), 1012 (m), 963 (w), 821 (s), 593 (s)  $cm^{-1}$ .

*Synthesis of  $Zn(NCS)_2(4\text{-acetylpyridine})_2$  (Zn1)*

45.4 mg  $Zn(NCS)_2$  (0.25 mmol) and  $110.15 \mu L$  4-acetylpyridine (1.00 mmol) were stirred in 1.5 mL  $H_2O$  for 2 d. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of the solvent from the filtrate. –  $C_{16}H_{14}N_4O_2S_2Zn$  (423.82 g mol $^{-1}$ ): calcd. C 45.3, H 3.3, N 13.2, S 15.4; found C 45.6, H 3.3, N 13.4, S 15.4. –

IR (ATR):  $\nu_{max} = 2063$  (s), 1698 (s), 1618 (m), 1557 (m), 1503 (w), 1422 (s), 1360 (s), 1259 (s), 1232 (s), 1065 (s), 1031 (m), 965 (m), 882 (w), 824 (s), 594 (s)  $cm^{-1}$ .

*Powder X-ray diffraction*

The experiments were performed using a Stoe Transmission Powder Diffraction System (STADI P) with  $CuK\alpha$  radiation ( $\lambda = 154.0598$  pm) that is equipped with a linear position-sensitive detector ( $\delta - 2\theta = 6.5 - 7^\circ$  simultaneous; scan range overall =  $2 - 130^\circ$ ) from Stoe & Cie.

*Elemental analysis*

CHNS analysis was performed using an EURO EA elemental analyzer, fabricated by Euro Vector Instruments and Software.

*Differential scanning calorimetry (DSC)*

The DSC experiments were performed using a DSC 1 Star System with STAREx Excellence Software from Mettler-Toledo AG.

Table 3. Selected crystal data and details on the structure determination for Cd1-I, Cd1-II, Cd2, and Zn1.

Compound	Cd1-I	Cd1-II	Cd2	Zn1
Formula	$C_{16}H_{14}CdN_4O_2S_2$	$C_{16}H_{14}CdN_4O_2S_2$	$C_{16}H_{14}CdN_4O_2Se_2$	$C_{16}H_{14}N_4O_2S_2Zn$
$M_r$	470.83	470.83	564.63	423.80
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$C2/c$	$P2_1/c$	$C2/c$	$P\bar{1}$
$a, \text{\AA}$	24.508(4)	5.8899(3)	24.027(2)	5.5720(4)
$b, \text{\AA}$	5.8069(6)	11.1429(7)	5.9301(3)	10.9241(8)
$c, \text{\AA}$	15.322(2)	14.3704(7)	15.3667(14)	16.2121(13)
$\alpha, \text{deg}$	90	90	90	95.927(6)°
$\beta, \text{deg}$	118.030(10)	100.837(4)	118.131(10)	96.322(6)
$\gamma, \text{deg}$	90	90	90	103.353(6)
$V, \text{\AA}^3$	1924.9(4)	926.32(9)	1930.9(3)	945.81(12)
$T, \text{K}$	293 (2)	293 (2)	–103 (2)	293 (2)
$Z$	4	2	4	2
$D_{\text{calcd.}}, \text{mg cm}^{-3}$	1.63	1.69	1.94	1.49
$\mu(MoK\alpha), \text{mm}^{-1}$	1.4	1.4	4.9	1.5
Min./max. trans.	0.5610/0.7381	0.6795/0.8779	0.3714/0.5581	0.6598/0.8377
$\theta_{\text{max}}, \text{deg}$	26.00	29.22	27.97	27.92
Measured reflns.	7954	13 104	7520	9507
Unique reflns.	1892	2498	2306	4487
$R_{\text{int}}$	0.0615	0.0443	0.0951	0.0292
Refl. $F_0 > 4 \sigma(F_0)$	1426	1905	1773	2985
Parameters	115	116	115	226
$R_{\text{l}}^{\text{a}}[F_0 > 4 \sigma(F_0)]$	0.0522	0.0434	0.0496	0.0431
$wR_2^{\text{b}}$ (all data)	0.1100	0.0997	0.1371	0.0949
$GoF^{\text{c}}$	1.171	1.109	1.048	0.975
$\Delta\rho_{\text{max/min}}, \text{e} \text{\AA}^{-3}$	0.70 / –0.43	0.55 / –0.86	1.11 / –1.70	0.31 / –0.18

<sup>a</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ ; <sup>b</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ ;

<sup>c</sup>  $GoF = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$ .

*Single-crystal structure determinations*

Data collection was performed with an imaging plate diffraction system (IPDS-2 for **Cd1-I**, **Cd1-II** and **Zn1**; IPDS-1 for **Cd2**) from Stoe & Cie with  $\text{MoK}\alpha$  radiation. The data were corrected for absorption using X-RED and X-SHAPE from Stoe [67, 68]. The structure solution was performed with Direct Methods using SHELXS-97, and structure refinements were performed against  $F^2$  using SHELXL-97 [69]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters with  $U_{\text{iso}}(\text{H}) = -1.2 U_{\text{eq}}(\text{C})$  (1.5 for methyl H atoms) using a riding model. Details of the structure determination are given in Table 3.

CCDC 927933 (**Cd1-I**), CCDC 927934 (**Cd1-II**), CCDC 927935 (**Cd2**) and CCDC 927932 (**Zn1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

*Differential thermal analysis and thermogravimetry*

The DTA-TG measurements were performed in nitrogen atmosphere (purity: 5.0) in  $\text{Al}_2\text{O}_3$  crucibles using a STA-409CD thermobalance from Netzsch. 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.

*Spectroscopy*

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

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