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New cadmium thio- and selenocyanato coordination compounds: Structural snapshots on the reaction pathway to more condensed anionic networks[†]

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In this contribution several new coordination compounds on the basis of cadmium(II) thio- and selenocyanate with pyrimidine as co-ligand were prepared and investigated for their structural, thermal and spectroscopic properties. The reaction of cadmium(II) thiocyanate with pyrimidine leads to the formation of four compounds, which from a structural point of view are closely related. In the most pyrimidine-rich 1:2 compound $[Cd(NCS)_2(pyrimidine)_2]_n$ (1A) (1:2 = ratio between metal salt and the co-ligand pyrimidine) the Cd cations are linked by the pyrimidine ligands into layers and are additionally coordinated by two terminal N-bonded anions. In the 2:3 compound $\{ [Cd(NCS)_2]_2 (pyrimidine)_3 \}_n$ (**1B**) the Cd cations are linked into chains by μ -1,3 bridging thiocyanato anions, which are connected into layers by only half of the pyrimidine ligands, whereas the other co-ligands are only terminal coordinated. Further reduction of the pyrimidine content leads to the formation of the 1:1 2D compound $[Cd(NCS)_2(pyrimidine)]_n$ (1CI) in which the terminal N-bonded thiocyanato anions become bridging. Surprisingly, crystallization experiments lead to the formation of an additional pyrimidine-deficient intermediate of composition $\{[Cd(NCS)_2]_3(pyrimidine)_2\}_n$ (1D), in which some of the μ -1,3 coordinated anions transform into μ -1,1,3 bridging thiocyanato anions. Consequently the four structures can be used as snapshots of intermediates on the way to a more condensed thiocyanato coordination network. In contrast, with cadmium selenocyanate only two different compounds were obtained. The 1:2 compound $[Cd(NCSe)_2(pyrimidine)_2]_{\mu}$ (2A) is not isotypic to 1A and shows a completely different coordination topology whereas the pyrimidine-deficient 1:1 compound (2B) shows a more condensed network with u-1,3 coordinating selenocyanato anions. On heating, the 1:2 compound 1A decomposes into Cd(NCS)₂ via a new polymorphic modification (1CII) as intermediate which is metastable, whereas the 1:2 selenocyanato compound 2A transforms into the 1:1 compound **2B** on heating which cannot be obtained phase pure under these conditions. If faster heating rates are used, there are indications for the formation of a 3:2 compound, which is amorphous to X-rays. The results are compared with those obtained for related thio- and selenocyanato coordination polymers with pyridine, pyridazine and pyrazine as co-ligand. Moreover, their impact on the structures and thermal reactivity of analogous paramagnetic compounds is discussed in detail. Based on the structural data of compound 1D the unknown structures of two intermediates were determined, which are formed in the thermal decomposition reaction of the Mn and Fe thiocyanato pyrimidine coordination polymers, reported recently.

Introduction

Investigations on the synthesis, structures and properties of coordination polymers including metal–organic frameworks or inorganic–organic hybrid compounds are an important field in chemical research and there are excellent reviews in this field.¹ One

important goal in this area is the preparation of new materials with desired physical properties. This approach, called "Crystal Engineering", must include a more rational approach to design structures and the systematic investigations of structure-property relationships in solids.² Moreover, methods are needed that allow the preparation of a large amount of a desired compound phase pure and in preferably high yields. Concerning the properties or even future applications of such compounds, coordination polymers with useful magnetic properties have become of increasing interest.³ Consequently a large amount of different antiferro-, ferro- or ferrimagnetic materials has been reported which also includes metamagnetic or SCM compounds (SCM = single chain

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magnetism).⁴ In most compounds paramagnetic transition metals are linked by small-sized anions that can mediate magnetic exchange interactions.

To add one piece of knowledge to the field, we have started systematic investigations on compounds in which transition metal cations are linked by thio- or selenocyanato anions. In some cases this is a great challenge because especially paramagnetic cations like e.g. Fe, Co or Ni prefer terminal N-bonding to such anions. This is a pity because coordination compounds with μ -1,3 bridging anions might show cooperative magnetic phenomena. However, in some cases the u-1,3 bridging compounds can simply be prepared using conventional solution techniques but very often only the compounds with terminal bonded anions are obtained. To close this gap we have developed an alternative method which is based on thermal decomposition of ligand-rich precursor compounds (ligand-rich = rich on neutral co-ligands) with terminal bonded thio- or selenocyanato anions and additional neutral co-ligands that can easily be extended to other anionic ligands.⁵⁻⁷ If such compounds are heated usually ligand-deficient (ligand-deficient = lacking neutral co-ligands) compounds are obtained as intermediates, in which the anions become μ -1,3 bridging. With this approach we have prepared e.g. 1D and 2D compounds that show a slow relaxation of the magnetization.⁵ In this context it is mentioned that also the corresponding compounds based on diamagnetic Cd(II) cations are of extraordinary importance for our project, because in contrast to the paramagnetic analogue they prefer a bridging coordination. Therefore, the Cd compounds with µ-1,3 bridging anions can easily be crystallized from solution. In those cases where they are isotypic to their paramagnetic analogue the structures of the latter can be determined by Rietveld refinement.8

Moreover, the thermal decomposition of the paramagnetic precursors lead in most cases to only one intermediate. In this context the question arises whether additional *e.g.* metastable intermediates might exist. From previous investigations on compounds based on manganese and iron thiocyanates with pyrimidine we had strong indications that additional ligand-deficient intermediates occur but we were not able to identify them.⁹ Because of the higher chalcophilicity of Cd it might be that such intermediates can be prepared in solution which would allow conclusions on the identity or structure of their paramagnetic intermediates. This is one additional reason why we have investigated cadmium thioand selenocyanates with pyrimidine as co-ligand. Here we report on our investigations.

Experimental section

Cd(NCS)₂

 $Ba(NCS)_2 \cdot 3H_2O(3.0755 \text{ g}, 10 \text{ mmol})$ and $CdSO_4 \cdot 8H_2O(3.5258 \text{ g}, 10 \text{ mmol})$ 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 by 80 °C. The homogeneity of the product was investigated by X-ray powder diffraction.

Synthesis of [Cd(NCS)₂(pyrimidine)₂]_n (1A)

 $Cd(NCS)_2$ (228 mg, 1 mmol) and pyrimidine (170 μ L, 2.00 mmol) were stirred together in 3 mL of water at RT in a snap cap vial

for 2 d. $C_{10}H_8CdN_6S_2$ (388.8): calcd. C 30.9, H 2.1, N 21.6, S 16.5; found C 30.7, H 2.0, N 22.3, S 16.7. Single crystals were prepared by the reaction of Cd(NCS)₂ (28.5 mg, 0.125 mmol) and pyrimidine (21 μ L, 0.25 mmol) in 2 mL of ethanol in a closed glass tube at 130 °C for 1 week. The precipitate consists of a mixture of single crystals of compounds **1A**, **1B** and **1CI**.

Synthesis of {[Cd(NCS)₂]₂(pyrimidine)₃}_n (1B)

Compound **1B** cannot be obtained as a phase pure powder from solution. Single crystals were selected from a mixture which was prepared as described for compound **1A**.

Synthesis of [Cd(NCS)₂(pyrimidine)]_n (1CI)

Cd(NCS)₂ (114 mg, 0.50 mmol) and pyrimidine (21 μ L, 0.25 mmol) were stirred in 2 mL of methanol in a snap cap vial at RT for 3 d. If stoichiometric ratios of the reactants were used, compound **1A** formed. C₆H₄CdN₄S₂ (308.65): calcd. C 23.3, H 1.3, N 18.5, S 20.7; found C 23.0, H 1.2, N 18.1, S 20.8. Single crystals were selected from a mixture prepared as described in the synthesis for **1A**.

Synthesis of $\{[Cd(NCS)_2]_3(pyrimidine)_2\}_n$ (1D)

Single crystals were prepared by the reaction of Cd(NCS)₂ (114 mg, 0.50 mmol) and pyrimidine (21 μ L, 0.25 mmol) in 2 mL of acetonitrile in a closed glass tube at 130 °C for 1 week. The precipitate consists of a mixture of single crystals of compound **1CI** and **1D**.

Synthesis of [Cd(NCSe)₂(pyrimidine)₂]_n (2A)

Cd(NO₃)₂·4H₂O (77.1 mg, 0.25 mmol) and KNCSe (72.0 mg, 0.50 mmol) were stirred together in 1 mL of ethanol at RT in a 3 mL snap cap vial. The resulting colorless precipitate of KNO₃ was filtered off and pyrimidine (2 mL, 25.0 mmol) was added to the filtrate. After stirring the reactants for 2 d the light beige crystalline powder was filtered off and the purity was checked by XRPD. C₁₀H₈CdN₆Se₂ (482.54): calcd. C 24.9, H 1.7, N 17.4; found C 24.3, H 1.5, N 17.3. Single crystals were prepared by the reaction of Cd(NO₃)₂·4H₂O (77.1 mg, 0.25 mmol), KNCSe (136.9 mg, 0.95 mmol) and pyrimidine (2 mL, 25.0 mmol) in 1 mL of water at RT in a 3 mL snap cap vial without stirring. After 3 d colorless well shaped single-crystals were obtained.

Synthesis of [Cd(NCSe)₂(pyrimidine)]_n (2B)

Single crystals were prepared by the reaction of $Cd(NO_3)_2 \cdot 4H_2O$ (77.1 mg, 0.25 mmol) and KNCSe (72.0 mg, 0.50 mmol) in 1 mL of ethanol at RT in a 3 mL snap cap vial. The resulting colorless precipitate of KNO₃ was filtered off and pyrimidine (19.7 µL, 0.25 mmol) was added to the filtrate. After 3 d the colorless singlecrystals were obtained in a mixture with unknown phases.

Spectroscopy

Fourier transform IR spectra were recorded on a Genesis series FTIR spectrometer from ATI Mattson in KBr pellets as well on an Alpha IR spectrometer from Bruker equipped with a Platinum ATR QuickSnapTM sampling module between 4000–375 cm⁻¹.

Compound	1A	1B	1CI	1D	2A	2B
Formula MW g ⁻¹ mol ⁻¹	$C_{10}H_8CdN_6S_2$ 388.74	$\begin{array}{c} C_{16}H_{12}Cd_2N_{10}S_4\\ 697.40\end{array}$	$\begin{array}{c} C_{6}H_{4}CdN_{4}S_{2}\\ 308.65 \end{array}$	$\begin{array}{c} C_{14}H_8Cd_3N_{10}S_6\\ 845.86\end{array}$	$C_{10}H_8CdN_6Se_2$ 482.54	$\begin{array}{c} C_{12}H_{8}Cd_{2}N_{8}Se_{4}\\ 804.90 \end{array}$
Ratio M:L	1:2	2:3	1:1	3:2	1:2	1:1
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	Cmca	$P 2_1 2_1 2$	$P 2_1/m$	$P\overline{1}$	$P 2_1/c$	C 2/c
a/Å	10.0015(6)	11.2398(6)	5.6358(9)	6.9128(4)	8.566(2)	8.6778(3)
b/Å	15.6680(7)	14.8326(7)	12.4946(15)	9.2461(6)	6.0220(10)	16.7503(5)
c/Å	8.6696(5)	7.3449(4)	7.1516(13)	10.6609(7)	13.829(4)	29.2877(8)
α (°)	90	90	90	108.162(5)	90	90
β(°)	90	90	105.634(14)	91.352(5)	92.07(3)	92.158(2)
γ (°)	90	90	90	103.857(5)	90	90
$V/Å^3$	1358.56(13)	1224.51(11)	484.96(13)	625.04(7)	712.9(3)	4254.1(2)
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Ζ	4	2	2	1	2	8
$D_{\rm c}/{\rm g~cm^{-3}}$	1.901	1.891	2.114	2.247	2.248	2.513
μ/mm^{-1}	1.908	2.103	2.637	3.055	6.632	8.857
min/max transmission	0.6235/0.8408	0.7001/0.7900		0.6103/0.6741	0.0441/0.1144	0.2326/0.3771
θ_{\max} (°)	29.21	25.10	25.89	27.99	27.98	26.81
Measured reflections	7848	6607	3936	7240	5395	23168
Unique reflections	967	2180	6520*	2980	1667	4500
Reflections $[F_0 > 4\sigma(F_0)]$	795	1896	5132	2761	1347	4092
Parameter	51	146	65	155	88	237
$R_{ m int}$	0.0816	0.0456	0.0296	0.0171	0.0393	0.0285
$R_1^{[b]}[F_0 > 4\sigma(F_0)]$	0.0485	0.0414	0.0355	0.0190	0.0272	0.0318
$WR_2^{[c]}$ [all data]	0.0895	0.0647	0.0636	0.0426	0.0666	0.0663
GOF	1.213	1.148	1.065	1.077	1.047	1.110
$\Delta ho_{ m max},\Delta ho_{ m min}$ /e Å $^{-3}$	0.653, -0.568	0.627, -0.629	0.397, -0.770	0.411, -0.963	0.441, -0.719	1.332, -1.074

 Table 1
 Selected crystal data and details on the structure determinations from single crystal data (*Please note, compound 1CI was twinned and refined using the HKLF5 option. Thus, the number of independent reflections is artificially too high)

Raman-spectra were recorded using a Bruker ISF66 FRA106 between $3500-100 \text{ cm}^{-1}$.

Elemental analysis

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

Elemental analysis of the residue obtained in the thermal decomposition

Isolated in first heating step of compound **1A**: calculated for a 1 : 1 compound: C 23.3, H 1.3, N 18.5, S 20.7; found C 23.7, H 1.2, N 18.4, S 22.6.

X-ray powder diffraction (XRPD)

XRPD experiments were performed using a Stoe Transmission Powder Diffraction System (STADI P) with Cu-K α -radiation (λ = 154.0598 pm) that is equipped with a linear position-sensitive detector (Delta 2 Theta = 6.5–7° simultaneous; scan range overall = 2–130°) from STOE & CIE and an Image Plate Detector (scan range overall = 0–127°).

Single-crystal structure analysis

All investigations were performed with an imaging plate diffraction system (IPDS-1 for **1A**, **2A**/IPDS-2 for **1B**, **1CI**, **1D** and **2B**) with Mo-K α -radiation from STOE & CIE. The structure solution was performed with direct methods using SHELXS-97,¹⁰ and structure refinements were performed against F^2 using SHELXL-97.¹¹ 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 $[U_{iso}(H) = -1.2 \cdot U_{eq}(C)]$ using a riding model. Details of the structure determinations are given in Table 1. The crystal of compound **1CI** was non-merohedrically twinned. Both individuals were indexed separately, the twin law was calculated and finally the structure was refined using the HKLF5 option. If the overlapping reflections are omitted a completeness of only 69.4% is reached but the R_1 value drops down to 2.98% for the observed reflections. However, to refine against all data the HKLF-5 option was used.

CCDC-836235 (1A), CCDC-836234 (1B), CCDC-836233 (1CI), CCDC-836232 (1D), CCDC-836237 (2A) and CCDC-836236 (2B) 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/.

Differential thermal analysis and thermogravimetry

The DTA-TG measurements were performed in nitrogen atmosphere (purity: 5.0) in Al_2O_3 crucibles using a STA-409CD thermobalance from Netzsch. All measurements were performed with a flow rate of 75 mL min⁻¹ and were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

Results and discussion

Investigations on Cd thiocyanato coordination compounds

Structural investigations. The reaction of cadmium thiocyanate with an excess of pyrimidine leads to the phase pure formation of the ligand-rich precursor compound $[Cd(NCS)_2(pyrimidine)_2]_n$ (1A; Fig. S1 in the ESI†). Compound 1A crystallizes in the orthorhombic space group *Cmca* with 4 formula units in the unit cell. The asymmetric unit consists of one Cd cation that occupies position 2/m, one thiocyanato anion located on a crystallographic mirror plane and one pyrimidine ligand which is situated on a 2-fold rotation axis. The Cd cations are coordinated by two N-bonded symmetry equivalent thiocyanato anions and four symmetry related pyrimidine ligands within slightly distorted octahedra (Fig. 1, Fig. S2 and Table S1 in the ESI†).



Fig. 1 Crystal structure of compound **1A** with view along the crystallographic *b*-axis (black = cadmium, dark-grey = sulphur, grey = carbon, light-grey = nitrogen) (an Ortep plot of **1A** is shown in Fig. S2 in the ESI[†]).

In the crystal structure the Cd cations are connected *via* the pyrimidine ligands into layers that are located in the *ac* plane (Fig. 1). These layers are stacked in the direction of the *c* axis. It must be noted that the topology of the coordination network is similar to that of the corresponding ligand-rich 1:2 coordination compounds of composition $[M(X)_2(pyrazine)_2]_n$ (X = NCS⁻, NCSe⁻; M = Zn, Cd) reported recently.¹²

Compound **1B** was obtained as single crystals in a mixture with compound **1A** and **1CI** by the reaction of $Cd(NCS)_2$ and pyrimidine under solvothermal conditions. The 2:3 compound { $[Cd(NCS)_2]_2(pyrimidine)_3$ }_n (**1B**) crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12$ with 2 formula units in the unit cell. The asymmetric unit consists of one Cd cation, two crystallographically independent thiocyanato anions and one pyrimidine ligand all in general positions, as well as of one pyrimidine ligand that is located on a 2-fold rotation axis. The Cd cations are surrounded by two N and two S atoms of two pairs of symmetry equivalent thiocyanato anions and two N atoms of two crystallographically independent pyrimidine ligands within slightly distorted octahedral polyhedron (Fig. 2, Fig. S3 and Table S2 in the ESI[†]).

The Cd cations are linked by μ -1,3 bridging thiocyanato anions into chains that elongate in the direction of the *a* axis. These chains are further linked into corrugated layers by pyrimidine ligands (Fig. 2). Interestingly only half of the co-ligands act as bridging ligands whereas the others are only terminal bonded. It must be noted that this structural motif was never observed before in thiocyanato coordination polymers.

The 1:1 compound $[Cd(NCS)_2(pyrimidine)]_n$ (1CI) can be prepared phase pure by the reaction of $Cd(NCS)_2$ and pyrimidine



Fig. 2 Crystal structure of compound 1B with view along the crystallographic *c* axis (black = cadmium, dark-grey = sulphur, grey = carbon, light-grey = nitrogen) (an Ortep plot of 1B is shown in Figure S3 in the ESI[†]).

in ratio 2:1 (Fig. S4 in the ESI[†]). The compound crystallizes in the monoclinic space group $P2_1/m$ with 2 formula units in the unit cell. The asymmetric unit consists of one Cd cation located on a centre of inversion, one thiocyanato anion in a general position and one pyrimidine ligand located on a mirror plane. The Cd cations are surrounded by two N and two S atoms of four symmetry equivalent thiocyanato anions and two N atoms of two pyrimidine ligands related by symmetry (Fig. 3, Fig. S5 and Table S3 in the ESI[†]).



Fig. 3 Crystal structure of compound **1CI** with view along (101) (black = cadmium, dark-grey = sulphur, grey = carbon, light-grey = nitrogen) (an Ortep plot of **1CI** is shown in Figure S5 in the ESI†).

The Cd cations are linked *via* μ -1,3 bridging thiocyanato anions into chains that elongate in the direction of the crystallographic *a* axis. These chains are further linked by bridging pyrimidine ligands into layers, which is a common motif for 1 : 1 thiocyanato coordination polymers with bidentate co-ligands.^{7,9} The 3:2 compound { $[Cd(NCS)_2]_3(pyrimidine)_2\}_n$ (**1D**) can only be obtained as single crystals in a mixture with compound **1CI** (Fig. S6 in the ESI[†]). This compound crystallizes in the triclinic centrosymmetric space group $P\overline{1}$ with Z = 1 formula unit in the unit cell. The asymmetric unit consists of three crystallographically independent thiocyanato anions and one pyrimidine ligand in general positions as well as of three crystallographically independent Cd cations that are located on a centre of inversion (Fig. 4 and Fig. S7 in the ESI[†]).



Fig. 4 Crystal structure of compound **1D** with view along the *a* axis (black = cadmium, dark-grey = sulphur, grey = carbon, light-grey = nitrogen) (an Ortep plot of **1D** is shown in Fig. S7 in the ESI†).

Two of the cations are each coordinated by two N and two S atoms of μ -1,3 bridging thiocyanato anions and two N atoms of two bridging pyrimidine ligands within a distorted octahedral coordination geometry (Table S4 in the ESI†). The remaining Cd cations are coordinated by two N and four S atoms of μ -1,3 bridging thiocyanato anions and the coordination polyhedra can also be described as a slightly distorted octahedron. Two of the three Cd cations are bridged by alternating μ -1,3 (N, S) and μ -1,1,3 (S, S, N) bridging thiocyanato anions into chains, which are further connected into layers by additional Cd cations that are coordinated to the S atoms of the μ -1,1,3 bridging anions (Fig. 4). This Cd cations *via* μ -1,3 bridging anions (Fig. 4).

Thermoanalytical investigations. To prove which of the liganddeficient intermediates can be obtained on thermal decomposition of the most ligand-rich precursor **1A**, this compound was investigated by DTA-TG measurements (Fig. 5).

On heating two mass steps are observed, which are accompanied with two endothermic events in the DTA curve at $T_{\rm P} = 182$ °C and 218 °C. From the DTG curve it is obvious that both steps are not well resolved. The experimental mass loss of 20.1% and 20.4% is in good agreement with that calculated for the loss of one pyrimidine ligand in each step ($\Delta m_{\rm calc} = 20.6\%$). Thus, it can be assumed that in the first step a 1 : 1 compound of composition [Cd(NCS)₂(pyrimidine)]_n is obtained that in the second step transforms into Cd(NCS)₂, which decomposes on further heating. Heating rate dependent measurements show that the resolution cannot be improved (Fig. S8 in the ESI†). However, to check if the 1 : 1 compound **1CI** has formed in the first step, the residue formed at about 178 °C was isolated and investigated by XRPD measurements. If the powder pattern is compared with



Fig. 5 DTG, TG and DTA curves for compound 1A. Given are the mass loss in % and the peak temperatures in $^{\circ}$ C.

that calculated for **1CI** from single crystal structure analysis it is obvious that a different modification (**1CII**) has formed (Fig. S9 in the ESI†). This is in agreement with the results of an elemental analysis, which is in perfect agreement with that expected for a 1:1 compound. Moreover, information on the coordination mode of the thiocyanato anions can be retrieved by IR- and Raman spectroscopy.¹³ For form **1CI** $v_{as}(CN) = 2080 \text{ cm}^{-1}$ whereas for the new form **1CII** $v_{as}(CN) = 2079 \text{ cm}^{-1}$, which clearly shows that in both modifications the coordination mode must be similar (Fig. S10 and S11 in the ESI†). It must be noted that the new form **1CII** is not isotypic to its selenocyanato analogue (see below). Unfortunately all attempts to determine the structure of this new form from X-ray powder data fail.

To prove which of the two 1:1 modifications is the thermodynamically most stable form at room temperature a mixture of both forms were stirred in a saturated acetonitrile solution at room temperature. Finally, the product formed after one week was investigated by X-ray powder diffraction. These investigations clearly show that the new modification transforms into form **1CI**, which proves that this modification represents the most stable form at room-temperature (Fig. 6). Additional DSC measurements gave no hints for a transformation of **1CI** into a further modification and thus, it is not proven if both forms behave enantiotropically or monotropically.

Investigations on Cd selenocyanato coordination compounds

Crystal structures. In contrast to the cadmium thiocyanato coordination polymers mentioned above, with cadmium selenocyanate only two different compounds were obtained. The reaction of $Cd(NO_3)_2$ ·4H₂O and KNCSe in ethanol with a large excess of pyrimidine leads to the phase pure formation of the most ligandrich compound [Cd(NCSe)₂(pyrimidine)₂]_n (**2A**) (Fig. S12 in the ESI†). Compound **2A** crystallizes in the monoclinic space group



Fig. 6 Experimental X-ray powder pattern of **1CII** (A), of the mixture of **1CI** and **1CII** (B), after stirring the mixture for one week (C) and X-ray powder pattern for form **1CI** calculated from single crystal data (D).

 $P2_1/c$ with Z = 2 formula units in the unit cell. The structure consists of Cd cations which are coordinated by two N and two Se atoms of the μ -1,3 bridging selenocyanato anions and by two N atoms of the pyrimidine ligands (Fig. S13 and Table S5 in the ESI†). This structure exhibits the same coordination topology as that of **1CI**, but in contrast the neutral co-ligands are terminal bonded. The Cd cations are connected into chains *via* μ -1,3 bridging selenocyanato anions (Fig. 7).



Fig. 7 Crystal structure of compound **2A** with view along the *c* axis (black = cadmium, dark-grey = selenium, grey = nitrogen, light-grey = carbon, white = hydrogen) (an Ortep plot of **2A** is shown in Figure S13 in the ESI†).

Using slightly different reaction conditions, a second compound of composition [Cd(NCSe)₂(pyrimidine)]_n (**2B**) was obtained. The 1 : 1 compound **2B** crystallizes in the monoclinic space group C2/cwith Z = 8 formula units in the unit cell. The asymmetric unit consists of four crystallographically independent selenocyanato anions, two pyrimidine ligands and three Cd cations, whereby two of them are located on special positions. One Cd cation is coordinated by two N and two Se atoms of four crystallographically independent and µ-1,3 bridging selenocyanato anions and two independent and bridging pyrimidine ligands within a slightly distorted octahedron (Fig. 8, Fig. S14 and Table S6 in the ESI†). The second Cd cation is coordinated by four Se atoms of two pairs of symmetry related µ-1,3 bridging selenocyanato anions and two N atoms of two symmetry related pyrimidine ligands and the



Fig. 8 Crystal structure of compound **2B** with view along the *a*-axis (black = cadmium, dark-grey = selenium, grey = nitrogen, light-grey = carbon, white = hydrogen) (an Ortep plot of **2B** is shown in Figure S14 in the ESI†).

coordination polyhedron can be described as a slightly distorted octahedron. Surprisingly, the third Cd cation is only coordinated by N atoms. Four of them originate from two pairs of symmetry related μ -1,3 bridging selenocyanato anions and the other two N atoms belong to symmetry equivalent and bridging pyrimidine ligands. The Cd cations are linked by the selenocyanato anions and the pyrimidine ligands into a three-dimensional coordination network, which is different from that of its thiocyanato analogue **1CI** and **1CII** and which is without any precedence in the literature (Fig. 8).

Thermoanalytical investigations. If the most ligand-rich compound $[Cd(NCSe)_2(pyrimidine)_2]_n$ (2A) is heated in a thermobalance at least three low resolved mass steps are observed, which are accompanied with endothermic events in the DTA curve (Fig. 9, left). The mass loss in the first and second TG step is in reasonable agreement with that calculated for the removal of one pyrimidine ligand in each step ($\Delta m_{\text{calc}} = 16.6\%$), leading in the first mass step to a ligand-deficient intermediate of composition $[Cd(NCSe)_2(pyrimidine)]_n$ which decomposes on further heating. In order to prove if the 1:1 compound 2B has formed in the first step, the residue formed at about 130 °C was isolated and investigated by XRPD measurements. Unfortunately the residue formed is always a mixture of 2A and 2B. Therefore heating rate dependent measurements were performed to investigate if the resolution of the thermal event can be improved. These measurements showed, that on faster heating the mass loss of the first step increases to a value calculated for a 3:2 compound (Fig. 9, right). Unfortunately, if the TG experiment is stopped after this mass step only a dark brown residue is obtained which is amorphous to X-rays and therefore was not further analyzed.



Fig. 9 DTG, TG and DTA curves for compound 2A with heating rate of 1 °C min⁻¹ (left) and 8 °C min⁻¹ (right). Given are the mass loss in % and the peak temperatures in °C.

Impact on the paramagnetic counterparts

As mentioned in the introduction one important reason for the present investigations on the diamagnetic cadmium thio- and selenocyanato coordination compounds is to extract structural information on intermediates of their analogue paramagnetic compounds, in the case that they cannot be crystallized from solution. In this context we have previously reported on manganese and iron thiocyanato coordination compounds with pyrimidine as coligand.⁹ We have reported that on heating the ligand-rich 1 : 2 compounds [Mn(NCS)₂(pyrimidine)₂]_n and [Fe(NCS)₂(pyrimidine)₂]_n a transformation into ligand-deficient 1 : 1 compounds of composition [M(NCS)₂(pyrimidine)]_n (M = Mn, Fe) is observed. However, from temperature dependent X-ray powder diffraction



Fig. 10 X-ray powder pattern of the 3:2 intermediate isolated in the thermal decomposition reaction of $[Mn(NCS)_2(pyrimidine)_2]_n$ (top) and $[Fe(NCS)_2(pyrimidine)_2]_n$ (middle) as well as calculated pattern for the 3:2 compound $\{[Cd(NCS)_2]_3(pyrimidine)_2\}_n$ (**1D**) (bottom).

Table 2Selected crystal data of the 3:2 intermediates of the ligand-richcompounds $[M(NCS)_2(pyrimidine)_2]_n$ (M = Mn, Fe)

Compound	$\{[Mn(NCS)_2]_3-$ (pyrimidine)_2 $\}_n$	${[Fe(NCS)_2]_3}$ - (pyrimidine) ₂ $_n$	
MW g ⁻¹ mol ⁻¹	673.50	676.22	
Crystal system	Triclinic	Triclinic	
Space group	$P\overline{1}$	$P\overline{1}$	
a/Å	6.8633(3)	6.7050(6)	
b/Å	9.1548(3)	9.0752(6)	
c/Å	10.4201(4)	10.3754(7)	
α (°)	108.538(1)	108.842(2)	
β(°)	91.106(1)	91.204(2)	
γ (°)	103.736(1)	104.148(2)	
$V/Å^3$	599.79(4)	575.93(7)	

and DTA-TG measurements we had strong hints that the overall reaction is much more complicated in order that a second intermediate of composition $\{[M(NCS)_2]_3(pyrimidine)_2\}_n$ (M = Mn, Fe) is formed. These intermediates can only be obtained as a microcrystalline powder on thermal decomposition and we were not able to determine their crystal structure. However, if the X-ray powder pattern of these intermediates is compared with that calculated for the 3 : 2 compound $\{[Cd(NCS)_2]_3(pyrimidine)_2\}_n$ it is obvious that all compounds are isotypic (Fig. 10).

To prove this assumption we isolated the 3:2 intermediates obtained by thermal decomposition of the ligand-rich compounds $[M(NCS)_2(pyrimidine)_2]_n$ (M = Mn, Fe) and determined its structure by Rietveld refinement (Table 2 and Fig. S16–17†).

Conclusions

In this contribution we reported on new Cd(II) thio- and selenocyanato coordination polymers with pyrimidine as co-ligand. With cadmium thiocyanate and pyrimidine we obtained a ligandrich precursor that on heating forms an intermediate which is a polymorphic modification of the 1:1 compound prepared in solution. IR- and Raman spectroscopic investigations clearly prove that the coordination mode of the thiocyanato anions is identical and therefore, the coordination topology of both forms should be identical. Solvent mediated conversion experiments reveal that form **1CI** represents the thermodynamic most stable form at room-temperature. However, if $Cd(NCS)_2$ and pyrimidine are reacted under different conditions in solution four different compounds were obtained and their structures are strongly related. Therefore, our results indicate that on the way from coordination compounds with terminal N-bonded thiocyanato anions to more condensed networks with μ -1,3 bridging anions a large amount of structural intermediates might be observed.

Moreover, based on the structure of the 3:2 compound we have determined the structures of two ligand-deficient intermediates with Mn and Fe reported recently.⁹

In contrast, with cadmium selenocyanate we obtained only two different compounds that are not isotypic to their thiocyanate analogue. Such observations might be of interest in those cases, in which thermal decomposition reactions lead to the formation of a new modification of a metal thiocyanate, which might be isotypic to its selenocyanate analogue. Even if this is not the case here, because the new modification **1CI** is not isotypic to **2B**, we have recently reported on an example in which we have determined the structure of an metastable modification of a metal thiocyanate coordination polymer based on the structural data of its thermodynamically more stable selenocyanate analog.¹²

Summarizing, the exchange of the paramagnetic metal cations like *e.g.* Mn(II), Fe(II), Co(II) or Ni(II) by cadmium seems to be a promising approach to retrieve structural information on the paramagnetic analogues and to get a deeper insight into the structural aspects of thermal decomposition reactions on the way to more condensed coordination networks based on transition metal thio- or selenocyanates. The former is of special interest, because structural information is really needed to understand their magnetic properties in more detail.

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