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New Coordination Compounds Based on $Cd(NCS)_2(4\text{-Ethylpyridine})_x$ ($x = 4, 2, 1$)

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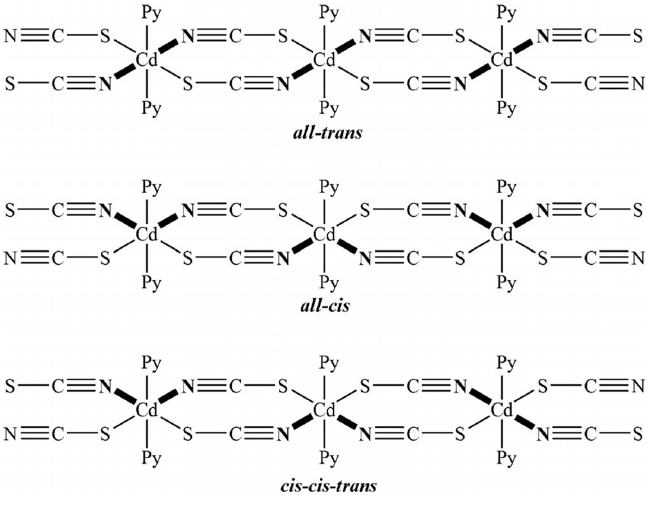
Abstract. The reactions of different ratios of cadmium(II) thiocyanate and 4-ethylpyridine as neutral co-ligand in water at room temperature leads to the formation of the three new coordination compounds of different topology. In the crystal structure of the 1:4 compound (1:4 = ratio between metal and neutral co-ligand) $Cd(NCS)_2(4\text{-ethylpyridine})_4$ (**1**) discrete complexes are found, in which the cadmium ions are coordinated by two terminal N-bonded anionic ligands and four 4-ethylpyridine co-ligands. In the crystal structure of the 1:2 compound $[Cd(NCS)_2(4\text{-ethylpyridine})_2]_n$ (**2**) the cadmium cations are coordinated by two S-bonded, two N-bonded thiocyanato anions and two 4-ethylpyridine ligands, all of them are *trans*-oriented. The Cd^{2+} cations are connected by μ-1,3 bridging thiocyanato anions into chains, which elongate in the direction of the crystallographic *a* axis. In the crystal structure of the 1:1 compound $[Cd(NCS)_2(4\text{-ethylpyridine})]_n$ (**3**) a more condensed coordination network is observed, in which each Cd^{2+} cation is coordinated by two N-bonded and three S-bonded as well as one 4-ethylpyridine ligand within slightly distorted octahedra. The cadmium cations are linked into chains by μ-1,3- and μ-1,1,3-bridging thiocyanato anions. On heating the 1:4 compound **1** two mass steps are observed in the TG curve, of which the first one is well resolved. The residue obtained after the first TG step is investigated by XRPD, elemental analysis, and IR spectroscopy, it is proven that the 1:2 compound $Cd(NCS)_2(4\text{-ethylpyridine})_2$ is obtained as a phase pure material. Based on the results of IR spectroscopic investigations the coordination mode of the thiocyanato anions was additionally investigated.

Introduction

Recently, we have reported on the synthesis of transition metal thiocyanato coordination polymers, in which the cations are linked by μ-1,3-bridging anionic ligands that can mediate magnetic exchange.[1–4] Unfortunately, if the synthesis is performed in solution, in most cases discrete complexes are obtained, in which the thiocyanato anions are terminal *N*-bonded indicating that this coordination is more stable. This is in accordance with a search in the CCDC database, which shows that in compounds with hard metals like e.g. Mn, Fe, Co, and Ni the bridging coordination is unfavored and therefore, less compounds are reported with some selected examples given in the reference list.[5–14] However, we have found that the μ-1,3-bridging compound can be prepared by thermal decomposition of precursors, in which the anions are only terminal *N*-bonded and in which a part of the neutral N-donor co-ligands are removed.[15–18] Unfortunately, by this procedure only microcrystalline products are obtained and therefore, structural information is difficult to extract. However, in these cases the μ-1,3-bridging compounds based on cadmium can be crystallized from solution, which are more stable because of the chalcophilicity of this cation. In those cases, where they are isotypic to their paramagnetic analogues, the structures of the latter can be determined by Rietveld refinement.[19–21]

In this context we have reported on cadmium thiocyanato coordination polymers based on pyridine as neutral co-ligand.[22] Within these investigations we have obtained three different modifications of $[Cd(NCS)_2(pyridine)_2]_n$, in which the cadmium cations are always coordinated by two *N*-bonded and two *S*-bonded thiocyanato anions as well as two pyridine ligands. The cadmium cations are linked by pairs of μ-1,3 bridging thiocyanato anions into chains, in which the thiocyanato anions are either all-*trans*, all-*cis*- or *cis-cis-trans* coordinated (Scheme 1).



Scheme 1. Arrangement of the thiocyanato anions in the three structures of $[Cd(NCS)_2(pyridine)_2]_n$.[22]

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The all-*trans* compound is metastable and can only be prepared by thermal decomposition of $Cd(NCS)_2(pyridine)_4$. In solution it converts into the thermodynamic stable *cis-cis-trans* compound via the metastable all-*cis* modification as intermediate. Finally, if less pyridine is used in the synthesis, a 1:1 compound of composition $[Cd(NCS)_2(pyridine)]_n$ is obtained.

Based on these results we decided to investigate compounds based on other pyridine derivatives and in the beginning we used 4-ethylpyridine as co-ligand. Within these investigations we obtained three compounds of different composition but we have found no hints for the formation of different modifications. Herein we report on our results.

Results and Discussion

Crystal Structure of $Cd(NCS)_2(4\text{-ethylpyridine})_4$ (1)

If an excess of 4-ethylpyridine is used in the synthesis the 1:4 compound $Cd(NCS)_2(4\text{-ethylpyridine})_4$ is obtained as a phase pure material (Figure 1). This compound crystallizes in the triclinic space group $P\bar{1}$ with four formula units in the unit cell (Table 5). The asymmetric unit consists of three crystallographically independent discrete complexes, with two of them located on centers of inversion. In each of the three complexes the cadmium(II) cations are coordinated by two terminal *N*-bonded thiocyanato anions and four 4-ethylpyridine ligands within slightly distorted octahedra (Table 1 and Figure 2). The values of the bond lengths and angles in all three complexes are comparable and as expected the Cd–N bond lengths to the negatively charged thiocyanato anions are significantly shorter than those to the neutral 4-ethylpyridine ligands (Table 1). Interestingly, in all three complexes a large deviation of the Cd–N–C bond angles from linearity is observed [Cd1–N1–C1 = 145.9(3)°, Cd1–N2–C2 = 151.0(3)°, Cd2–N3–C3 = 154.0(3)°, and Cd3–N4–C4 = 159.0(3)°]. Significant differences in all complexes are predominantly found in the conformation of the ethyl substituent.

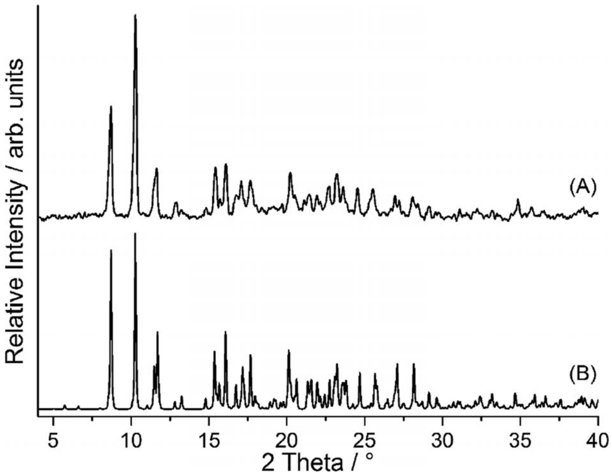

Figure 1. Experimental XRPD pattern of compound **1** (A) and XRPD pattern of **1** calculated from single-crystal data (B).

Table 1. Selected bond lengths /Å for compound **1**.

Cd(1)–N(1)	2.315(3)	Cd(2)–N(3)	2.282(3)
Cd(1)–N(2)	2.273(3)	Cd(2)–N(50)	2.396(4)
Cd(1)–N(10)	2.367(3)	Cd(2)–N(60)	2.377(3)
Cd(1)–N(20)	2.353(3)	Cd(3)–N(4)	2.283(3)
Cd(1)–N(30)	2.408(3)	Cd(3)–N(70)	2.390(4)
Cd(1)–N(40)	2.385(3)	Cd(3)–N(80)	2.390(3)

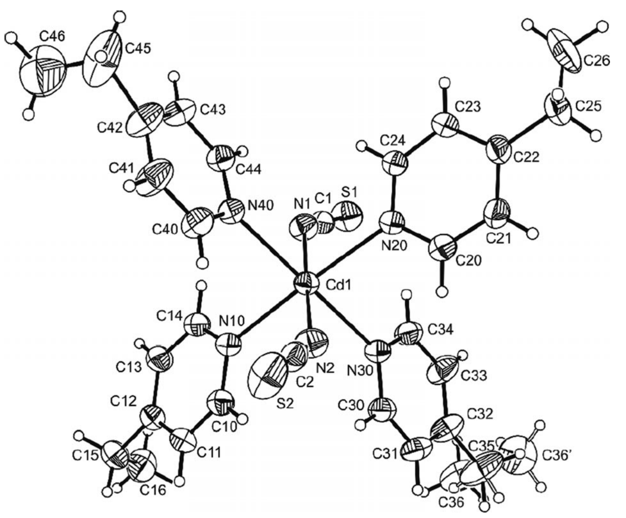

Figure 2. ORTEP plot of one of the three crystallographic independent complexes in **1** as a representative with labeling and displacement ellipsoid drawn at the 50 % probability level.

Crystal Structure of $[Cd(NCS)_2(4\text{-ethylpyridine})_2]_n$ (2)

Crystals of the 1:2 compound $[Cd(NCS)_2(4\text{-ethylpyridine})_2]_n$ (**2**) were obtained by the reaction of stoichiometric amounts of $Cd(NCS)_2$ and 4-ethylpyridine but can also be obtained by thermal decomposition of compound **1** (see below). This compound crystallizes in the centrosymmetric space group $P2_1/c$ with two formula units in the unit cell (Table 5). The asymmetric unit consists of one cadmium(II) cation located on a center of inversion, as well as of one thiocyanato anion and one 4-ethylpyridine ligand in general positions. The cadmium(II) cations are coordinated by two *N*-bonded and two *S*-bonded thiocyanato anions as well as two *N*-bonded 4-ethylpyridine ligands, all of them are *trans*-oriented. The CdN_4S_2 octahedra are slightly distorted with distances in the range of 2.290(3) Å to 2.7622(8) Å and angles between 87.33(7)° and 92.67(7)° and of 180° (Figure 3 and Table 2).

In the crystal structure, the cadmium(II) cations are linked via μ-1,3-bridging thiocyanato anions into chains, which elongate in the direction of the crystallographic *b* axis (Figure 4). Neighboring chains are arranged in order that the aromatic rings are coplanar oriented indicating for π···π interactions.

Crystal Structure of $[Cd(NCS)_2(4\text{-ethylpyridine})]_n$ (3)

Single-crystals suitable for structure determination of a ligand-deficient 1:1 compound $[Cd(NCS)_2(4\text{-ethylpyridine})]_n$

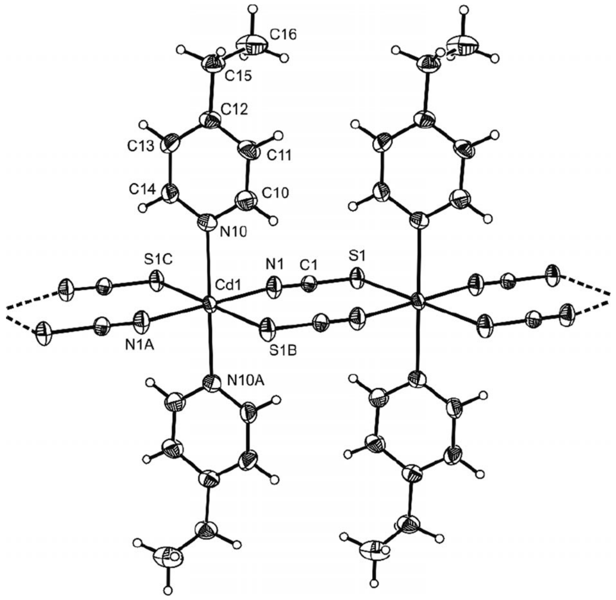

Figure 3. ORTEP plot of compound **2** with labeling and displacement ellipsoids drawn at the 50 % probability level. Symmetry codes: A = –*x* + 1, –*y*, –*z* + 1; B = –*x*, –*y*, –*z* + 1; C = *x* + 1, *y*, *z*.

Table 2. Selected bond lengths /Å for compound **2**. Symmetry codes: A = –*x* + 1, –*y*, –*z* + 1; B = –*x*, –*y*, –*z* + 1.

Cd(1)–N(1)	2.290(3)	N(1)–Cd(1)–S(1B)	92.7(1)
Cd(1)–N(10)	2.366(3)	N(1A)–Cd(1)–N(10)	89.9(1)
Cd(1)–S(1B)	2.762(1)	N(10)–Cd(1)–S(1B)	89.6(1)
N(1)–Cd(1)–N(10)	90.1(1)	N(10A)–Cd(1)–S(1B)	90.4(1)
N(1A)–Cd(1)–S(1B)	87.3(1)		

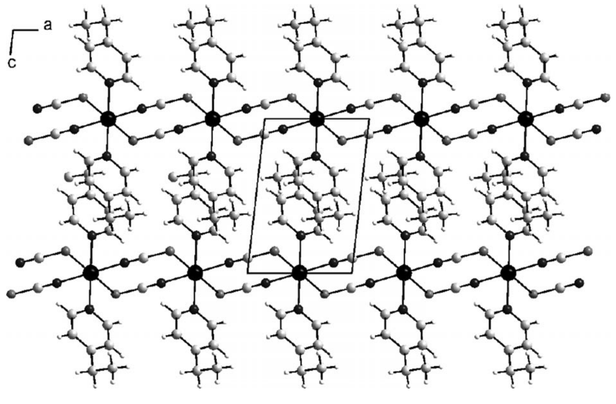

Figure 4. Crystal structure of [Cd(NCS)$_2$(4-ethylpyridine)$_2$]$_n$ (**2**) with view along the crystallographic *b* axis.

(**3**) can be synthesized by an excess of cadmium(II) thiocyanate with 4-ethylpyridine. This compound **3** crystallizes in the centrosymmetric space group $P2_1/n$ with all atoms in a general position (Table 5). In the crystal structure each cadmium(II) cation is coordinated by two *N*-bonded and three *S*-bonded thiocyanato anions as well as one 4-ethylpyridine ligand in a slightly distorted octahedral arrangement (Figure 5, Table 3).

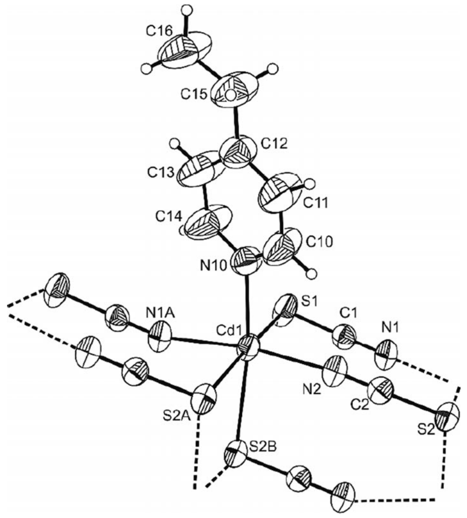

Figure 5. ORTEP plot of compound **3** with labeling and displacement ellipsoids drawn at the 50 % probability level. Symmetry codes: A = *x*, *y* + 1, *z*; B = –*x*, –*y* + 2, –*z* + 1.

Table 3. Selected bond lengths /Å for compound **3**. Symmetry codes: A = *x*, *y* – 1, *z*; B = –*x* + 1, –*y* + 2, –*z* + 1.

Cd(1)–N(1A)	2.259(2)	N(2)–Cd(1)–S(1)	97.6(1)
Cd(1)–S(2B)	2.779(1)	N(2)–Cd(1)–S(2A)	82.0(1)
Cd(1)–S(2A)	2.904(1)	N(10)–Cd(1)–S(2A)	84.6(1)
Cd(1)–N(2)	2.288(2)	S(1)–Cd(1)–S(2A)	177.4(1)
Cd(1)–N(10)	2.325(2)	N(10)–Cd(1)–S(1)	97.9(1)
Cd(1)–S(1)	2.6403(7)	N(2)–Cd(1)–S(2B)	90.6(1)
N(1A)–Cd(1)–N(2)	168.9(1)	N(10)–Cd(1)–S(2B)	167.8(1)
N(1A)–Cd(1)–N(10)	91.4(1)	S(1)–Cd(1)–S(2B)	93.7(1)
N(2)–Cd(1)–N(10)	91.5(1)	N(1A)–Cd(1)–S(2A)	87.65(6)
N(1A)–Cd(1)–S(1)	92.6(1)	S(2B)–Cd(1)–S(2A)	83.81(2)
N(1A)–Cd(1)–S(2B)	84.35(6)		

Two neighboring octahedra are connected by pairs of μ-1,1,3(S,S,N)-coordinating thiocyanato anions into dimers, which are further connected via μ-1,3(N,S) and the μ-1,1,3-(S,S,N)-bridging thiocyanato anions into double chains, which elongate in the direction of the crystallographic *a* axis (Figure 6, Figure 7).

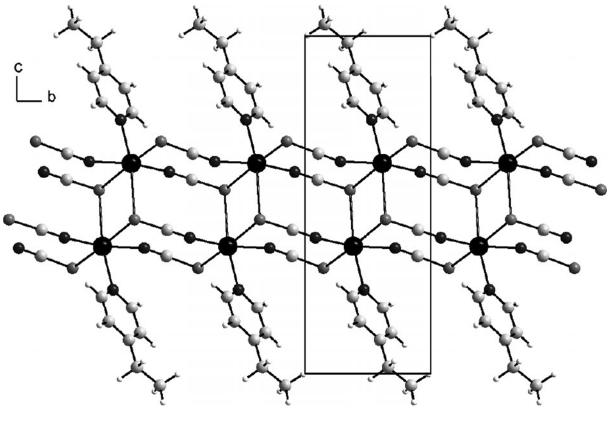

Figure 6. Crystal structure of [Cd(NCS)$_2$(4-ethylpyridine)]$_n$ (**3**) with view along the crystallographic *a* axis.

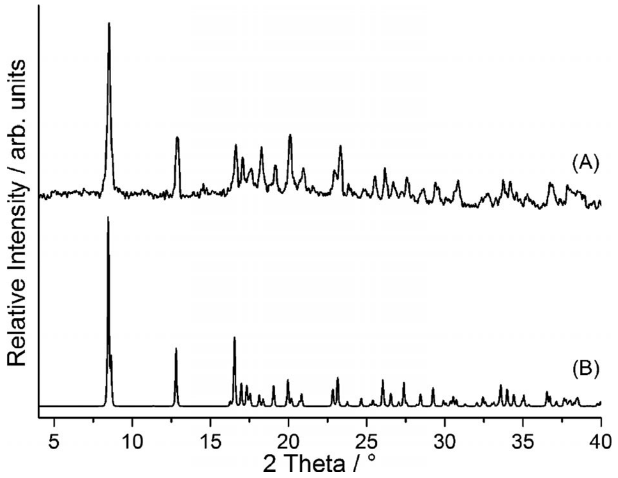

Figure 7. Experimental XRPD pattern of compound **3** (A) and XRPD pattern of **3** calculated from single-crystal data (B).

Thermoanalytical Investigations

In order to investigate if compounds **2** and **3** can also be obtained by thermal decomposition, the 4-ethylpyridine-rich 1:4 compound **1** was investigated for their thermal properties. In this context the question raises if the same modification is found by thermal decomposition as it can be obtained from solution. On heating of compound **1** in a thermobalance to 300 °C, three mass steps are observed in the TG curve that were accompanied with endothermic events in the DTA curve (Figure 8). From the DTG curve it is obvious that the first mass step is well, all others poorly resolved. The experimental mass loss of $\Delta m_{(\text{exp})} = 32.4\,\%$ in the first step and of $\Delta m_{(\text{exp})} = 15.9\,\%$ in the second step are in good agreement with the removal of two 4-ethylpyridine ligands in the first and one 4-ethylpyridine ligand ($\Delta m_{(\text{calcd.})} = 16.3\,\%$) in the second step. To verify the nature of the intermediates additional TG experiments were performed and stopped after the first and second TG step. Elemental analysis of the residue obtained after the first TG step yielded a composition of $Cd(NCS)_2$(4-ethylpyridine)$_2$ (see Experimental Section). XRPD investigations of the residue prove that compound **2** is obtained (Figure 9). Additional XRPD investigations of the residue obtained after the second TG step shows that it is amorphous against X-ray.

Infrared Spectroscopic Investigations

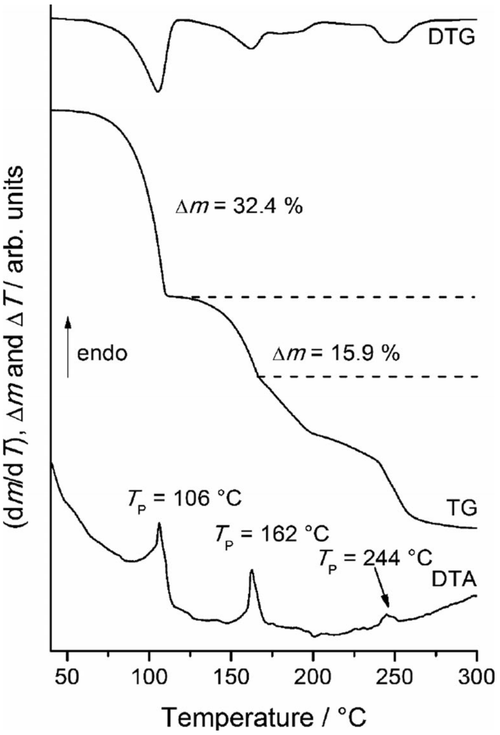

Figure 8. DTG, TG and DTA curves of compound **1**. Heating rate = 1 K·min^{-1}; given are the peak temperatures T_P in °C and the mass loss in %.

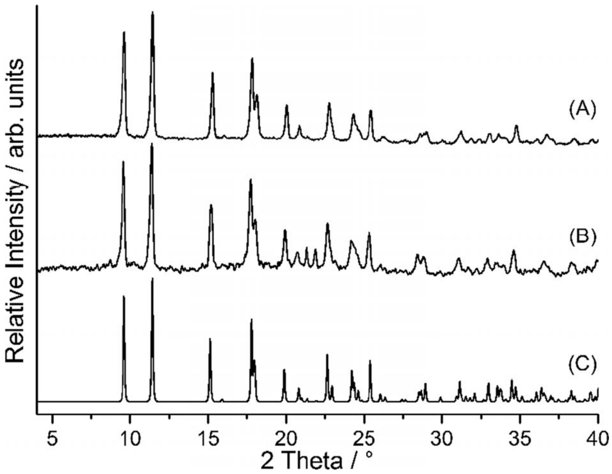

Figure 9. Experimental XRPD pattern of compound **2** obtained from solution (A) and XRPD pattern of the residue obtained after the first TG step in the thermal decomposition reaction of compound **1** (B) and XRPD pattern calculated from single-crystal data for compound **2** (C).

The coordination mode of the thiocyanato anions was additionally investigated by IR spectroscopic investigations by analyzing the asymmetric stretching vibration ν_{as}(CN) of the thiocyanato anions. According to the literature for terminal *N*-bonded thiocyanato anions the asymmetric stretching vibration is found at about 2050 cm^{-1}, whereas for μ-1,3-(N,S)-bridging thiocyanato anions this value shifted to about 2100 cm^{-1}. Finally, if μ-1,1-(N,N)-bridging anions are present this vibration is observed below 2050 cm^{-1}.[23,24] However, we have found that all these values depend strongly on the nature of the metal cation and the co-ligand and therefore, can overlap for the different coordination modes. To investigate this dependence in more detail all compounds were investigated by IR spectroscopy. However, from these investigations it is obvious that in this case only small deviations are found from the values given in literature and that these values are comparable to those obtained for the corresponding cadmium thiocyanato coordination compounds based on pyridine as co-ligand (Table 4). Moreover, from these investigations it is also obvious that ν_{as}(CN) is shifted by about 20 cm^{-1} to higher values if μ-1,1,3-[S,S,N)-coordinating anions are present.

Table 4. Values of the asymmetric stretching vibration $\nu_{as}(CN)$ in compounds **1**, **2** and **3** as well as for the corresponding pyridine compounds retrieved from literature.[22].

Compound	$\nu_{as}(CN)$ /cm^{-1}	Coordination
$Cd(NCS)_2$(4-ethylpyridine)$_4$ (**1**)	2037	terminal
[$Cd(NCS)_2$(4-ethylpyridine)$_2$]$_n$ (**2**)	2102	μ-1,3
[$Cd(NCS)_2$(4-ethylpyridine)]$_n$ (**3**)	2124, 2107	μ-1,1,3
$Cd(NCS)_2$(pyridine)$_4$	2054	terminal
[$Cd(NCS)_2$(pyridine)$_2$]$_n$ all-*trans*	2093	μ-1,3
[$Cd(NCS)_2$(pyridine)$_2$]$_n$ all-*cis*	2089, 2107	μ-1,3
[$Cd(NCS)_2$(pyridine)$_2$]$_n$ *cis-cis-trans*	2089	μ-1,3
[$Cd(NCS)_2$(pyridine)]$_n$	2120, 2105	μ-1,1,3

Investigations on the Stability of Compound 2

As mentioned in the introduction, for [$Cd(NCS)_2$(pyridine)$_2$]$_n$ three different modifications are found, that differ in the coordination mode of the anionic ligands. The all-*trans* form was obtained by thermal decomposition and transform into solution within hours into the *cis-cis-trans* form via the all-*cis* form as an intermediate, which proves that the latter represents the thermodynamic stable form at room temperature. In this context it is noted that the all-*trans* form of [$Cd(NCS)_2$(4-ethylpyridine)$_2$]$_n$ is also obtained by thermal decomposition, but in contrast to pyridine this form is also obtained from the liquid phase. At first sight this is not surprising, because if this compound would be metastable it is usually being observed in the beginning. However, if the formation of compound **2** is followed in solution there are no indications that it will transform within a short period into a new modification. Unfortunately, it was observed that this compound transforms slowly into the 4-ethylpyridine-rich compound **1**, which seems to be more stable and which prevent to follow this reaction for a longer time. Additional DSC investigations gave also no hints that additional forms are present and therefore, it cannot be answered if compound **2** represent the stable form or if other modifications will exist.

Conclusions

Three new cadmium thiocyanato coordination polymers with 4-ethylpyridine were presented, that exhibit the same composition and same coordination topology as those for pyridine reported recently.[22] In contrast to [$Cd(NCS)_2$(pyridine)$_2$]$_n$ only one modification was observed for [$Cd(NCS)_2$(4-ethylpyridine)$_2$]$_n$, in which the anionic ligands are always *trans*-configured. This is the most common motive in this class of compounds and observed in several other μ-1,3-(N,S)-bridging compounds.[3,10,11,13] However, during our investigations we have found a more ligand-deficient compound of composition [$Cd(NCS)_2$(4-ethylpyridine)]$_n$, which normally cannot be obtained with other transition metals like Mn, Fe, Co, and Ni because of their relatively low chalcophilicity. This compound exhibits a more condensed coordination network, which is very rare and which was observed only in a few compounds.[22,25]

Experimental Section

Synthesis: $CdSO_4 \cdot 8/3H_2O$, $Ba(NCS)_2 \cdot 3H_2O$, and 4-ethylpyridine were obtained from Alfa Aesar. All chemicals were used without further purification. $Cd(NCS)_2$ was prepared by a reaction of equimolar amounts of $CdSO_4 \cdot 8/3H_2O$ and $Ba(NCS)_2 \cdot 3H_2O$ in water. The resulting precipitate of $BaSO_4$ was filtered off and the filtrate was concentrated to complete dryness resulting in a white residue of $Cd(NCS)_2$. The purity was checked by XRPD and elemental analysis.

Synthesis of [Tetrakis(4-ethylpyridine-κ*N*)-bis(thiocyanato-κ*N*)-cadmium(II)] (1): Colorless block-shaped single crystals suitable for X-ray structure determination were obtained by a reaction of $Cd(NCS)_2$ (68.6 mg, 0.30 mmol) with an excess of 4-ethylpyridine in a closed test tube at 120 °C. Colorless block-shaped single-crystals were obtained on cooling after 3 d.

A white crystalline powder was obtained by the reaction of $Cd(NCS)_2$ (343 mg, 1.50 mmol) with an excess of 4-ethylpyridine by stirring the reactants at 120 °C in a closed test tube. The residues were filtered off and washed with water and diethyl ether and dried in air. Yield based on $Cd(NCS)_2$: 969 mg (98.4 %). $C_{30}H_{36}CdN_6S_2$ (657.18): calcd. C 54.83, H 5.52, N 12.79, S 9.76 %; found C 55.16, H 5.45, N 12.81, S 10.47 %. **IR** (ATR): $\tilde{\nu}$ = 2969 (w), 2931 (w), 2873 (w), 2037 (s), 1609 (s), 1556 (m), 1499 (w), 1454 (m), 1421 (m), 1375 (w), 1317 (w), 1220 (m), 1107 (w), 1066 (w), 1013 (m), 971 (w), 877 (w), 827 (s), 783 (m), 571 (m), 501 (m) cm^{-1}.

Synthesis of Catena-poly[bis(4-ethylpyridine-κ*N*)-bis(thiocyanato-κ*N*,*S*)-cadmium(II)] (2): Colorless block-shaped single crystals suitable for X-ray structure determination were obtained by a reaction of $Cd(NCS)_2$ (34.3 mg, 0.15 mmol) and 4-ethylpyridine (34.1 μL, 0.30 mmol) in water (1 mL) in a snap-vial at room temperature after 1 week.

A white crystalline powder was obtained by the reaction of $Cd(NCS)_2$ (343 mg, 1.50 mmol) and 4-ethylpyridine (341 μL, 3.0 mmol) by stirring the reactants in water (3 mL) for 3 d at room temperature. The residues were filtered off and washed with water and diethyl ether and dried in air. Yield based on $Cd(NCS)_2$: 639 mg (96.3 %). $C_{16}H_{18}CdN_4S_2$ (442.87): calcd. C 43.39, H 4.10, N 12.65, S 14.48 %; found C 42.96, H 3.70, N 12.47, S 13.87 %. **IR** (ATR): $\tilde{\nu}$ = 2969 (w), 2931 (w), 2872 (w), 2102 (s), 1611 (s), 1556 (m), 1501 (m), 1455 (m), 1421 (m), 1375 (w), 1224 (m), 1108 (w), 1070 (m), 1015 (m), 981 (w), 932 (w), 819 (s), 785 (m), 567 (m), 504 (m), 463 (m) cm^{-1}.

Synthesis of Catena-poly[(4-ethylpyridine-κ*N*)-(bis-thiocyanato-k*N*,*S*)-(tris-thiocyanato-κ*N*,*S*,*S*)-cadmium(II)] (3): Single crystals suitable for X-ray structure determination were obtained by a reaction of $Cd(NCS)_2$ (137 mg, 0.6 mmol) and 4-ethylpyridine (17.1 μL, 0.15 mmol) in ethanol (1 mL) in a snap-vial at room temperature. Colorless block-shaped single-crystals were obtained after 3 d.

A white crystalline powder was obtained by the reaction of $Cd(NCS)_2$ (411 mg, 1.8 mmol) and 4-ethylpyridine (51.3 μL, 0.45 mmol) in 3 mL ethanol, by stirring the reactants in solution for 3 d at room temperature. The residues were filtered off and washed with water and diethyl ether and dried in air. Yield based on $Cd(NCS)_2$: 147 mg (97.5 %). $C_9H_9CdN_3S_2$ (335.72): calcd. C 32.20, H 2.70, N 12.52, S 19.10 %; found C 32.31, H 2.81, N 12.51, S 18.63 %. **IR** (ATR): $\tilde{\nu}$ = 2977 (w), 2134 (s), 2124 (s), 2107 (s), 1615 (s), 1556 (w), 1504 (w), 1428 (m), 1227 (m), 1068 (w), 1021 (m), 828 (s), 786 (m), 569 (m), 447 (m) cm^{-1}.

Table 5. Selected crystal data and details on the structure determinations from single crystal data for compound Cd(NCS)$_2$(4-ethylpyridine)$_4$ (**1**), [Cd(NCS)$_2$(4-ethylpyridine)$_2$]$_n$ (**2**), and [Cd(NCS)$_2$(4-ethylpyridine)]$_n$ (**3**).

	1	**2**	**3**
Formula	$C_{30}H_{36}CdN_6S_2$	$C_{16}H_{18}CdN_4S_2$	$C_9H_9CdN_3S_2$
MW /g·mol^{-1}	657.17	442.86	335.71
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a /Å	11.5997(10)	5.8913(5)	13.8186(6)
b /Å	16.3699(12)	18.3943(16)	5.81020(10)
c /Å	18.7395(14)	8.5953(8)	15.5742(7)
α /°	72.712(8)	90	90
β /°	75.252(9)	96.5420(10)	91.153(3)
γ /°	76.458(9)	90	90
Crystal size /mm	0.19 × 0.12 × 0.08	0.12 × 0.09 × 0.07	0.12 × 0.10 × 0.08
V /Å^3	3236.9(4)	925.38(14)	1250.18(8)
T /K	293	200	293
Z	4	2	4
D_{calc} /mg·m^{-3}	1.349	1.589	1.784
μ /mm^{-1}	0.832	1.409	2.052
θ_{max} /°	28.06	27.96	27.50
Reflections collected	42893	9733	19807
Unique reflections	15164	2196	2888
T_{min} / T_{max}	0.7793 / 0.8922	0.7654 / 0.8472	0.6883 / 0.7611
R_{int}	0.0395	0.0517	0.0256
Refl. [$F_o > 4\sigma(F_o)$]	11478	1768	2529
Parameters	720	107	136
R_1 [$F_o > 4\sigma(F_o)$]	0.0485	0.0387	0.0253
wR_2	0.1362	0.0975	0.0522
GOF	1.033	1.021	1.112
$\Delta\rho_{max/min}$ /e·Å^{-3}	0.91 / –0.72	0.95 / –1.16	0.40 / –0.42

Single Crystal Structure Analysis: The data collection was performed with an imaging plate diffraction system: STOE IPDS-1 for **2** and STOE IPDS-2 for **1** and **3** using Mo-K_α radiation. The structure solution was done with direct methods using SHELXS-97 and structure refinement was performed against F^2 using SHELXL-97.[26] Numerical absorption correction was applied using X-red and X-shape of the Program Package X-area.[27,28] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were positioned with idealized geometry and were refined isotropic with $U_{iso}(H) = -1.2U_{eq}(C)$ using a riding model with d_{C-H} = 0.93 Å for **1** and **3** and d_{C-H} = 0.95 Å for **2**. In compound **1** one ethyl group is disordered and was refined using a split model. Details of the structure determination are given in Table 5.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-908581 (**1**), CCDC-908582 (**2**), and CCDC-908583 (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Spectroscopy: IR spectra were recorded with an Alpha IR spectrometer from Bruker equipped with a Platinum ATR QuickSnap™ sampling module between 4000–375 cm^{-1}.

Elemental Analysis: CHNS analysis was performed with an EURO EA elemental analyzer, fabricated by EURO VECTOR Instruments and Software.

Differential Scanning Calorimetry: The DSC experiments were performed with a DSC 1 Star System with STARe Excellence Software from Mettler-Toledo AG.

X-ray Powder Diffraction (XRPD): XRPD experiments were performed with 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 2θ = 6.5–7° simultaneous; scan range overall = 2–130°) from STOE & CIE and an Image Plate Detector (scan range overall = 0–127°).

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