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# Synthesis, Crystal Structures, and Properties of Mn(NCS)<sub>2</sub> Coordination Compounds with 4-Picoline as Coligand and Crystal Structure of Mn(NCS)<sub>2</sub>

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Dedicated to Prof. Dr. Hans-Jörg Deiseroth on the Occasion of his 75th Birthday

Abstract. Reaction of  $Mn(NCS)_2$  with 4-picoline (4-methylpyridine) leads to the formation of  $[Mn(NCS)_2(4\text{-picoline})_4]\cdot 0.67\cdot 4\text{-picoline} 0.33\cdot H_2O$  (1-Mn) reported in literature,  $Mn(NCS)_2(4\text{-picoline})_2(H_2O)_2$ (2-Mn/H<sub>2</sub>O), and of  $[Mn(NCS)_2(4\text{-picoline})_2]_n$  (2-Mn/I). 1-Mn and 2-Mn/H<sub>2</sub>O consist of discrete complexes, in which the metal cations are octahedrally coordinated, whereas in 2-Mn/I the metal cations are linked by pairs of  $\mu$ -1,3-bridging thiocyanate anions into corrugated chains. Measurements using thermogravimetry and differential scanning calorimetry as well as temperature dependent X-ray powder diffraction on 1-Mn and 2-Mn/H<sub>2</sub>O reveal that upon heating both compounds transform into  $[Mn(NCS)_2(4\text{-picoline})]_n$  (3-Mn) via 2-Mn/I as intermediate. **3-Mn** shows a very rare chain topology in which the metal cations are linked by  $\mu$ -1,3,3 (N,S,S) coordinating anionic ligands which was never observed before with Mn<sup>II</sup>. From these investigations there is no hint that a further modification of **2-Mn** can be prepared as recently observed for [M(NCS)<sub>2</sub>(4-picoline)<sub>2</sub>]<sub>n</sub> (M = Fe, Cd) and such a form is also not available if the metastable forms of the Fe<sup>II</sup> or Cd<sup>II</sup> compounds were used as template during thermal decomposition. Magnetic investigations on **2-Mn/H<sub>2</sub>O** show only paramagnetic behavior, whereas for **2-Mn/I** antiferromagnetic ordering is observed. Finally, the crystal structure of Mn(NCS)<sub>2</sub> was determined from XRPD data, which shows that it is strongly related to that of **3-Mn**.

## Introduction

For several reasons, coordination compounds based on transition metal thiocyanates have become of increasing interest in the last few years. First of all, the thiocyanate anion is a versatile ligand that can coordinate to metal cations in different ways leading to compounds with a large structural variety.<sup>[1–13]</sup> Moreover, this ligand is able to mediate a magnetic exchange that can be used to prepare compounds that, depending on the nature of the metal cations and the topology of the coordination network, show very different magnetic properties.<sup>[14–24]</sup> These are the reasons why we became interested in this class of compounds several years ago. In the course of these investigations, we also have obtained several

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isomeric or polymorphic modifications that are of special interest, because in this case the chemical composition is constant and all changes in the properties of such compounds can directly be correlated with their structures. For the preparation of such modifications, we frequently use a typical solid state synthesis, where the ligands are stepwise removed by thermal annealing. This procedure very often leads to the formation of metastable modifications but also to compounds with condensed thiocyanate networks that in most cases cannot be obtained from solution.<sup>[25,26]</sup> The synthesis of coordination compounds by solid state synthesis is nothing unusual and also other approaches are reported.<sup>[27–35]</sup>

In this context, we have reported on isomeric modifications of [Fe(NCS)<sub>2</sub>(4-picoline)<sub>2</sub>]<sub>n</sub>.<sup>[36]</sup> From solution a compound is obtained, in which the Fe cations are octahedrally coordinated by two 4-picoline coligands and each two N- and S-bonding thiocyanate anions and are linked by pairs of anionic ligands into chains. Within these chains, two crystallographically independent Fe<sup>II</sup> cations with an alternating all-trans and cis-cistrans coordination are present, which leads to the formation of corrugated chains. If a precursor complex with the composition  $Fe(NCS)_2(4-picoline)_2(H_2O)_2$  is thermally decomposed, the water molecules are removed leading to the formation of the same composition as that obtained from solution but a completely different structure. This compound also consists of the same Fe(NCS)<sub>2</sub> chains but the Fe<sup>II</sup> cations show only an alltrans coordination that leads to the formation of linear chains. Upon further heating, half of the 4-picoline coligands are removed and a compound with the composition [Fe(NCS)<sub>2</sub>(4allgemeine Chemie

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picoline)]<sub>n</sub>. is obtained that shows a very rare chain topology, which for Fe<sup>II</sup> was never observed before. Since by this procedure only microcrystalline powders can be obtained we prepared an analogous compound with Cd<sup>II</sup> as this cation is much more chalcophilic, which means that such compounds can easily be crystallized from solution. Both, the Fe<sup>II</sup> and Cd<sup>II</sup> compound are isotypic and therefore, the structure of the former was determined by Rietveld refinements. In the course of these investigations also two isomers of  $[Cd(NCS)_2(4-picoline)_2]_n$  were isolated. The isomer with corrugated chains is isotypic to that with Fe<sup>II</sup>, whereas that with linear chains crystallizes differently.

Based on all these results, the question arose if two different isomeric forms can also be prepared with Mn<sup>II</sup> and if this is not the case it would be of interest if the isomer with linear or corrugated chains is obtained. More importantly, it should also be checked if a 1D 4-picoline-deficient compound similar to that with Fe<sup>II</sup> and Cd<sup>II</sup> is available, because structures with Mn<sup>II</sup> and this chain topology are unknown in thiocyanate chemistry. It is noted that within these investigations, anhydrous Mn(NCS)<sub>2</sub> was obtained that was structurally characterized by X-ray powder diffraction. However, two coordination compounds with Mn(NCS)<sub>2</sub> and 4-picoline are already reported in literature. This contains [Mn(NCS)<sub>2</sub>(4-picoline)<sub>4</sub>. solvate that consists of discrete complexes with terminally coordinated thiocyanate anions and some solvent in voids of the structure and [Mn(NCS)<sub>4</sub>]<sup>2-</sup> [bis-4-picolinium]<sup>2+</sup>(4-picoline)<sub>2</sub> that consists of negatively charged discrete complexes that are charge balanced by two 4-picolinium cations.<sup>[37-39]</sup> Herein we report on our investigations.

## **Results and Discussion**

### Synthesis and Characterization

By the reaction of  $Mn(NCS)_2$  with an excess of 4-picoline, the literature known compound  $[Mn(NCS)_2(4-picoline)_4]\cdot 0.67\cdot 4$ -picoline $\cdot 0.33\cdot H_2O$  (**1-Mn**) was obtained as a pure phase (Figure S1, Supporting Information). It is noted that the 101 reflection observed at  $2\theta = 8.7^\circ$  is absent in the calculated powder pattern, because it is sensitive to the amount of solvent incorporated in the voids (Figures S1 and S2, Supporting Information). When  $Mn(NCS)_2$  is reacted with 4-picoline in ratio 1:2 in water, a hydrate complex with the composition  $Mn(NCS)_2(4\text{-picoline})_2(H_2O)_2$  (**2-Mn/H\_2O**) is obtained that was characterized by single-crystal X-ray diffraction (see below). Comparison of its powder pattern with the calculated one reveals that a pure phase was isolated (Figure S3, Supporting Information).

Compared to **1-Mn** the CN stretching vibration of the thiocyanate anions observed by IR and Raman spectroscopy is shifted by about 50 wavenumbers to 2095, respectively 2100 cm<sup>-1</sup>. (Figures S4 and S5, Supporting Information). If the 4-picoline content is reduced, crystals of a further compound with the composition [Mn(NCS)<sub>2</sub>(4-picoline)<sub>2</sub>]<sub>n</sub> (**2-Mn/I**) were obtained and investigated by IR and Raman spectroscopy as well as single crystal structure analysis (see below). Surprisingly, the CN stretching vibrations are observed at lower values than those in **2-Mn/H<sub>2</sub>O** even if bridging thiocyanate anions are present (Figure S6, Supporting Information). However, XRPD investigations prove that **2-Mn/I** was obtained as a pure phase (Figure S7, Supporting Information). It is noted that even if Mn(NCS)<sub>2</sub> is used in excess there is no hint that a further 4-picoline-deficient compound exists. Therefore, the precursor complexes **1-Mn** and **2-Mn/H<sub>2</sub>O** were investigated by TG-DSC measurements and temperature dependent in situ XRPD measurements. In this context it was also of interest if a second modification of **2-Mn** can be obtained by this route as recently reported for the corresponding Fe and Cd compounds.<sup>[36]</sup>

### Thermoanalytical Investigations

Measurements of 1-Mn using TG-DSC show three mass losses, which are each accompanied by an endothermic DSC signal (Figure 1). The first mass loss is in reasonable agreement with that calculated for the removal of the solvate molecules and two coordinated 4-picoline ligands ( $\Delta m = 38-42\%$ ,  $\Delta m_{\text{calcd}} = 40.6\%$ ). The mass losses in the second and third mass step point to the emission of one 4-picoline ligand in each step, indicating the formation of a further crystalline phase with the composition  $[Mn(NCS)_2(4-picoline)]_n$  (3-Mn) that decomposes into Mn(NCS)2 upon further heating. Similar measurements were performed for 2-Mn/H<sub>2</sub>O that also show three reasonable resolved mass losses (Figure 1). The first mass loss is in reasonable agreement with the emission of the two coordinated water molecules  $[(\Delta m_{calc} (-2H_2O) = 9.2\%],$ while the second and third are in good agreement with the release of one 4-picoline ligand each [ $\Delta m_{calc}$  (-4-picoline) = 23.6%].



Figure 1. DTG, TG, and DSC curve for 1-Mn (left) and 2-Mn/H<sub>2</sub>O (right) measured with a heating rate of 4 K·min<sup>-1</sup>.

The compounds formed after the first mass loss were isolated and investigated with XRPD. The results confirmed that **2-Mn/I** has been formed as a pure phase (Figure S8, Supporting Information). This is somehow surprising, because similar measurements on the corresponding Fe and Cd compounds always lead to mixtures of two different isomers. Therefore, ad-



ditional TG curves were recorded using different heating rates with no sign for the formation of a further modification (Figures S9 and S10, Supporting Information). However, to identify the compound formed in the second TG step the corresponding residues were investigated by XRPD, which indicated that **3-Mn** is isotypic to  $[Fe(NCS)_2(4-picoline)]_n$  and  $[Cd(NCS)_2(4-picoline)]_n$  reported recently (Figure S11, Supporting Information). Therefore, its crystal structure was determined by Rietveld refinements (see Experimental Section and Figure S13, Supporting Information). Each two bands are observed for the CN stretching vibrations at 2093 and 2115 cm-<sup>1</sup> in the IR and at 2097 and 2116 cm<sup>-1</sup> in the Raman spectra, which is in agreement with the presence of two different thiocyanate anions (Figure S12, Supporting Information). To complete these investigations we also determined the crystal structure of Mn(NCS)<sub>2</sub> formed in the third TG step by XRPD, for which no crystallographic data were available (see Experimental Section and Figure S14, Supporting Information).

From the TG measurements there is no hint for the formation of a further crystalline phase of  $[Mn(NCS)_2(4-picoline)_2]_n$ as observed for Fe and Cd, which is somehow surprising, because these cations usually behave chemically very similar. Therefore, much of effort was made to prove the existence of such a form. In the beginning, temperature dependent in situ XRPD measurements of **1-Mn** and **2-Mn/H<sub>2</sub>O** were performed. Upon heating both compounds transform into Mn(NCS)<sub>2</sub> via **2-Mn/I** and **3-Mn** as intermediates as already observed in the TG-DSC measurements (Figure 2).

We also tried to remove a part of the coligands under mild conditions but even in this case **2-Mn/I** was exclusively isolated (Figure S15, Supporting Information). Similar results were obtained when **2-Mn/H<sub>2</sub>O** was annealed at 75 °C and 220 °C (Figure S16, Supporting Information). Finally, we also tried to decompose physical mixtures of the precursor **2-Mn/ H<sub>2</sub>O** and the linear chain isomers with Cd (**2-Cd/III**) and Fe (**2-Fe/II**) to enforce the formation of these modifications but only mixtures of **2-Mn/I** and **2-Cd/III** respectively **2-Fe/II** were obtained (Figures S17 and S18, Supporting Information).

However, to check if the transformation of  $2-Mn/H_2O$  into 2-Mn/I is reversible; 2-Mn/I was stored in a desiccator over a saturated H<sub>2</sub>O atmosphere. In this case the transformation is completed within 29 h, leading to pure samples of  $2-Mn/H_2O$ , which shows that the water removal is reversible (Figure S19, Supporting Information).

### **Crystal Structures**

 $Mn(NCS)_2(4\text{-picoline})_2(H_2O)_2$  (2-Mn/H<sub>2</sub>O) crystallizes in the monoclinic space group  $P2_1/c$  with Z = 2 formula units in the unit cell and is isotypic to  $Fe(NCS)_2(4\text{-pico$  $line})_2(H_2O)_2$ .<sup>[36]</sup> The asymmetric unit consists of one Mn cation, located on a center of inversion and one thiocyanate anion, one 4-picoline coligand and one water molecule located on general positions (Figure S20, Supporting Information). The Mn cations are sixfold coordinated by two terminally Nbonded thiocyanate anions, two 4-picoline coligands and two coordinated water molecules into discrete complexes (Figure 3

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Figure 2. Temperature dependent XRPD pattern of 1-Mn (top) and 2-Mn/H<sub>2</sub>O (bottom) together with the calculated powder pattern of 1-Mn (A1), 2-Mn/H<sub>2</sub>O (A2), 2-Mn/I (B), 3-Mn (C), and Mn(NCS)<sub>2</sub> (D).

top). The bond lengths around the central Mn atoms are comparable to those reported in literature and the bonding angles show that the octahedra are slightly distorted (Table S1, Supporting Information). In the crystal structure, the discrete complexes are linked by intermolecular O–H···S hydrogen bonds between the H atoms of the water molecules and the thiocyanate S atoms into layers parallel to the b/c plane (Figure 3 bottom and Table S2, Supporting Information). These layers are further connected by intermolecular C–H···S hydrogen bonding into a 3D network (Figure S21, Supporting Information).

**2-Mn/I** crystallizes *C*-centered in the monoclinic space group C2/c and is isotypic to form **I** of  $[Fe(NCS)_2(4\text{-pico$  $line})_2]_n$ .<sup>[36]</sup> The asymmetric unit consists of two crystallographically independent Mn cations (one located on a center of inversion and the other located on a twofold rotational axis), and two crystallographically independent thiocyanate anions and 4-picoline coligands in general positions (Figure S22, Supporting Information). Each Mn cation is sixfold coordinated to both two N- and two S-bonding thiocyanate anions and two 4picoline coligands but the metal coordination for each independent Mn center is different (Table S3, Supporting Information). For Mn2 the thiocyanate N and S atoms as well as the 4neine Chemi

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Figure 3. View of a discrete complex in the crystal structure of 2-Mn/  $H_2O$  (top) and projection of the crystal structure with view along the crystallographic *a* axis and intermolecular hydrogen bonding shown as dashed lines (bottom). An ORTEP plot can be found in Figure S20 (Supporting Information).



Figure 4. Part of a chain in the crystal structure of 2-Mn/I. An ORTEP plot can be found in Figure S22 (Supporting Information).

picoline co-ligand are in *trans*-position whereas for Mn1 the thiocyanate-related S and the 4-picoline N atoms are *cis*, whereas the thiocyanate N atoms are still *trans*, leading to an alternating all-*trans* and *cis-cis-trans* coordination (Figure 4). The central Mn atoms are linked by pairs of  $\mu$ -1,3-bridging thiocyanate anions into corrugated chains (Figure 4).

The crystal structure of the most 4-picoline deficient compound  $[Mn(NCS)_2(4-picoline)]_n$  (**3-Mn**) was determined by a Rietveld refinement using the crystallographic data of the isotypic Fe compound as starting model.<sup>[36]</sup> This compound crystallizes in space group *P*- $\overline{1}$  with *Z* = 2 and all atoms located in general positions. The Mn cations are octahedrally coordinated by two N and three S-bonding thiocyanate anions as well as by one 4-picoline coligand. Additionally, the metal atoms are linked into chains by  $\mu$ -1,3 (N,S) and  $\mu$ -1,3,3 (N,S,S) bridging thiocyanate anions (Figure 5). These chains are further connected into double chains by the sulfur atoms via Mn<sub>2</sub>S<sub>2</sub> units. It is noted that this topology of the thiocyanate network is quite rare and usually observed with the more chalcophilic Cd<sup>II</sup> cations.<sup>[25]</sup>



Figure 5. Part of a chain in the crystal structure of 3-Mn.

As mentioned above, compound **3-Mn** loses the 4-picoline upon heating leading to the formation of Mn(NCS)<sub>2</sub>. Surprisingly, no crystal structure data for this compound were available and only the structure of the tetrahydrate Mn(NCS)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> is reported.<sup>[40]</sup> Therefore, the structure of the anhydrate was determined from XRPD data. This compound crystallizes in the monoclinic space group C2/m with Z = 2 formula units in the unit cell and is isotypic to Ni(NCS)<sub>2</sub> reported by Dubler et al. in 1982.<sup>[41]</sup> The asymmetric unit consists of one crystallographically independent Mn<sup>II</sup> cation that is located on position 2/m, as well as of one thiocyanate anion that is located on a crystallographic mirror plane. The Mn<sup>II</sup> cations are in a square pyramidal environment with four S atoms of four symmetry-related thiocyanate anions in the basal plane and the two N atoms of further anionic ligands in the apical position (Figure 6).

The central  $Mn^{II}$  atoms are linked by the thiocyanate S atoms sharing common edges into chains along the crystallographic *b* axis that are further linked into layers by the N atom of the  $\mu$ -1,3,3 (N,S,S) bridging thiocyanate anions into layers that are parallel to the *a/b* plane (Figure 6 top). These layers are stacked perpendicular to the crystallographic *c*-axis (Figure 6 bottom).

Finally, analysis of the crystal structures of **3-Mn** and  $Mn(NCS)_2$  reveal that their thiocyanate networks are strongly related. In **3-Mn** both,  $\mu$ -1,3 (N,S) and  $\mu$ -1,3,3 (N,S,S) thiocyanate anions are present but the sulfur atoms of the former anionic ligands are close to the 4-picoline ligands of a neighbored

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**Figure 6.** Projections of the crystal structure of  $Mn(NCS)_2$  with view onto (top) and along the layers (bottom).



Figure 7. Projections of the crystal structures of 3-Mn (top) and of  $Mn(NCS)_2$  each showing two neighbored chains. The C–H hydrogen atoms are omitted for clarity and the 4-picoline ligands are shown in wire-stick model.

chain (Figure 7). This indicates that on ligand removal these sulfur atoms will complete the Mn coordination of a neighbored chain forming  $Mn_2S_2$  via common edges of two neighbored octahedra (Figure 7). However, even if this indicates that

a smooth reacting pathway might be present, it does not automatically mean that the reaction is topotactic.

### Magnetic Measurements

The magnetic properties of 1-Mn, 2-Mn/H<sub>2</sub>O, and 3-Mn were investigated by DC magnetic measurements. For the discrete complexes 1-Mn and 2-Mn/H<sub>2</sub>O only simple paramagnetic behavior is observed with a Weiss constant of 0.1 K, respectively -4.0 K, indicating very weak dominating antiferromagnetic interactions for the latter (Figure S23 and Table S4, Supporting Information). In contrast, for the chain compounds 2-Mn/I and 3-Mn the Weiss constants amount to -37.7 and -57.0 K, which proves that dominating antiferromagnetic interactions are present (Figure S23 and Table S4, Supporting Information). Moreover, for these compounds a maximum in the susceptibility is observed at 27.0 (2-Mn/I) and 32.4 K (3-Mn), indicating magnetic ordering, which is also observed in other Mn(NCS)<sub>2</sub> chain compounds with linear chains (Figure S24, Supporting Information).<sup>[42]</sup> It is noted that for 3-Mn a small increase of the susceptibility is observed after the maximum, which indicates a small paramagnetic impurity that cannot be detected by XRPD. However, the experimental magnetic moment for the Mn<sup>II</sup> cations is close to that calculated for a high-spin configuration (Table S4).

### Conclusions

These investigations originated from previous investigations of the corresponding Fe and Cd compounds, where two different isomers were obtained for  $[M(NCS)_2(4-picoline)_2]_n$  (M = Fe, Cd). It was found that with Mn only the form with the corrugated chains that is thermodynamically stable at roomtemperature can be prepared and this does not change when crystals of the metastable forms with Fe and Cd were used as nuclei during thermal decomposition. This is somehow surprising, because Mn<sup>II</sup> usually behaves like Cd<sup>II</sup> in thiocyanate chemistry and therefore, a similar reactivity is expected. This is also obvious from the fact that a 4-picoline deficient compound was additionally obtained that is isotypic to the corresponding Fe<sup>II</sup> and Cd<sup>II</sup> compounds and that shows a very rare chain topology that was never observed before for Mn(NCS)<sub>2</sub> coordination compounds and that is comparable to that of a spin-ladder.

### **Experimental Section**

 $Ba(SCN)_2{\cdot}3H_2O$  was purchased from Alfa Aesar,  $MnSO_4{\cdot}H_2O$  and  $MnCl_2{\cdot}2H_2O$  were purchased from Merck and 4-picoline was purchased from Fluka.

 $Mn(NCS)_2$  was synthesized by the reaction of  $Ba(SCN)_2$ ·3H<sub>2</sub>O with  $MnSO_4$ ·H<sub>2</sub>O in demin. H<sub>2</sub>O. The colorless precipitate of  $BaSO_4$  was filtered of and the filtrate was concentrated to dryness in a rotary evaporator giving the colorless powder of  $Mn(NCS)_2$ . The purity was checked by DSC/TG and XRPD. All solvents were used without further purification.

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> Synthesis of  $[Mn(NCS)_2(4-picoline)_4]$ ·4-picoline·H<sub>2</sub>O (1-Mn): Mn(NCS)<sub>2</sub> (1.0 mmol, 171 mg) was dissolved in demin. H<sub>2</sub>O and a 1:1 mixture of 4-picoline and water (2.0 mL each) was added. The precipitate was stirred for one day and filtered off.

> Synthesis of  $Mn(NCS)_2(4\text{-picoline})_2(H_2O)_2$  (2-Mn/H<sub>2</sub>O): Crystals suitable for single crystal X-ray diffraction were obtained by the reaction of  $MnCl_2 \cdot 2H_2O$  (0.5 mmol, 81 mg) and KSCN (1.0 mmol, 97 mg) which were solved in water (1.5 mL) to which 4-picoline (0.25 mmol, 24.3  $\mu$ L) in demin H<sub>2</sub>O (1.5 mL) was added. Larger amounts of **2-Mn/H<sub>2</sub>O** were prepared by dissolving  $Mn(NCS)_2$  (1.0 mmol, 342 mg) in demin. H<sub>2</sub>O (5.0 mL) and adding 4-picoline (1.5 mmol, 3x97  $\mu$ L).

**Synthesis of [Mn(NCS)<sub>2</sub>(4-picoline)<sub>2</sub>]<sub>n</sub> (2-Mn/I):** Crystals suitable for single X-ray diffraction were obtained by the reaction of Mn(NCS)<sub>2</sub>·H<sub>2</sub>O (0.5 mmol, 94.6 mg) and 4-picoline (0.25 mmol, 24.3 µL) in EtOH (1.5 mL) at 120 °C. Mn(NCS)<sub>2</sub> (2.0 mmol, 342 mg) was stirred in MeOH (3.5 mL) to which 4picoline (1.0 mmol, 97 µL) was added. No immediate precipitate was observed and therefore the solution was stirred without closing the lid of the vessel. Alternatively, **2-Mn/I** was synthesized by the reaction of Mn(NCS)<sub>2</sub> (2.0 mmol, 342 mg) with 4-picoline (1.5 mmol, 3x97 µL) at 120 °C in EtOH in a solvothermal glass tube.

Synthesis of  $[Mn(NCS)_2(4-picoline)]_n$  (3-Mn): It is noted that no single crystals were available and that all samples of 3-Mn were prepared by thermal decomposition of either 1-Mn or 2-Mn/H<sub>2</sub>O in a thermobalance.

Single Crystal Structure Analysis: For the collection of single crystal XRD data for 2-Mn/I and 2-Mn/H<sub>2</sub>O a Stoe&Cie IPDS 1 was used. The instrument was equipped with a Mo- $K_{\alpha}$  radiation source. Direct methods were used for the structure solution with the SHELX-package and structure refinement was performed against  $F^2$  using SHELXL-2014/7. For 2-Mn/I a numerical absorption correction was performed using X-Red and X-Shape of the software package X-Area. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were positioned with idealized geometry and were refined isotropically with  $U_{iso}$  (H) = 1.2 U<sub>eq</sub> (C) (1.5 for methyl H). Selected crystal data are given in Table S5 (Supporting Information).

**IR- and Raman Spectroscopy:** IR spectra were recorded at room temperature on a Bruker Vertex70 FT-IR spectrometer using a broadband spectral range extension VERTEX FM for full mid and far IR. Raman spectra were recorded at room temperature on a Bruker RAM II FT-Raman spectrometer using a liquid nitrogen cooled, highly sensitive Ge detector, 1064 nm radiation and 3 cm<sup>-1</sup> resolution.

**Differential Scanning Calorimetry and Thermogravimetry (DSC/TG):** For DSC/TG measurements a STA-PT1000 respectively a STA-PT1600 thermobalance from Linseis were used. Measurements were performed in Al<sub>2</sub>O<sub>3</sub> crucibles and under a dynamic nitrogen atmosphere. The instruments were calibrated using standard referencing materials and corrected for buoyancy.

In situ X-ray Powder Diffraction (XRPD): The temperature dependent in-situ XRPD measurements of 1-Mn and 2-Mn/H<sub>2</sub>O were carried out using a laboratory powder diffractometer in Debye–Scherrer setup (Bruker D8-Advance; Cu- $K_{a1}$  radiation from primary Ge(111)-Johannson-type monochromator, Våntec detector). The sample was loaded into a 0.5 mm diameter quartz capillary (WJM-Glas/Mueller GmbH), which was spun during the measurements. The patterns were measured in a 2 $\theta$  range from 2.0° to 60.0° applying a total scan time of 3 h per measurement. The temperature was adjusted using the TC-transmission furnace (MRI). The sample was heated from 30 °C to 160 °C in 10 K steps and from 160 °C to 250 °C in 5 K steps with a heating rate of 2 K·min<sup>-1</sup>. During each step a diffraction pattern was collected, after a delay time of 5 min to ensure thermal equilibration of the sample. After the experiment, the capillary was measured with a diffractometer equipped with molybdenum radiation (see below).

**Laboratory X-ray Powder Diffraction:** The XRPD measurements for the characterization of all samples were performed with a Stoe Transmission Powder Diffraction System (STADI P) with Cu- $K_{\alpha 1}$  radiation and a Dectris Mythen 1 K detector with a Johann-type-Ge(111) monochromator from STOE & CIE.

XRPD measurements of  $[Mn(NCS)_2(4\text{-picoline})]_n$  and  $Mn(NCS)_2$ were carried out at room temperature on a laboratory powder diffractometer in Debye–Scherrer setup (Stadi P-Diffractometer (Stoe), Mo- $K_{\alpha 1}$  radiation from primary Ge(111)-Johann-type monochromator, array of 3 Mythen 1 K detectors (Dectris). The sample was loaded into a 0.5 mm diameter glass capillary (WJM-Glas/Mueller GmbH), which was spun during the measurements. The pattern of  $[Mn(NCS)_2(4\text{-pico$  $line})]_n$  was measured in a 2 $\theta$  range from 2.0° to 50.0° applying a total scan time of 16 h per measurement and using only one detector. The pattern of  $Mn(NCS)_2$  was collected in a 2 $\theta$  range from 0° to 55° applying a total scan time of 4 h per measurement and using 3 detectors.

All Rietveld refinements<sup>[43]</sup> were performed with the program TOPAS 6.0.<sup>[44]</sup> The profile function was described with the fundamental parameter approach implemented into TOPAS<sup>[45]</sup> and the background was modelled using Chebyshev polynomials. The hump in the background of the diffraction pattern caused by the glass capillary and small amount of amorphous phase was modelled with very broad Lorentzian type peaks (two for  $[Mn(NCS)_2(4-picoline)]_n$  and one for Mn(NCS)<sub>2</sub>). The thiocvanate and 4-picoline molecules were described using rigid bodies in z-matrix notation and their rotation and translation modes were let to refine. The bond lengths and angles were taken from cadmium-related single crystal structure data.<sup>[36]</sup> Distinct isotropic displacement parameters were applied for manganese, thiocyanate and 4picoline molecules. Eventually, the background, all lattice parameters, rotations (except the thiocyanate in  $[Mn(NCS)_2(4-picoline)]_n)$ , translations, the atomic positions of manganese atoms were refined without any constraints during the final Rietveld refinement. For  $[Mn(NCS)_2(4-picoline)]_n$ , hydrogen atoms on the methyl group of the 4-picoline ligands were omitted due to the presence of positional disorder. The final agreement factors are listed in Table S6 (Supporting Information) and the fits of the whole powder patterns are shown in Figures S13 and S14 (Supporting Information).

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-1962529 (**2-Mn/H**<sub>2</sub>**O**), CCDC-1962528 (**2-Mn/I**), CCDC-1962526 (**3-Mn**), and CCDC-1962527 [Mn(NCS)<sub>2</sub>] (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk).

**Supporting Information** (see footnote on the first page of this article): Lists with crystal data and details of the structure refinements, lists with bond lengths and angles, Ortep plots, experimental and calculated XRPD pattern, IR and Raman spectra, TG-DSC curves as well as selected results of the magnetic measurements. Journal of Inorganic and General Chemistry

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Synthesis, Crystal Structures, and Properties of  $Mn(NCS)_2$  Coordination Compounds with 4-Picoline as Coligand and Crystal Structure of  $Mn(NCS)_2$ 



