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

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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-picoline)$_2$]·0.67·4-picoline·0.33·H$_2$O (1-Mn) reported in literature. Mn(NCS)$_2$(4-picoline)$_2$(H$_2$O)$_2$
(2-Mn/H$_2$O), and of [Mn(NCS)$_2$(4-picoline)$_2$(H$_2$O)]$_n$ (2-Mn/I). 1-Mn and 2-Mn/H$_2$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 μ-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$_2$O reveal that upon heating both compounds transform into [Mn(NCS)$_2$(4-picoline)$_2$]$_n$ (3-Mn) via 2-Mn/I as intermediate. 3-Mn shows a very rare chain topology in which the metal cations are linked by μ-1,3,3 (N,S,S) coordinating anionic ligands which was never observed before with Mn$^{II}$. From these investigations there is no hint that a further modification of 2-Mn can be prepared as recently observed for [M(NCS)$_2$(4-picoline)$_2$]$_n$. (M = Fe, Cd) and such a form is also not available if the metastable forms of the Fe$^{II}$ or Cd$^{II}$ compounds were used as template during thermal decomposition. Magnetic investigations on 2-Mn/H$_2$O show only paramagnetic behavior, whereas for 2-Mn/I antiferromagnetic ordering is observed. Finally, the crystal structure of Mn(NCS)$_2$ 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.[$^{[1–13]}$] 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.[$^{[14–24]}$] 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 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.[$^{[25,26]}$] The synthesis of coordination compounds by solid state synthesis is nothing unusual and also other approaches are reported.[$^{[27–35]}$]

In this context, we have reported on isomeric modifications of [Fe(NCS)$_2$(4-picoline)$_2$]$_n$.[$^{[36]}$] 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$^{II}$ cations with an alternating all-trans and cis-cis-trans 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$_2$O)$_2$ 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)$_2$ chains but the Fe$^{III}$ cations show only an all-trans 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)$_2$(4-
picoline]n, is obtained that shows a very rare chain topology, which for FeII was never observed before. Since by this procedure only microcrystalline powders can be obtained we prepared an analogous compound with CdII as this cation is much more chalcophilic, which means that such compounds can easily be crystallized from solution. Both, the FeII and CdII 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)]n were isolated. The isomer with corrugated chains is isotypic to that with FeII, 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 MnII 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 FeII and CdII is available, because structures with MnII and this chain topology are unknown in thiocyanate chemistry. It is noted that within these investigations, anhydrous Mn(NCS)2 was obtained that was structurally characterized by X-ray powder diffraction. However, two coordination compounds with Mn(NCS)2 and 4-picoline are already reported in literature. This contains [Mn(NCS)2(4-picoline)]2+ solvate that consists of discrete complexes with terminally coordinated thiocyanate anions and some solvent in voids of the structure and [Mn(NCS)4]2– [bis-4-picolinium][2+4-picoline]2 that consists of negatively charged discrete complexes that are charge balanced by two 4-picolinium cations.[37–39] 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)]0.674-picoline0.33·H2O (1-Mn) was obtained as a pure phase (Figure S1, Supporting Information). It is noted that the 101 reflection observed at 2θ = 8.7° 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-picoline)2·H2O2 (2-Mn/H2O) 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−1 (Figures S4 and S5, Supporting Information). If the 4-picoline content is reduced, crystals of a further compound with the composition [Mn(NCS)2(4-picoline)]n (2-Mn/I) were obtained and investigated by IR and Raman spectroscopy as well as single crystal structure analysis (see below). Surpris-

ingly, the CN stretching vibrations are observed at lower values than those in 2-Mn/H2O 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)2 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/H2O 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.[36]

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 (Δm = 38–42%, Δm_calc = 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/H2O 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 [Δm_calc (–2H2O) = 9.2%], while the second and third are in good agreement with the release of one 4-picoline ligand each [Δm_calc (–4-picoline) = 23.6%].

Figure 1. DTG, TG, and DSC curve for 1-Mn (left) and 2-Mn/H2O (right) measured with a heating rate of 4 K·min−1.

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)]2n 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\(^{-1}\) in the IR and at 2097 and 2116 cm\(^{-1}\) 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)\(_2\) 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)]2n 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\(_2\)O were performed. Upon heating both compounds transform into Mn(NCS)\(_2\) 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\(_2\)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\(_2\)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\(_2\)O into 2-Mn/I is reversible; 2-Mn/I was stored in a desiccator over a saturated H\(_2\)O atmosphere. In this case the transformation is completed within 29 h, leading to pure samples of 2-Mn/H\(_2\)O, which shows that the water removal is reversible (Figure S19, Supporting Information).

### Crystal Structures

Mn(NCS)\(_2\)(4-picoline)\(_2\)(H\(_2\)O)\(_2\) (2-Mn/H\(_2\)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-picoline)\(_2\)(H\(_2\)O)\(_2\).\(^{[36]}\) 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 N-bonded thiocyanate anions, two 4-picoline coligands and two coordinated water molecules into discrete complexes (Figure 3).

Figure 2. Temperature dependent XRPD pattern of 1-Mn (top) and 2-Mn/H\(_2\)O (bottom) together with the calculated powder pattern of 1-Mn (A1), 2-Mn/H\(_2\)O (A2), 2-Mn/I (B), 3-Mn (C), and Mn(NCS)\(_2\) (D).
As mentioned above, compound 3-Mn loses the 4-picoline upon heating leading to the formation of Mn(NCS)₂. Surprisingly, no crystal structure data for this compound were available and only the structure of the tetrahydrate Mn(NCS)₂(H₂O)₄ is reported.⁴⁰ 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)₂ reported by Dubler et al. in 1982.⁴¹ The asymmetric unit consists of one crystallographically independent Mn²⁺ cation that is located on position 2/m, as well as of one thiocyanate anion that is located on a crystallographic mirror plane. The Mn²⁺ 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 Mn²⁺ 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 μ-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, μ-1,3 (N,S) and μ-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
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.

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 room-temperature 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 MnII usually behaves like CdII 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 FeII and CdII compounds and that shows a very rare chain topology that was never observed before for Mn(NCS)₂ coordination compounds and that is comparable to that of a spin-ladder.

Experimental Section
Ba(SCN)₂·3H₂O was purchased from Alfa Aesar, MnSO₄·H₂O and MnCl₂·2H₂O were purchased from Merck and 4-picoline was purchased from Fluka.

Mn(NCS)₂ was synthesized by the reaction of Ba(SCN)₂·3H₂O with MnSO₄·H₂O in demin. H₂O. The colorless precipitate of BaSO₄ 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.

Magnetic Measurements
The magnetic properties of 1-Mn, 2-Mn/H₂O, and 3-Mn were investigated by DC magnetic measurements. For the discrete complexes 1-Mn and 2-Mn/H₂O 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)₂ chain compounds with linear chains (Figure S24, Supporting Information).[42] 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 MnII cations is close to that calculated for a high-spin configuration (Table S4).
Synthesis of \([\text{Mn(NCS)}_2(4\text{-picoline})_4]\cdot 4\text{-picoline}\cdot \text{H}_2\text{O} \) (1-Mn):

Mn(NCS)\(_2\) (1.0 mmol, 171 mg) was dissolved in demin. \text{H}_2\text{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 \([\text{Mn(NCS)}_2(4\text{-picoline})_2]\cdot \text{H}_2\text{O}\) (2-Mn/\text{H}_2\text{O}):

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

Synthesis of \([\text{Mn(NCS)}_2(4\text{-picoline})_4]\) (2-Mn/I):

Crystals suitable for single X-ray diffraction were obtained by the reaction of Mn(NCS)\(_2\) (2.0 mmol, 342 mg) in EtOH (1.5 mL) at 120 °C. Mn(NCS)\(_2\) (2.0 mmol, 342 mg) was stirred in MeOH (3.5 mL) to which 4-picoline (1.0 mmol, 97 \(\mu\)L) 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)\(_2\) (2.0 mmol, 342 mg) with 4-picoline (1.5 mmol, 3x97 \(\mu\)L) at 120 °C in EtOH in a solvothermal glass tube.

Synthesis of \([\text{Mn(NCS)}_2(4\text{-picoline})_4]\) (2-Mn/I):

Crystals suitable for single X-ray diffraction were obtained by the reaction of Mn(NCS)\(_2\) (0.5 mmol, 94.6 mg) and 4-picoline (0.25 mmol, 24.3 \(\mu\)L) in EtOH (1.5 mL) at 120 °C. Mn(NCS)\(_2\) (2.0 mmol, 342 mg) was stirred in MeOH (3.5 mL) to which 4-picoline (1.0 mmol, 97 \(\mu\)L) 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)\(_2\) (2.0 mmol, 342 mg) with 4-picoline (1.5 mmol, 3x97 \(\mu\)L) at 120 °C in EtOH in a solvothermal glass tube.

Synthesis of \([\text{Mn(NCS)}_2(4\text{-picoline})_4]\) (2-Mn/I):

It is noted that no single crystals were available and that all samples of 2-Mn were prepared by thermal decomposition of either 1-Mn or 2-Mn/\text{H}_2\text{O} in a thermo-balance.

Single Crystal Structure Analysis:

For the collection of single crystal XRD data for 2-Mn/I and 2-Mn/\text{H}_2\text{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. Direct 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 geometric parameters. The thiocyanate and 4-picoline molecules were described by rigid bodies in \(z\)-matrix notation and their rotation and translation modes were left to refine. The bond lengths and angles were taken from cadmium-related single crystal structure data. Distinct isotropic displacement parameters were applied for manganese, thiocyanate and 4-picoline molecules. Eventually, the background, all lattice parameters, rotations (except the thiocyanate in [Mn(NCS)\(_2\)_2(4-picoline)]) transla- tions, the atomic positions of manganese atoms were refined without any constraints during the final Rietveld refinement. For [Mn(NCS)\(_2\)_2(4-picoline)], 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/\text{H}_2\text{O}), CCDC-1962528 (2-Mn/I), CCDC-1962526 (3-Mn), and CCDC-1962527 [Mn(NCS)\(_2\)] (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.
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Keywords: Thiocyanate; Coordination polymer; Manganese; Crystal structure; Solid state synthesis

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