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Synthesis, Crystal Structure and Properties of a new Hydrate of Manganese Thiocyanate with the Composition $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$

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The reaction of $\text{Mn}(\text{NCS})_2$ with 3-cyanopyridine in water accidentally leads to the formation of single crystals of $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$ (1). If the synthesis is performed without 3-cyanopyridine, the known tetrahydrate $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$ is formed. In the crystal structure of the new hydrate, the Mn^{2+} cations are linked by pairs of μ -1,3-bridging anionic ligands to chains, which are further connected via $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$ units into layers, that are additionally stabilized by intralayer hydrogen bonding. These layers are linked by interlayer hydrogen bonding into a 3D network. The structure of 1 shows strong similarities to that of both the tetrahydrate and of $\text{Mn}(\text{NCS})_2$.

The synthesis from water always leads to the tetrahydrate, which is also obtained, when $\text{Mn}(\text{NCS})_2$ is stored in a humid atmosphere. Thermoanalytical measurements on the tetrahydrate show a more complicated behavior, which includes melting at about 46 °C and on cooling sometimes the dihydrate is observed. If the tetrahydrate is stored in vacuum at room temperature, the dihydrate forms before the transformation to the anhydrate is observed. Isothermic water sorption measurements prove, that at low humidity the dihydrate is obtained, which transforms into the tetrahydrate at higher humidities.

Introduction

Thiocyanate anions are useful anionic ligands in coordination chemistry because of their versatile coordination behavior and their ability to mediate reasonable magnetic exchange.^[1–4] Moreover, in combination with organic donor ligands a variety of structures with different metal-thiocyanate networks are available, which is surely the reason why the interest in this class of compounds strongly increased in the last years. For the majority of compounds with bridging anionic ligands, the main structural motif consists of chains, in which the metal cations are octahedrally coordinated and linked by pairs of thiocyanate anions into chains, whereas compounds with layered thiocyanate networks are rare.^[5–8] We are interested in thiocyanate coordination compounds for several years to study, e.g. the influence of the coligand on the structural and magnetic properties of such compounds in more detail.^[9–12] In the course

of this project we became interested in compounds with $\text{Mn}(\text{NCS})_2$ and 3-cyanopyridine as coligand, because $\text{Mn}(\text{NCS})_2$ compounds frequently behave structurally similar to $\text{Cd}(\text{NCS})_2$ compounds and with $\text{Cd}(\text{NCS})_2$ and 3-cyanopyridine compounds with an unusual stoichiometry and structure are reported, that are not available with pyridine derivatives substituted in 4-position.^[13] For the synthesis, usually $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$ prepared according to literature procedures^[14] or $\text{Mn}(\text{NCS})_2$ synthesized by water removal from the tetrahydrate are used as reactants and in one of these reactions crystals of two different crystalline phases were obtained, of which one contains 3-cyanopyridine as ligand, which was not the case for the second phase. Single-crystal structure determinations prove the formation of a compound with the composition $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$, which represents a hitherto unknown hydrate of $\text{Mn}(\text{NCS})_2$. In this context it is noted, that some new hydrates and solvates of alkali- and alkaline-earth metal thiocyanates were recently reported.^[15–17]

However, with the 3d metals Mn, Fe, Co, Ni, Cu and Zn not many hydrates of transition-metal thiocyanates are known. With other coordinating donor ligands these metal cations frequently form compounds with a similar stoichiometry and similar crystal structures and several of them are isotypic. In contrast, for the hydrates no clear trend is observed. With $\text{Mn}(\text{NCS})_2$ only a tetrahydrate with the composition $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$ is reported, which is formed when $\text{Mn}(\text{NCS})_2$ is synthesized from aqueous solution at room temperature.^[14] Its crystal structure consists of discrete complexes, in which the Mn^{2+} cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions in *trans*-position and four water molecules (Figure S1).^[14] With $\text{Fe}(\text{NCS})_2$ and $\text{Ni}(\text{NCS})_2$, no hydrates are reported in the Cambridge Structural Database or the Inorganic Crystal Structure

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Database. For $\text{Co}(\text{NCS})_2$, only a trihydrate with the composition $[\text{Co}(\text{NCS})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ is found, in which each Co^{2+} cation is octahedrally coordinated by two water molecules, as well as two N- and two S-bonded thiocyanate anions in an all-*trans* configuration.^[18] The Co^{2+} cations are linked by single μ -1,3-bridging anions into layers, which are separated by additional water solvate molecules (Figure S1). With Cu and Zn hydrates with the composition $\text{M}(\text{NCS})_2(\text{H}_2\text{O})_2$ ($\text{M} = \text{Cu}, \text{Zn}$) are reported, in which the copper(II) cations show a square-planar^[19] and the zinc(II) cations a tetrahedral coordination (Figure S1).^[20]

Results and Discussion

Crystal Structure

Single crystals of $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$ were accidentally obtained by the reaction of $\text{Mn}(\text{NCS})_2$ with 3-cyanopyridine in water

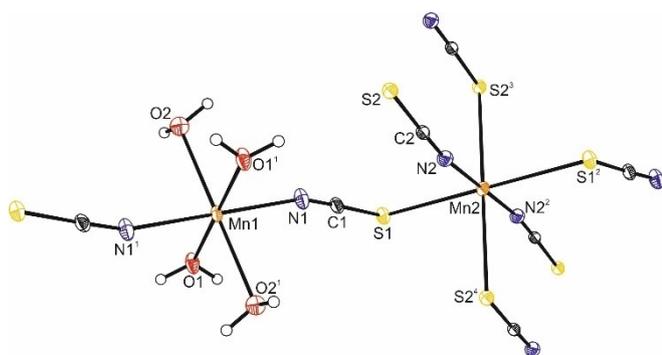


Figure 1. Crystal structure of $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$ with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry codes for the generation of equivalent atoms: ¹ $1-x, 1-y, 1-z$; ² $-x, 2-y, 1-z$; ³ $-x, 1-y, 1-z$; ⁴ $+x, 1+y, +z$.

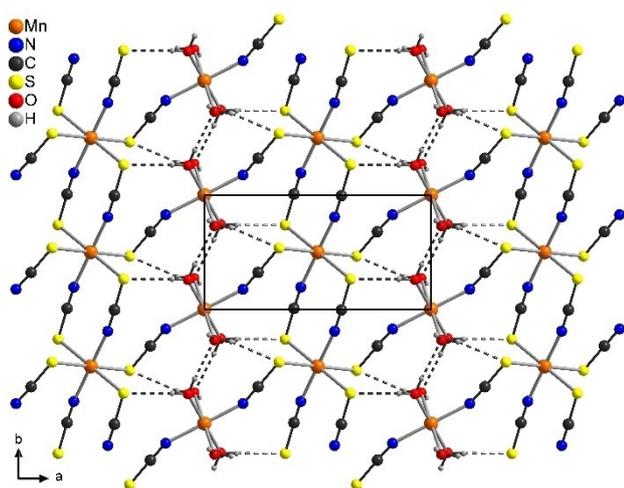


Figure 2. Crystal structure of $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$ with view along the crystallographic *c*-axis with intralayer and interlayer hydrogen bonding shown as dashed lines.

at room temperature and characterized by single-crystal X-ray analysis. The new hydrate crystallizes in the monoclinic space group $P2_1/n$ with $Z=4$ and two crystallographically independent Mn^{2+} cations, that are located on centers of inversion (Figure 1 and Table S1).

$\text{Mn}1^{2+}$ is coordinated by two *trans* nitrogen atoms of μ -1,3-bridging thiocyanate anions and four water molecules within slightly distorted octahedra and is linked via the single bridging anionic ligand to $\text{Mn}2^{2+}$ (Figure 1). The Mn–O distances to O1 of 2.1785(9) Å and to O2 of 2.2682(10) Å are significantly different and the Mn–N distance of 2.1362(11) Å is slightly shorter than that one to $\text{Mn}2^{2+}$ (2.1001(11) Å). $\text{Mn}2^{2+}$ is also six-fold coordinated, but linked to two *trans* nitrogen- and four sulfur-bonding μ -1,3-bridging thiocyanate anions and the coordination polyhedra can be described as slightly distorted octahedra (Figure 1 and 2). The Mn–S distance to the double bridging thiocyanate anions of 2.7237(3) Å is much longer than that to the single bridging anionic ligands of 2.6743(3) Å.

The Mn^{2+} cations are linked by pairs of μ -1,3-bridging thiocyanate anions to linear chains that proceed along the *b*-axis direction (Figure 3; mid). These chains are further connected into layers via single thiocyanate anions of the $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$ units (Figure S2). Within these layers alternating $\text{Mn}(\text{NCS})_2$ and $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$ chains are observed, with the latter formed by intrachain O–H...O hydrogen bonding. These layers are stacked along the crystallographic *c*-axis and are additionally stabilized by intrachain O–H...O and O–H...S hydrogen bonding (Figure 1 and S2). Additional interlayer O–H...O and O–H...S hydrogen bonds link the layers into a 3D network (Figure 2).

Comparison of the crystal structures of $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$, $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$, $\text{Mn}(\text{NCS})_2$ and the hydrates of manganese halides

The crystal structure of the dihydrate of $\text{Mn}(\text{NCS})_2$ is strongly related to that one of the tetrahydrate and especially to the anhydrate. The crystal structure of the tetrahydrate consists of discrete complexes, in which the Mn^{2+} cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions in *trans*-position and four water molecules (Figure 3; top)^[21] and exactly this building block can be found in the crystal structure of the dihydrate (Figure 3; mid).

In the latter the $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$ units are linked by single thiocyanate anions to $\text{Mn}(\text{NCS})_2$ double chains and exactly such chains can also be identified in the crystal structure of the anhydrate (Figure 3; bottom).^[22–23] However, in the latter the $\text{Mn}(\text{NCS})_2$ chains are directly linked to neighbouring chains *via* μ -1,3,3-(N,S,S) thiocyanate anions forming Mn_2S_2 rings, which means that neighbouring octahedra share common edges (Figure 3; bottom). The $\text{Mn}^{2+} \cdots \text{Mn}^{2+}$ distance within these rings amounts to 3.9104 Å. The Mn–S bonds within the Mn_2S_2 rings in the anhydrate are formerly replaced by O–H...S hydrogen bonds in the dihydrate.

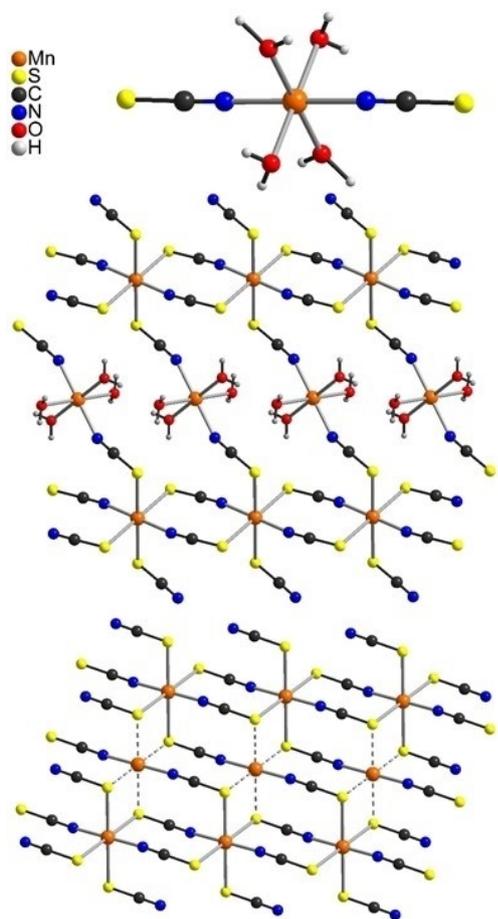


Figure 3. Crystal structure of $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$ (top),^[14] $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$ (mid) and $\text{Mn}(\text{NCS})_2$ (bottom).^[22–23] Please note that for $\text{Mn}(\text{NCS})_2$ some of the Mn–S bonds are indicated as broken lines to show the similarities between the $\text{Mn}(\text{NCS})_2$ networks in the dihydrate and the anhydrate.

It is noted that some more hydrates are reported with manganese halides and even these structures are strongly related. This includes the tetrahydrates $\text{MnX}_2(\text{H}_2\text{O})_4$ with $\text{X} = \text{Cl}$,^[21,24–26] Br ,^[27–28] I ,^[29] in which the Mn^{2+} cations are octahedrally coordinated by two halide anions and four water molecules into discrete complexes, like it is the case for the tetrahydrate of $\text{Mn}(\text{NCS})_2$. However, in contrast to $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$, for some of the halides two isomers are reported, in which the halide anions are in *trans*- or in *cis*-position (Figure S3). The crystal structure of the corresponding dihydrates $\text{MnX}_2(\text{H}_2\text{O})_2$ ($\text{X} = \text{Cl}$,^[30] Br ^[31]) is also reported, but in contrast to $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$ only one crystallographically independent manganese(II) cation is present that is octahedrally coordinated by four halide anions and two water molecules and linked by μ -1,1-bridging halide anions to chains (Figure S3). However, an additional hydrate with the composition $\text{MnCl}_2(\text{H}_2\text{O})$ is reported that shows an unusual structure, in which each Mn^{2+} cation is octahedrally coordinated by one water molecule and five chloride anions. As it is the case for the dihydrate, the Mn^{2+} cations are linked by μ -1,1-bridging chloride anions into chains, that are linked by μ -

1,1,1-chloride anions to MnCl_2 double chains (Figure S3).^[32] If the water molecules are formally removed, these chains condense into the layered structure of MnCl_2 (Figure S3).^[33]

Synthetic investigations

As pointed out above, single crystals of $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$ were accidentally obtained by the reaction of $\text{Mn}(\text{NCS})_2$ with 3-cyanopyridine in water at room temperature, where a mixture of the title compound and some cyanopyridine-containing phase with the composition $\text{Mn}(\text{NCS})_2(3\text{-cyanopyridine})_2(\text{H}_2\text{O})_2$ was obtained (Figure S4). Therefore, we tried to synthesize pure samples by different approaches.

If $\text{Mn}(\text{NCS})_2$ is stored in humid atmosphere in a desiccator within a few hours the tetrahydrate forms with no hint for the formation of the dihydrate as intermediate and within 8 h a liquid is obtained (Figure S5 and S6). The storing of $\text{Mn}(\text{NCS})_2$ at room temperature for 1 h in air also leads to the formation of the tetrahydrate, but in some batches traces of the dihydrate were observed (Figure S7).

Thermoanalytical investigations

In order to prove, if the dihydrate can be obtained by water removal, measurements using thermogravimetry and differential thermoanalysis were performed. Upon heating the sample mass decreases slightly in the beginning, because the tetrahydrate is extremely hygroscopic and thus, completely dried samples are difficult to obtain (Figure 4). On further heating one mass loss is observed, that is accompanied with a strong endothermic event in the DTA curve. The experimental mass loss of 28.5% is in reasonable agreement with that one calculated for the removal of 4

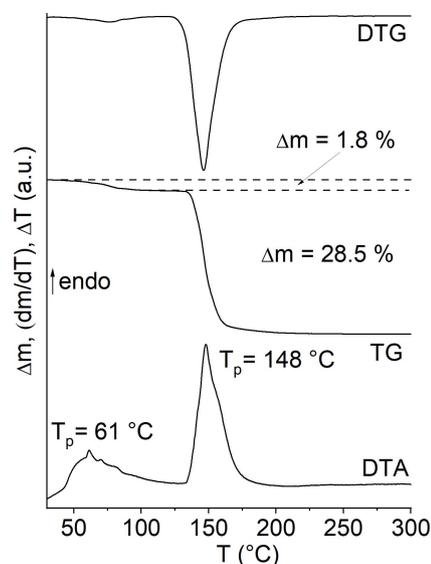


Figure 4. DTG, TG and DTA curve of $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$ measured with $8^\circ\text{C}/\text{min}$ in nitrogen.

water molecules of 29.6%. If this measurement is repeated with 1 °C/min an additional mass loss occurs, but this value does not point to the formation of the dihydrate and might be traced back to the kinetics of the water removal (Figure S8).

Measurements using differential scanning calorimetry (DSC) show a more complicated behavior. Upon heating, several endothermic peaks are visible with the first peak at 46 °C where the sample mass does not change and the last peak, where the water is removed completely and Mn(NCS)₂ forms (Figure 5).

Additional DSC heating and cooling curves show that the first event is irreversible and that in this reaction samples of the tetrahydrate are formed, which are of low crystallinity (Figure S9 and S10). The third endothermic event is also irreversible, but in this case samples of the tetrahydrate are obtained, that contain traces of the dihydrate (Figure S11 and S12). Thermomicroscopic measurements prove that the first endothermic event

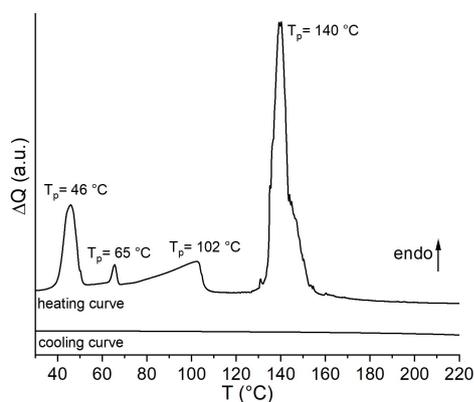


Figure 5. DSC heating and cooling curve of Mn(NCS)₂(H₂O)₄ measured with 10 °C/min in nitrogen.

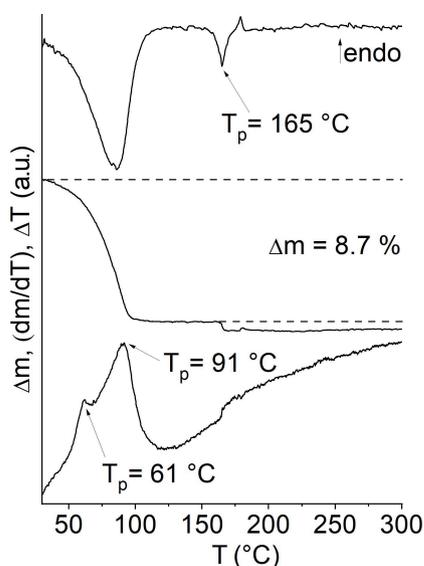


Figure 6. DTG, TG and DTA curve of Mn(NCS)₂(H₂O)₂ measured with 8 °C/min in nitrogen.

corresponds to melting, which explains, that on cooling at least a part of the tetrahydrate crystallizes again (Figure S13).

Because no pure samples of the dihydrate can be obtained by these procedures, it was tried to remove some of the water in vacuum. In this case samples of the dihydrate form within about 1 h, but this is difficult to control and thus, some of such samples are pure, whereas others contain small amounts of the tetrahydrate or the anhydrate (Figure S14).

Thermogravimetric measurements of a sample of the dihydrate obtained by removing the water in vacuum show one mass loss, that is accompanied with a strong endothermic event in the DTA curve (Figure 6). The experimental mass loss of 16.8% is in reasonable agreement with that calculated for the removal of two water molecules ($\Delta m_{\text{calc.}}(-2 \text{ H}_2\text{O}) = 17.4\%$). The water loss already starts at 40 °C, which indicates that the dihydrate is relatively unstable.

In contrast to the tetrahydrate, DSC measurements on the dihydrate show no hints for melting before the water is removed (Figure 7), which was also confirmed by thermomicroscopic measurements, where in contrast to the tetrahydrate no liquid phase is obtained (Figure S15).

Water-sorption measurements

To study the water-sorption behavior of Mn(NCS)₂, this compound was investigated by isothermic water-sorption measurements. Below $p/p_0 = 0.22$, almost no water uptake can be observed (Figure 8). At approximately $p/p_0 = 0.23$ Mn(NCS)₂ absorbs about two equivalents of water, which is in reasonable agreement with the expectation for the formation of the dihydrate and at around $p/p_0 = 0.38$ the tetrahydrate is formed (Figure 8). For the tetrahydrate no plateau is observed, which can be attributed to the high hygroscopicity of this compound, that leads to a linear increase of the curve at higher humidities.

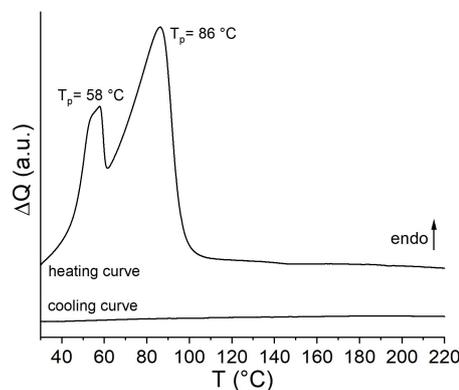


Figure 7. DSC heating and cooling curves of Mn(NCS)₂(H₂O)₂ measured with 10 °C/min in nitrogen.

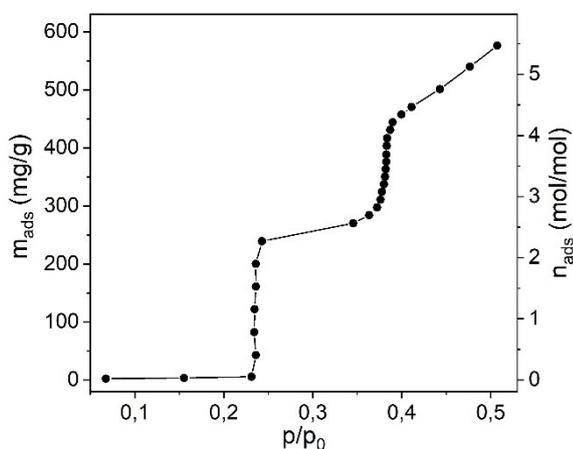


Figure 8. Water-sorption isotherm of $\text{Mn}(\text{NCS})_2$ measured at room temperature.

IR spectroscopy

In the IR spectrum of the dihydrate the bands above 2903 cm^{-1} correspond to the O–H stretching vibrations of the water molecules, that are involved in intermolecular hydrogen bonding and at 1611 cm^{-1} the bending vibration of the water molecules is observed (Figure 9). The strong absorption at 2132 cm^{-1} is in the range expected for the asymmetric $\text{C}\equiv\text{N}$ stretching vibration of μ -1,3-bridging thiocyanate anions (Figure 9). Surprisingly only one band is observed, even if single and double bridging anionic ligands are present, but this band is relatively broad and a small shoulder appears at about 2070 cm^{-1} . The band at 919 cm^{-1} can be assigned to the bending vibration and that at 778 cm^{-1} to the C–S stretching vibration of the thiocyanate anions.^[17]

For the tetrahydrate and the anhydrate, no IR spectroscopic data were found but for comparison they were also measured. The IR spectrum of the tetrahydrate is similar to that one of the dihydrate. The O–H stretching vibrations of the water molecules are observed in the range between

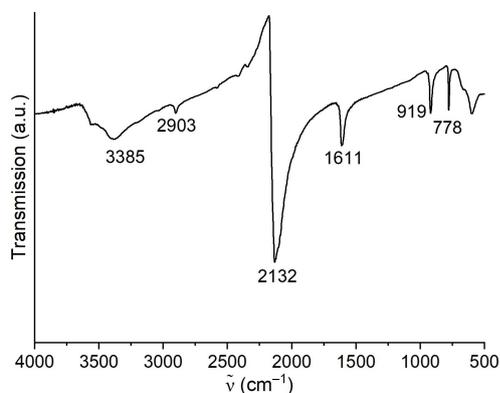


Figure 9. IR spectrum of $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$.

2899 and 3391 cm^{-1} and the bending vibration is slightly shifted to 1625 cm^{-1} (Figure S16). The $\text{C}\equiv\text{N}$ stretching vibration of the thiocyanate anion is observed at 2101 cm^{-1} , which is at the borderline expected for terminal N-bonded thiocyanate anions. However, this vibration is usually shifted to much higher values, if the metal cation is additionally coordinated by O-donor coligands. Compared to the dihydrate, the $\text{N}\equiv\text{C}-\text{S}$ bending vibration is shifted to 927 cm^{-1} , whereas the C–S stretching vibration is not clearly visible (Figure S16). For $\text{Mn}(\text{NCS})_2$, all vibrations of the thiocyanate anion are observed at very similar wavenumbers as those of the dihydrate, which can be traced back to the fact that their structures consists of very similar $\text{Mn}(\text{NCS})_2$ chains (Figure S16).

Conclusions

In the present contribution a hitherto unknown hydrate of $\text{Mn}(\text{NCS})_2$ was reported, that was accidentally obtained, but that can be prepared pure, e.g. if the water is carefully removed from the tetrahydrate at room temperature in vacuum or by water-sorption experiments. The crystal structure of this dihydrate is strongly related to that one from the anhydrate. In its crystal structure two crystallographically independent Mn^{2+} cations are present, of which one is coordinated by two N-bonded single bridging thiocyanate anions and four water molecules and this structural element exactly corresponds to that observed in the tetrahydrate. The second Mn^{2+} cation is coordinated by two N- and four S-bonded thiocyanate anions and linked to chains by pairs of μ -1,3-bridging thiocyanate anions and these chains condense into layers by the μ -1,3-single bridging anionic ligands. This structural element is exactly observed in the crystal structure of $\text{Mn}(\text{NCS})_2$. If $\text{Mn}(\text{NCS})_2$ is stored at room temperature, it transforms relatively fast into the tetrahydrate, which usually is obtained, when $\text{Mn}(\text{NCS})_2$ is synthesized according to literature procedures. According to this procedure $\text{Mn}(\text{NCS})_2$ is obtained, when the tetrahydrate is dried at elevated temperatures and during this process all water molecules are removed in one step, without any hint for the formation of the dihydrate. All this might be the reason, why the dihydrate was not detected before. However, after the new dihydrate was found by serendipity, its synthesis was not so difficult to achieve.

Experimental Section

Synthesis

$\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ was purchased from Alfa Aesar, $\text{Mn}(\text{SO}_4) \cdot \text{H}_2\text{O}$ and $\text{Mn}(\text{SO}_4) \cdot \text{H}_2\text{O}$ were purchased from Merck.

$\text{Mn}(\text{NCS})_2$ was synthesized by the reaction of $\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ with $\text{Mn}(\text{SO}_4) \cdot \text{H}_2\text{O}$ in deionized H_2O . The colorless precipitate of $\text{Ba}(\text{SO}_4)$ was filtered off and the filtrate was concentrated to dryness in a rotary evaporator and dried at 40°C , giving a powder of $\text{Mn}(\text{NCS})_2$. If this powder is stored in a humid atmosphere of a desiccator at room temperature, a fast trans-

formation into $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_4$ is observed. If the water is carefully removed from the tetrahydrate for one hour at about 10 mbar $\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2$ is obtained. This, however, is not a stable procedure, because the time needed to remove two H_2O molecules depends on several parameters, like e.g. the particle size and the actual vacuum and must therefore be optimized. The purity of all samples was checked by XRPD measurements.

Structure analysis

Single-crystal X-ray diffraction data collections were performed with an XtaLAB Synergy-S diffraction system equipped with micro-focus source (PhotonJet-S) and a HyPix-6000HE Hybrid Photon Counting (HPC) detector using $\text{Cu-K}\alpha$ radiation. Structure solution was performed with SHELXT^[34] and structure refinements performed against F^2 using SHELXL-2018.^[35] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located in the difference map, their bond lengths were set to ideal values and finally they were refined isotropically with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$ using a riding model.

CSD-2143151 contains 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/data_request/cif.

Other physical measurements

The XRPD measurements for the characterization of all samples were performed with a Stoe Transmission Powder Diffraction System (STADI P) with $\text{Cu-K}\alpha 1$ radiation and a Dectris Mythen 1 K detector with a Johann-type-Ge(111) monochromator from STOE & CIE. IR spectra were recorded at RT on a Bruker Vertex70 FT-IR spectrometer using a broadband spectral range extension VERTEX FM for full, mid and far IR. For the TG-DTA measurements, a STA-PT1000 thermobalance from Linseis was used. Measurements were performed in Al_2O_3 crucibles and under a dynamic nitrogen atmosphere. The DSC experiments were performed using a DSC 1 star system with STARe Excellence software from Mettler-Toledo AG under a dynamic nitrogen atmosphere in Al pans. Thermomicroscopic measurements were performed using a hot-stage from Linkam and a microscope from Olympus. All instruments were calibrated using standard reference materials. Prior to the sorption measurement of the $\text{Mn}(\text{SCN})_2$ sample, all water molecules were removed by a treatment at 80°C for 2 h under reduced pressure (10^{-2} kPa). The sorption isotherm was measured using a BelSorp Max instrument. The endpoint of $p/p_0 = 0.5$ was chosen to prevent the sample from becoming waterlogged and forming a solution.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords: Manganese thiocyanate · hydrates · layered compounds · synthesis · crystal structures · thermal properties

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