

Synthesis, Crystal Structures and Properties of Polymorphic and Isomeric Nickel(II)thiocyanate Coordination Compounds with 3-Bromopyridine as Coligand

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Dedicated to Prof. Dr. Christoph Janiak on the occasion of his 60th birthday.

Reaction of different molar ratios of Ni(NCS)₂ and 3-bromopyridine in water, methanol or acetonitrile leads to the formation of two polymorphs of composition Ni(NCS)₂(3-bromopyridine)₄ (1-I and 1-II), as well as Ni(NCS)₂(3-bromopyridine)₂(H₂O)₂ (2), Ni(NCS)₂(3-bromopyridine)₂(CH₃OH)₂ (3), Ni(NCS)₂(3-bromopyridine)₂·CH₃CN (4) and Ni(NCS)₂(3-bromopyridine)₂ (5). Compounds 1-I, 1-II, 2 and 3 consist of discrete octahedral complexes with terminal N-bonded anionic ligands. In compound 4 the Ni cations are *cis-cis-trans* coordinated and linked into corrugated chains by pairs of μ -1,3-bridging thiocyanate anions. Solvent mediated conversion experiments prove that form 1-I represents the thermodynamically stable polymorph at

room temperature. TG-DTA measurements reveal that upon heating compounds 1-I, 1-II, 2 and 3 lose their coligands stepwise and transform into the new crystalline phase 5 that can also be obtained from solution if the reaction is performed in *n*-butanol. If the acetonitrile solvate molecules are removed from compound 4, it also transforms into 5. DC magnetic measurements for compound 4 show a maximum, which is indicative for antiferromagnetic ordering, whereas for compound 5 no magnetic ordering is observed. For both compounds, the ferromagnetic exchange constants were determined.

Introduction

There is a problem in numbering which was solved. Coordination compounds based on thiocyanate anions have attracted much interest in recent years, which can partly be traced back due to their versatile coordination behaviour leading to structures of different dimensionality.^[1–13] In most compounds the anionic ligands are only terminal N-bonded to the metal cations, whereas the synthesis of compounds with bridging thiocyanate ligands is sometimes more complicated if less chalcophilic paramagnetic 3d metal cations are used. This is a pity, because this ligand is able to mediate reasonable magnetic exchange leading to compounds that can show different

magnetic properties.^[12–21] However, in those cases in which compounds with bridging thiocyanate anions are not available from solution, thiocyanate coordination compounds that contain only terminal N-bonded anionic ligands can be heated, which usually leads to a stepwise removal of the coligands, and the irreversible formation of compounds with bridging thiocyanate anions.^[3] In most cases, compounds with 1D or 2D thiocyanate networks are obtained. For the 2D compounds only very few networks of different topology are reported, in which e.g. the metal cations are linked into dimers that are further connected into layers by single thiocyanate anions or in which the layers consist of only single anionic ligands.^[22–23] Regarding such 2D networks, compounds based on Co(NCS)₂ and Ni(NCS)₂ are of special interest, because with both cations the magnetic exchange is usually ferromagnetic and at low temperatures ferromagnetic ordering is observed. In this case, the critical temperatures are always higher for Ni(II) than for Co(II), which allows the tuning of the critical temperatures by mixed crystal formation.^[24–26]

In contrast, much more examples for compounds that consist of chains are reported. In nearly all cases the metal cations are octahedrally coordinated and linked into chains by pairs of thiocyanate anions.^[27–38] In such compounds the metal cations are always linked to three pairs of chemically identical donor atoms, which corresponds to a MA₂B₂C₂ system, for which five geometrical isomers can exist. This includes the all-*trans*, three *cis-cis-trans*, and the all-*cis* coordination. The all-*cis* isomer would form a pair of stereoisomers, but because of geometrical reasons, it is unlikely that for this kind of chains this isomer will exist. For the other isomers, several examples are reported in the literature. In most cases, compounds with an all-*trans*

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coordination are reported, which leads to the formation of linear chains.^[30,38–43] Linear chains are also obtained if the thiocyanate S and N atoms are *cis*, whereas the coligands are still *trans*.^[13,44] For the other *cis-cis-trans* coordinations corrugated chains are formed.^[31–32,39, 45–46] The linear chains with Co and Ni are of special interest, because in both cases ferromagnetic magnetic exchange interactions along the chains are observed and the compounds with Co show 1D or 3D ferromagnetic ordering.^[34–38,46]

Concerning the chemical and structural properties of Co(NCS)₂ and Ni(NCS)₂ coordination compounds, several similarities are observed. If the same coligand is used, in most cases compounds of the same compositions are obtained that in several cases are isotypic. So if polymorphic or isomeric compounds with Co(NCS)₂ are accessible, these compounds can often also be prepared with Ni(NCS)₂. However, we have found examples where a certain compound with Ni(NCS)₂ can easily be prepared whereas no access to the corresponding Co(NCS)₂ compound was found. This is the case for, e.g. the acetonitrile solvate Ni(NCS)₂(4-(*boc*-amino)pyridine)₂·CH₃CN, which shows an interesting structural behaviour.^[34] In the crystal structure of this compound a very rare *cis-cis-trans* coordination is observed in which the S atom of the thiocyanate anions and the N atoms of the neutral coligands are in *cis*-position, whereas the thiocyanate N atoms are in *trans*-position. The metal cations are linked by the anionic ligands into corrugated chains that are further connected into layers by intermolecular N–H...O hydrogen bonding. These layers are stacked in a way that channels are formed, in which the acetonitrile solvate molecules are located. The solvent can be removed in a topotactic reaction leading to a change from space group *P2₁/c* to *C2/c*.^[45]

In the course of our systematic investigations on thiocyanate coordination compounds we became interested in Ni(NCS)₂ compounds with 3-bromopyridine as coligand, for which only some structures with Cd, Zn and Cu are reported in the Cambridge Structural Database.^[47–51] Despite the formation of several discrete complexes, we obtained two different chain compounds, of which one contains the usual linear chains with an all-*trans* coordination, whereas the second compound consists of corrugated chains and a structure, which is very similar to that of Ni(NCS)₂(4-(*boc*-amino)pyridine)₂·CH₃CN. Here we report on our investigations.

Results and Discussion

Synthesis and Characterization

Reaction of Ni(NCS)₂ with 3-bromopyridine in different molar ratios in water, methanol or acetonitrile leads to the formation of five different crystalline phases. If Ni(NCS)₂ is reacted with 3-bromopyridine in ratio 1:4 in water or methanol using very short reaction times of a few minutes the same crystalline phase is obtained (Figure S1). If the products are isolated after 2 d, a further reaction product has formed, which in water and methanol is identical. Elemental analysis reveals that for all of them the chemical composition is identical (Ni(NCS)₂(3-bromo-

pyridine)₄) indicating the formation of two polymorphic modifications, of which one is obtained after a short (1-I) and another after a much longer reaction time (1-II). The CN stretching vibration is observed at 2074 cm⁻¹ (1-I) and at 2086 cm⁻¹ (1-II), which points to the presence of N-terminal bonded anionic ligands (Figure S2 and S3). Therefore, it can be assumed that these modifications consist of discrete complexes, in which the Ni cations are octahedrally coordinated by two N-bonded thiocyanate anions and four 3-bromopyridine ligands.

If Ni(NCS)₂ and 3-bromopyridine are reacted in ratio 1:2 two different crystalline phases are obtained from water and methanol (Figure S1). For these compounds, preliminary thermogravimetric measurements indicate the presence of water and methanol, which together with the results from elemental analysis leads to a composition of Ni(NCS)₂(3-bromopyridine)(H₂O)₂ (2) and Ni(NCS)₂(3-bromopyridine)(CH₃OH)₂ (3). For these compounds, the CN stretching vibration is observed at 2127 cm⁻¹ for 2 and at 2092 cm⁻¹ for 3 (Figure S4 and S5). Especially for 2 this value is in the range expected for μ -1,3-bridging anionic ligands, but it is well known that the CN stretching vibration is shifted to higher values if the metal cations are additionally coordinated by O-donor coligands. Therefore, these compounds should consist of discrete octahedral complexes, in which the Ni cations are coordinated by two terminal N-bonded anionic ligands as well as two 3-bromopyridine ligands and two water or methanol molecules.

If the reaction is performed in acetonitrile in a metal to coligand ratio of 1:4 compound 1-I is obtained but lowering the ratio to 1:2 leads to the formation of a new crystalline phase that might contain additional acetonitrile as solvate molecules. This is confirmed by elemental analysis, from which a composition of (Ni(NCS)₂(3-bromopyridine)₂·CH₃CN (4) can be assumed. For this compound the CN stretching vibration of the thiocyanate anions is observed at 2113 cm⁻¹ and because in this case only N-donor coligands are present this points to the presence of μ -1,3-bridging thiocyanate anions (Figure S6). The presence of acetonitrile as a solvent is indicated by a band at 2248 cm⁻¹, which corresponds to the CN stretching vibration of the acetonitrile molecules.

In further experiments, single crystals were obtained for all five phases that were characterized by single crystal X-ray diffraction, which, e.g., proves the formation of two polymorphic modifications for compound 1 (Table S1 and S2).

Crystal structures

Crystal structures of 1-I and 1-II

Form 1-I crystallizes in the triclinic space group *P*-1 with *Z* = 2 and its crystal structure contains two crystallographically independent complexes, that are located on centres of inversion (Figure S7). Form 1-II crystallizes in the tetragonal space group *I4₁/acd* with *Z* = 8 and contains only one crystallographically independent Ni cation that is located on the 4-fold screw inversion axis (Figure S7). In both forms, the Ni cations

are octahedrally coordinated by two terminal N-bonded thiocyanate anions and four 3-bromopyridine ligands (Figure 1: left and Figure S7). Bond lengths are comparable in all complexes and from the bond lengths and angles it is obvious that all octahedra are slightly distorted (Table S3 and S4). This is in agreement with calculations of the octahedral angle variance which leads to values of 10.3190 (Ni1) respectively 3.5062 (Ni2) for 1-I and of 2.5842 for 1-II. The value of the mean octahedral quadratic elongation amounts to 1.0050 (Ni1) respectively 1.0025 (Ni2) for 1-I and 1.0016 for 1-II.^[52]

In the crystal structure of 1-I the discrete complexes are linked by intermolecular C–H...S hydrogen bonding into a 3D network (Table S5 and Figure S8). There are many additional C–H...N hydrogen bonds but from the H...S distances and the C–H...N angles it is obvious that these hydrogen bonds correspond to only weak interactions (Table S5). In the crystal structure of 1-II a completely different arrangement of the discrete complexes is observed (Figure S8). In this form, strong intermolecular C–H...S hydrogen bonding is observed that also connects the complexes into a 3D network (Table S6 and Figure S8) but two of such networks interpenetrate to form a dense structure.

Crystal structures of 2 and 3

Compounds 2 and 3 crystallize in the monoclinic space groups $P2_1/c$ (2) and $C2/c$ (3) with $Z=2$ respectively 4. As expected from the TG measurements, elemental analysis and IR spectroscopy both compounds consist of discrete solvato complexes, in which the Ni cations are coordinated by two terminal N-bonded thiocyanate anions, two 3-bromopyridine ligands and two water, respectively methanol molecules (Figure 1 and Figure S9). In both complexes, the bond lengths and angles correspond to literature values (Table S7 and S8). The Ni octahedra are slightly distorted which is obvious from the octahedral angle variance value of 1.4126 for 2 and of 3.9537 for 3 as well as from the mean octahedral quadratic elongation of 1.0013 for 2 and of 1.0017 for 3.^[52]

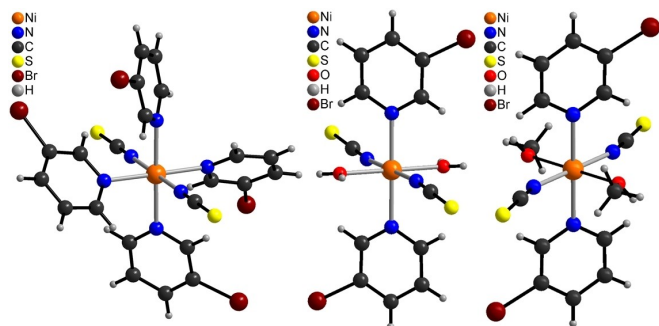


Figure 1. View of the discrete complexes in the crystal structure of 1-I (left), 2 (mid) and 3 (right). Please note that the complexes in 1-I look similar to that in 1-II. ORTEP plots of 1-I, 1-II, 2 and 3 can be found in Figures S7 and S9.

In the crystal structure of both compounds the discrete complexes are linked by intermolecular O–H...S hydrogen bonding between the water, respectively methanol O–H H atoms and the thiocyanate S atoms (Table S9 and S10 and Figure S10 and S11). In compound 3 additional C–H...N hydrogen bonding is present but from the H...N distances and the C–H...N angles it is obvious that these correspond to a very weak interaction (Table S10). For compounds 1-I, 1-II, 2 and 3 the calculated X-ray powder patterns were compared with the experimental patterns, which proves that in all cases pure samples have been obtained (Figure S12–S15).

Crystal structure of 4

Compound 4 crystallizes in the monoclinic space group $C2/c$ with 4 formula units in the unit cell. The asymmetric unit consists of one Ni cation that is located on the 2-fold rotation axis as well as one thiocyanate anion, one 3-bromopyridine ligand and one acetonitrile molecule in general positions (Figure S16). The acetonitrile solvate molecule is disordered around a centre of inversion and therefore was refined with only half occupation. If the structure is refined in space groups of lower symmetry the disorder still remains.

In the crystal structure of 4 the Ni cations are octahedrally coordinated by two N- and two S-bonding thiocyanate anions and two 3-bromopyridine ligands, as already indicated from the IR spectroscopic measurements. The Ni cations show a *cis-cis-trans* coordination with the thiocyanate S and the 3-bromopyridine N atoms in *cis* position, whereas the thiocyanate N atoms are *trans* to each other. As mentioned in the introduction, in most chain compounds an all-*trans* coordination is observed, whereas compounds with this kind of *cis-cis-trans* coordination are rare. This is observed in $\text{Ni}(\text{NCS})_2(4\text{-}(\text{Boc-amino})\text{pyridine})_2 \cdot \text{MeCN}$,^[45] $\text{Ni}(\text{NCS})_2(4\text{-benzylpyridine})_2$,^[38] $\text{Ni}(\text{NCS})_2(1\text{-}(2\text{-aminoethyl})\text{pyrrolidine})$,^[53] and in $\text{Ni}(\text{NCS})_2(2\text{-aminopyridine})_2 \cdot \text{Et}_2\text{O}$.^[54]

The Ni–N and Ni–S bond lengths are comparable to those found in similar compounds and from the distances and angles it is obvious that the octahedra are slightly distorted (Table S11). This is also confirmed by the value for the mean octahedral quadratic of 1.0166 and the octahedral angle variance of 9.1914 calculated using the method given by Robinson *et al.*^[52] The Ni cations are linked by pairs of anionic ligands into chains, which are corrugated because of the *cis-cis-trans* coordination (Figure 2: top).

These chains proceed along the crystallographic *c*-axis and are linked by weak intermolecular C–H...S, C–H...Br and C–H...N hydrogen bonding (Table S12). The chains are arranged in a way that channels are formed in which the acetonitrile solvate molecules are embedded (Figure 2: bottom).

The crystal structure of compound 4 is very similar to that of $\text{Ni}(\text{NCS})_2(4\text{-}(\text{Boc-amino})\text{pyridine})_2 \cdot \text{MeCN}$ reported recently, in which the Ni cations also show a *cis-cis-trans* coordination and are linked into corrugated chains (Figure S17). Moreover, the arrangement of chains and the opening of the channels is practically identical to that in compound 4, which is also reflected in very

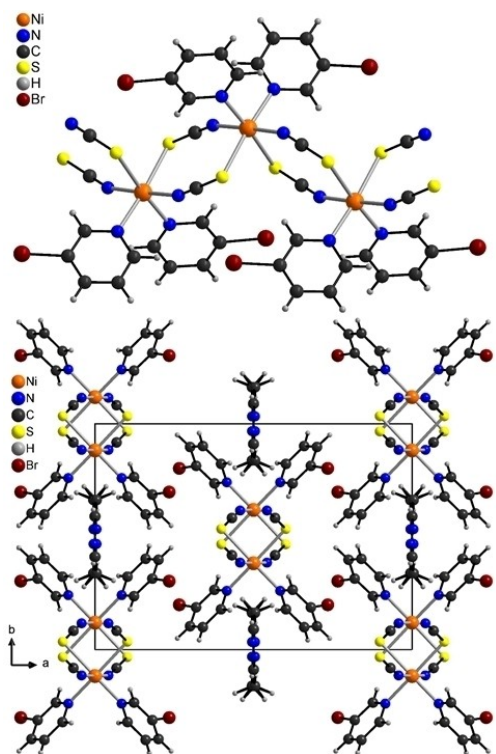


Figure 2. View of a chain in the crystal structure of **4** (top) and arrangement of the chains with view along the crystallographic *c*-axis (bottom). An ORTEP plot can be found in Figure S14.

similar values of the crystallographic *b* and *c* axes (Table S13). In contrast to compound **4**, $\text{Ni}(\text{NCS})_2(4\text{-}(\text{Boc-amino})\text{pyridine})_2 \cdot \text{MeCN}$ crystallizes in space group $P2_1/c$ with four formula units in the unit cell and fully ordered acetonitrile solvate molecules. However, the acetonitrile solvate molecules can be removed in vacuum which proceeds *via* a topotactic reaction and is accompanied with a change of the Bravais type from primitive to C-centered. If about half of the solvent molecules are removed the space group changes to $C2/c$ and in this case, the MeCN molecules are disordered like it is the case in compound **4**.

Determination of the thermodynamic stability of 1-I and 1-II

To prove which of the two polymorphic modifications 1-I and 1-II represents the thermodynamically stable form at room temperature, solvent mediated conversion experiments were performed in which a mixture of both forms in ratio 50:50 was suspended in MeOH and EtOH with excess of solid. The resulting suspension was stirred at room temperature and the residue was investigated by XRPD after 1, 5 and 15 min, which shows that within 5 min form 1-II has transformed into form 1-I, which therefore is thermodynamically stable at room temperature (Figure S19 and S20).

Thermoanalytical investigations for 1-I, 1-II, 2 and 3

To investigate if 3-bromopyridine deficient compounds with bridging thiocyanate anions can be prepared by ligand removal, TG-DTA measurements were performed for compounds **1-I**, **1-II**, **2** and **3** at different heating rates (Figure S21–S24). Upon heating the polymorphic modifications 1-I and 1-II two well resolved mass steps are observed in the TG curves, which are accompanied with endothermic events in the DTA curve (Figure 3 and Figure S21 and S22).

For all mass loss steps of compounds 1-I and 1-II similar values are found which are in well agreement with that calculated for the removal of half of the 3-bromopyridine ligands ($\Delta m_{\text{calc.}} = 39.2\%$). For the solvate complexes, similar observations were made (Figure 3). For these compounds the mass loss observed in the first step is in agreement with the loss of two water ($\Delta m_{\text{calc.}} = 6.8\%$), respectively methanol molecules ($\Delta m_{\text{calc.}} = 11.5\%$), whereas in the second step the remaining 3-bromopyridine ligands are removed ($\Delta m_{\text{calc.}} = 60.0\%$ for **2** and 56.9% for **3**). Therefore, these results indicate that after the first TG step compounds with the composition $\text{Ni}(\text{NCS})_2(3\text{-bromopyridine})_2$ were obtained.

In further experiments, the residues obtained after each mass loss were isolated and investigated by XRPD, which proves that always the same crystalline phase (**5**) has formed (Figure S25).

Synthesis and crystal structure of 5

In our previous synthetic experiments, no hint for the formation of compound **5** in solution was found. Therefore, further synthetic experiments using different solvents were performed and it was discovered that the reaction of $\text{Ni}(\text{NCS})_2$ with 3-bromopyridine in ratio 1:2 leads to a mixture of compound 1-I and **5** in *n*-butanol

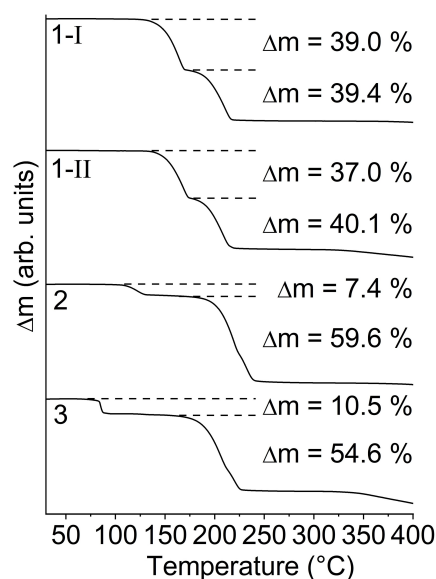


Figure 3. TG curves for compounds **1-I**, **1-II**, **2** and **3** measured with $4^\circ\text{C}/\text{min}$.

(Figure S26). To suppress the formation of the discrete complex, the reactants were used in ratio 1:1 but in this case, a mixture of **5** as the major phase and $\text{Ni}(\text{NCS})_2$ as the minor phase was obtained. In the following experiments the ratio between the metal salt and the coligand was optimized and with a ratio of 1:1.75 compound **5** can be obtained as a pure phase (Figure S26). The CN stretching vibration of the anionic ligands is observed at 2099 and 2127 cm^{-1} , clearly indicating that bridging thiocyanate anions are present.

As a crystalline powder was obtained in this solvent, we also performed crystallization experiments in *n*-butanol and obtained single crystals, which were characterized by single crystal X-ray diffraction.

Compound **5** crystallizes in the non-centrosymmetric space group $Pna2_1$ with 12 formula units in the unit cell. The asymmetric unit consists of three crystallographically independent Ni cations, six thiocyanate anions and 12 3-bromopyridine ligands that are located in general positions (Figure S27). In the crystal structure of this compound, each of the three distinct Ni cations is coordinated octahedrally by two N- and two S-bonding thiocyanate anions as well as two 3-bromopyridine ligands that are located in the apical position (Figure 4). The Ni–N and Ni–S bond lengths are in the range of literature values and from the bond lengths and angles it is obvious that the octahedra are slightly distorted. In contrast to compound **4**, the Ni cations show an all-*trans* coordination, which corresponds to the usual arrangement in this class of compounds. The Ni cations are linked by pairs of thiocyanate anions into linear chains, which is in agreement with the IR spectrum, in which the thiocyanate CN stretching vibration is observed at 2099 and 2127 cm^{-1} (Figure S28). If the experimental XRPD pattern is compared with that calculated from the single crystal data, it is proven that compound **5** was obtained as a pure phase (Figure S29).

Finally, it is noted that the structure refinement leads to relatively high R values and significant electron density peaks in the difference map especially in the center of the $\text{Ni}(\text{NCS})_2\text{Ni}$ units are observed. Much effort has been made to get a better model and details can be found in the Experimental Section.

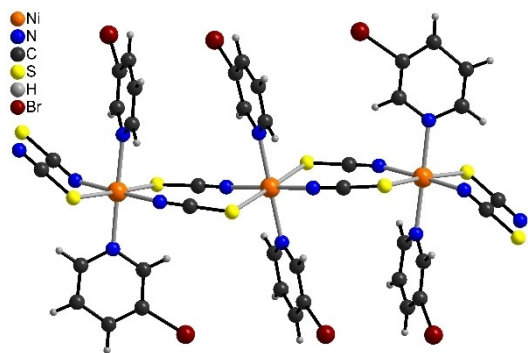


Figure 4. View of a chain in the crystal structure of **5**. An ORTEP plot can be found in Figure S26.

Investigations on the solvent removal of **4**

As mentioned above, the crystal structure of compound **4** is very similar to that of $\text{Ni}(\text{NCS})_2(4\text{-}(\text{Boc}\text{-amino})\text{pyridine})_2\cdot\text{MeCN}$. In the latter compound, the solvent can be removed at room temperature in vacuum *via* a topotactic reaction. The solvent removal can easily be followed by X-ray powder diffraction, in which a significant change in the intensity of some of the reflections is observed. Therefore, we also investigated if the acetonitrile solvate molecules can also be removed from compound **4** at room temperature. If a sample of this compound that was stored overnight under vacuum is investigated by XRPD no changes are observed in the powder pattern, indicating that the solvate molecules are still present (Figure 5). However, if compound **4** is investigated by TG-DTA measurements two mass losses are observed of which the first one of 7.7% and the second one of 59.5% are in perfect agreement with those calculated for the removal of the acetonitrile solvate molecules ($\Delta m_{\text{calc.}} = 7.7\%$) in the first and the 3-bromopyridine ligands ($\Delta m_{\text{calc.}} = 59.4\%$) in the second step (Figure S30). The XRPD pattern of the residue formed after the first mass loss is in very good agreement with that calculated for compound **5**. It was also checked whether an anhydrate of **4** can be obtained at elevated temperatures and therefore, compound **4** was annealed in vacuum much below the decomposition temperature observed in the TG measurement. XRPD measurements show that even this sample has been transformed into the chain compound **5** (Figure 5) which indicates that the acetonitrile solvate molecules are much stronger bound in compound **4** than in $\text{Ni}(\text{NCS})_2(4\text{-}(\text{Boc}\text{-amino})\text{pyridine})_2\cdot\text{MeCN}$.

Magnetic measurements

The magnetic properties of the chain compounds **4** and **5** were investigated by DC magnetic measurements at 1 and 10 kOe in a temperature range between 2.0 and 300 K (Figure 6). For both compounds, the χT product increases initially with decreasing

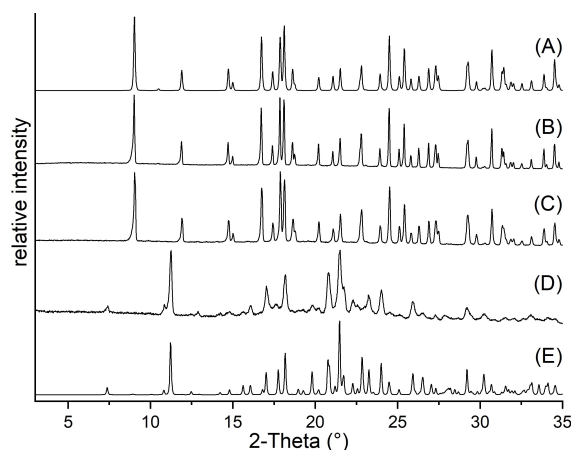


Figure 5. Calculated XRPD pattern for compound **4** (A) and **5** (E) as well as experimental patterns of a sample of **4** (B) that was stored for 1 d in vacuum at room temperature (C) and at 100 °C (D).

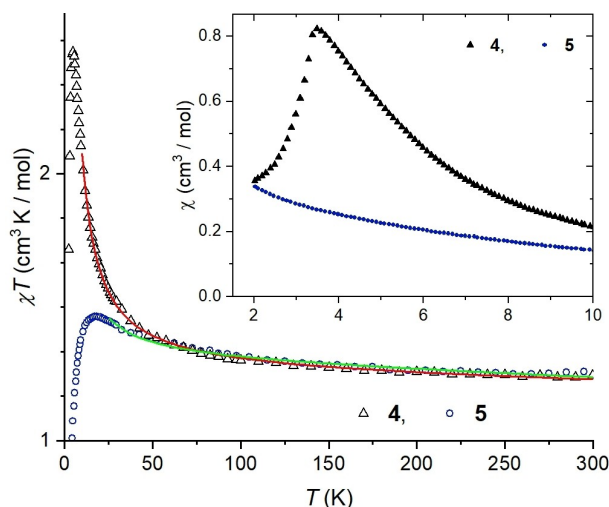


Figure 6. Temperature dependence of the magnetic susceptibility measured at 10 kOe for **4** (triangles) and **5** (circles). Lines were fitted (see text). Inset: Low temperature susceptibility measured at 1 kOe.

temperature, which is indicative for dominating ferromagnetic interactions within the chains, in agreement with observations made for similar $\text{Ni}(\text{NCS})_2$ chain compounds (Figure S31).^[38] For compound **4** a maximum of $\chi(T)$ is observed at $T=3.5$ K that points to an antiferromagnetic ordering. In contrast, for compound **5** no magnetic ordering is observed down to 2 K.

The magnetic data were analyzed in the frame of the isotropic spin $S=1$ chain model with Heisenberg exchange interaction:

$$\hat{H} = -J \sum_n \vec{S}_n \cdot \vec{S}_{n+1} + g\mu_B H_z \sum_n S_n^z$$

The J and g values were determined by fitting the experimental data above 10 K for **4** and above 25 K for **5** using the approximation formula proposed in.^[55] The obtained values are $J=4.35(3)$ K, $g=2.24(1)$ for **4**, and $J=2.3(1)$ K, $g=2.28(1)$ for **5**. The J value for **5** is the smallest in comparison with twelve $\text{Ni}(\text{NCS})_2\text{L}_2$ compounds with chain structures reported in ref.^[38] The small value of J is one of reasons why the fitted curve starts to deviate from the experimental points below 25 K, where the experimental χT has a smooth maximum around 18 K, and further decreases at lower T . This behavior is an effect of zero-field splitting of the Ni(II) cations, which cannot be easily incorporated in the solution of the Hamiltonian given above. A similar smooth $\chi T(T)$ maximum was observed for other linear $\text{Ni}(\text{NCS})_2$ chains with an all-*trans* N_4S_2 coordination of the Ni(II) cation, particularly for compounds with 4-dimethylaminopyridine and 4-ethylpyridine as ligand.^[38] Therefore, this maximum seems to be due to the nonmagnetic ground state of Ni(II) in zfs, rather than an effect of antiferromagnetic interactions.

Conclusions

In this contribution, several new compounds including polymorphic modifications based on $\text{Ni}(\text{NCS})_2$ and 3-bromopyridine were reported. In most cases, simple discrete complexes were obtained but in one compound a relatively rare *cis-cis-trans* coordination is observed that leads to the formation of corrugated chains. If the precursor complexes are heated, the coligands are emitted stepwise, which in all cases leads to an intermediate compound with the same ratio between $\text{Ni}(\text{NCS})_2$ and 3-bromopyridine as that of the corrugated chain compound. However, XRPD investigations revealed that a different crystalline phase has formed. Based on these results further synthetic experiments were performed in which the new crystalline phase was also obtained from solution. Single crystal X-ray diffraction has proven that a different isomer with an all-*trans* coordination has formed that consists of linear chains. These results demonstrate the potential of thermally induced ligand removal for the formation of new crystalline phases that might easily be overlooked if the synthesis is only performed in the liquid state. Even if in this case always the same crystalline phase was obtained, there are several examples reported in literature, where this approach can lead to metastable phases that cannot be obtained from the liquid phase.

Experimental Section

General

$\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ was purchased from Alfa Aesar. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 3-bromopyridine were purchased from Merck. $\text{Ni}(\text{NCS})_2$ was synthesized by the reaction of equimolar amounts of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$ in water. The resulting white precipitate of BaSO_4 was filtered off and the solvent was removed from the filtrate under reduced pressure. The purity was checked by XRPD and TG-DTA. All solvents were used without further purification.

Synthesis of $\text{Ni}(\text{NCS})_2(3\text{-bromopyridine})_4$ (**1-I**)

$\text{Ni}(\text{NCS})_2$ (1.0 mmol, 174.9 mg) was dissolved in MeOH and 3-bromopyridine (4.0 mmol, 390 μL) was added. The mixture was stirred for five days, the precipitate was filtered off and dried in air. Compound **1-I** consists of a blue crystalline powder. Elemental analysis for $\text{C}_{22}\text{H}_{16}\text{Br}_4\text{N}_6\text{NiS}_2$ (806.8472 g/mol): C 32.75, H 2.00, N 10.42, S 7.95. Found: C 32.39, H 2.05, N 10.37, S 7.98. For the preparation of single crystals $\text{Ni}(\text{NCS})_2$ (2.0 mmol, 349.7 mg) and 3-bromopyridine (8.0 mmol, 780.2 μL) were stirred in 2.0 mL methanol for two days. The precipitate was filtered off and the filtrate was stored at room temperature leading to suitable crystals within 3 d.

Synthesis of $\text{Ni}(\text{NCS})_2(3\text{-bromopyridine})_4$ (**1-II**)

For the synthesis of compound **1-II** the same amounts of reactants were used as for **1-I**, but the precipitate was stirred for only ten minutes, filtered off and dried in air. A purple crystalline powder was obtained. Elemental analysis for $\text{C}_{22}\text{H}_{16}\text{Br}_4\text{N}_6\text{NiS}_2$ (806.8472 g/mol): C 32.75, H 2.00, N 10.42, S 7.95. Found: C 32.65, H 2.14, N 10.32, S 7.52. Single crystals of this compound were obtained after a mixture of $\text{Ni}(\text{NCS})_2$ (0.25 mmol, 43.7 mg) and 3-Bromopyridine (2.5 mmol, 243.8 μL) was stored in a closed culture tube in 1.5 mL demin. water at 120 °C for 3 d.

Synthesis of Ni(NCS)₂(3-bromopyridine)₂(H₂O)₂ (2)

Compound **2** was obtained by the reaction of Ni(NCS)₂ (1.0 mmol, 174.9 mg) which was dissolved in 1.5 mL demin. water and 3-bromopyridine (1.0 mmol, 98 µL). After three days the residue was filtered off and dried in air. A lightblue crystalline powder was obtained. Elemental analysis for C₁₂H₁₂Br₂N₄NiO₂S₂ (526.8829 g/mol): C 27.36, H 2.30, N 10.63, S 12.17. Found: C 27.14, H 2.27, N 10.54, S 12.16. Single crystals were obtained by storing a mixture of Ni(NCS)₂ (1.0 mmol, 174.9 mg) and 3-bromopyridine (0.25 mmol, 24.4 µL) in a closed culture tube in 1.5 mL demin. water at 120 °C for 3 d.

Synthesis of Ni(NCS)₂(3-bromopyridine)₂(CH₃OH)₂ (3)

After stirring a mixture of Ni(NCS)₂ (2.0 mmol, 349.7 mg) and 3-bromopyridine (2.0 mmol, 195 µL) in 4.0 mL methanol for four days the residue was filtered off and a lightblue crystalline powder was obtained. Elemental analysis for C₁₄H₁₆Br₂N₄NiO₂S₂ (554.9366 g/mol): C 30.30, H 2.91, N 10.10, S 11.56. Found: C 29.91, H 2.82, N 9.93, S 11.80. For the preparation of single crystals Ni(NCS)₂ (0.5 mmol, 87.4 mg) and 3-bromopyridine (0.5 mmol, 48.8 µL) were stirred in 1.0 mL methanol for two days. The filtrate was stored at room temperature and single crystals were obtained within 4 d.

Synthesis of [Ni(NCS)₂(3-bromopyridine)₂]_n · CH₃CN (4)

A greenblue crystalline powder was obtained after stirring Ni(NCS)₂ (1.0 mmol, 174.9 mg) and 3-bromopyridine (2.0 mmol, 195 µL) in 2.0 mL acetonitrile for four days. The residue was filtered off and dried in air. The filtrate was stored at room temperature and single crystals were obtained after several weeks. Elemental analysis for C₁₄H₁₁Br₂N₅NiS₂ (531.9048 g/mol): C 31.61, H 2.08, N 13.17, S 12.06. Found: C 31.47, H 2.20, N 13.06, S 13.29.

Synthesis of [Ni(NCS)₂(3-bromopyridine)₂]_n (5)

A green crystalline powder was obtained by stirring Ni(NCS)₂ (0.5 mmol, 87.4 mg) and 3-bromopyridine (0.875 mmol, 86 µL) in 1.0 mL *n*-butanol for 7 d. The filtered off residue was washed with 3.0 mL *n*-heptane and dried in air. Elemental analysis for C₁₂H₈Br₂N₄NiS₂ (490.8523 g/mol): C 29.36, H 1.64, N 11.41, S 13.07. Found: C 29.44, H 1.82, N 11.44, S 12.39. Single crystals were prepared by heating Ni(NCS)₂ (0.2 mmol, 34.9 mg) and 3-bromopyridine (0.2 mmol, 19.5 µL) in 0.3 mL *n*-butanol up to 90 °C. The solution was cooled to 60 °C and annealed at this temperature for two days.

Single crystal structure analysis

Data collection was performed using an Imaging Plate Diffraction System (IPDS-2) from Stoe&Cie with Mo-K α radiation. A numerical absorption correction was performed using X-Red and X-Shape of the software package X-Area.^[56] The structures were solved with SHELXT^[57] and structure refinement was performed against *F*² using SHELXL-2018.^[58] The C–H hydrogen atoms were positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined isotropically with *U*_{iso} (H) = 1.2 *U*_{eq} (C) (1.5 for methyl H atoms) using a riding model. The O–H hydrogen atoms were located in difference map, their bond lengths were set to ideal values and finally, they were refined isotropically with *U*_{iso} (H) = 1.5 *U*_{eq} (O) using a riding model.

For compound **5** only relatively poor reliability factors were obtained and significant electron density was found in the middle of each Ni(NCS)₂Ni unit, which cannot originate from disorder. Because the lengths of the *a*- and *c*-axis are similar, it was also refined as a pseudo-

merohedral twin but no improvement was obtained. We also assumed monoclinic symmetry and performed twin refinement in all three possible settings but no changes were detected. In this case, the BASF parameter refined to 0.5, which clearly indicates that orthorhombic symmetry is present. Therefore, this structure was refined in the orthorhombic space group *Pna*2₁ as a racemic twin. It is noted that much of intensity was observed between the reflections along the crystallographic *b*-axis, which corresponds to the direction of the chains (Figure S32). We also measured a second crystal at 100 K using a Rigaku Synergy diffractometer but no improvement was obtained. From the experimental data, the reciprocal space was reconstructed, which clearly shows that much of diffuse scattering is observed along the *b*-axis (Figure S33). It is noted that there are no hints for the formation of an incommensurate structure. However, we are absolutely sure that our structure model is correct.

Selected crystal data and details of the structure refinements are given in Table S1 and S2.

CCDC 2052580 (1-I), CCDC 2052581 (1-II), CCDC 2052582 (2), CCDC 2052584 (3) CCDC 2052583 (4) and CCDC 2052585 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Other physical measurements

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 TG-DTA measurements either a STA-PT1000 or a STA-PT1600 thermobalance from Linseis were used. Measurements were performed in Al₂O₃ crucibles and under a dynamic nitrogen atmosphere. The instruments were calibrated using standard referencing materials and corrected for buoyancy.

The XRPD measurements for the characterization of all samples were performed with a Stoe Transmission Powder Diffraction System (STADI P) with Cu-K α radiation and a Dectris Mythen 1 K detector with a Johann-type-Ge(111) monochromator from STOE & CIE.

The magnetic measurements were performed with a PPMS from Quantum Design that is equipped with a 9 T magnet. The data were corrected for the diamagnetic contributions.

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- [1] D. A. Buckingham, *Coord. Chem. Rev.* **1994**, *135*, 587–621.
- [2] S. A. Barnett, A. J. Blake, N. R. Champness, C. Wilson, *Chem. Commun.* **2002**, 1640–1641.
- [3] C. Näther, S. Wöhlert, J. Boeckmann, M. Wriedt, I. Jess, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2696–2714.

- [4] F. A. Mautner, R. C. Fischer, L. G. Rashmawi, F. R. Louka, S. S. Massoud, *Polyhedron* **2017**, *124*, 237–242.
- [5] F. A. Mautner, M. Traber, P. Jantscher, R. C. Fischer, K. Reichmann, R. Vicente, N. Arafat, S. S. Massoud, *Polyhedron* **2019**, *161*, 309–316.
- [6] J. Palion-Gazda, I. Gryca, A. Maroń, B. Machura, R. Kruszynski, *Polyhedron* **2017**, *135*, 109–120.
- [7] S. P. Petrosyants, Z. V. Dobrokhotova, A. B. Ilyukhin, N. N. Efimov, A. V. Gavrikov, P. N. Vasilyev, V. M. Novotortsev, *Eur. J. Inorg. Chem.* **2017**, *2017*, 3561–3569.
- [8] Y. P. Prananto, A. Urbatsch, B. Moubaraki, K. S. Murray, D. R. Turner, G. B. Deacon, S. R. Batten, *Aust. J. Chem.* **2017**, *70*, 516–528.
- [9] J. Werner, T. Runčevski, R. Dinnebier, S. G. Ebbinghaus, S. Suckert, C. Näther, *Eur. J. Inorg. Chem.* **2015**, *2015*, 3236–3245.
- [10] S. Banerjee, B. Wu, P.-G. Lassahn, C. Janiak, A. Ghosh, *Inorg. Chim. Acta* **2005**, *358*, 535–544.
- [11] M. Mousavi, C. Duhayon, K. Bretosh, V. Béreau, J.-P. Sutter, *Inorg. Chem.* **2020**, *59*, 7603–7613.
- [12] K. Nebbali, C. D. Mekuimemba, C. Charles, S. Yefsah, G. Chastanet, A. J. Mota, E. Colacio, S. Triki, *Inorg. Chem.* **2018**, *57*, 12338–12346.
- [13] F. A. Mautner, M. Traber, R. C. Fischer, A. Torvisco, K. Reichmann, S. Speed, R. Vicente, S. S. Massoud, *Polyhedron* **2018**, *154*, 436–442.
- [14] T. Neumann, M. Rams, Z. Tomkowicz, I. Jess, C. Näther, *Chem. Commun.* **2019**, *55*, 2652–2655.
- [15] J. Palion-Gazda, B. Machura, F. Lloret, M. Julve, *Cryst. Growth Des.* **2015**, *56*, 2380–2388.
- [16] C. D. Mekuimemba, F. Conan, A. J. Mota, M. A. Palacios, E. Colacio, S. Triki, *Inorg. Chem.* **2018**, *57*, 2184–2192.
- [17] R. González, A. Acosta, R. Chiozzone, C. Kremer, D. Armentano, G. De Munno, M. Julve, F. Lloret, J. Faus, *Inorg. Chem.* **2012**, *51*, 5737–5747.
- [18] J. L. Guillet, I. Showmick, M. P. Shores, C. J. A. Daley, M. Gembicky, J. A. Golen, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.* **2016**, *55*, 8099–8109.
- [19] S. Petrosyants, Z. Dobrokhotova, A. Ilyukhin, N. Efimov, Y. Mikhlina, V. Novotortsev, *Inorg. Chim. Acta* **2015**, *434*, 41–50.
- [20] E. N. Basse, J. A. M. Paddison, E. N. Keyzer, J. Lee, P. Manuel, I. da Silva, S. E. Dutton, C. P. Grey, M. J. Cliffe, *Inorg. Chem.* **2020**, *59*, 11627–11639.
- [21] M. Mousavi, V. Béreau, C. Desplanches, C. Duhayon, J.-P. Sutter, *Chem. Commun.* **2010**, *46*, 7519–7521.
- [22] S. Suckert, M. Rams, M. Böhme, L. S. Germann, R. E. Dinnebier, W. Plass, J. Werner, C. Näther, *Dalton Trans.* **2016**, *45*, 18190–18201.
- [23] J. Werner, Z. Tomkowicz, T. Reinert, C. Näther, *Eur. J. Inorg. Chem.* **2015**, *2005*, 3066–3075.
- [24] T. Neumann, M. Rams, C. Wellm, C. Näther, *Cryst. Growth Des.* **2018**, *18*, 6020–6027.
- [25] C. Wellm, M. Rams, T. Neumann, M. Ceglarska, C. Näther, *Cryst. Growth Des.* **2018**, *18*, 3117–3123.
- [26] C. Wellm, A. M. Majcher-Fitas, M. Rams, C. Näther, *Dalton Trans.* **2020**, *49*, 16707–16714.
- [27] X.-Y. Wang, B.-L. Li, X. Zhu, S. Gao, *Eur. J. Inorg. Chem.* **2005**, 3277–3286.
- [28] E. Shurdha, C. E. Moore, A. L. Rheingold, S. H. Lapidus, P. W. Stephens, A. M. Arif, J. S. Miller, *Inorg. Chem.* **2013**, *52*, 10583–10594.
- [29] H.-J. Chen, X.-M. Chen, *Inorg. Chim. Acta* **2002**, *329*, 13–21.
- [30] G. Yang, Q. Zhang, X.-P. Zhang, Y. Zhu, N. Seik Weng, *J. Chem. Res.* **2007**, 384–386.
- [31] Y. Jin, Y.-X. Che, J.-M. Zheng, *J. Coord. Chem.* **2007**, *60*, 2067–2074.
- [32] J. M. Shi, J. N. Chen, C. J. Wu, J. P. Ma, *J. Coord. Chem.* **2007**, *60*, 2009–2013.
- [33] A. Datta, P.-H. Liu, J.-H. Huang, E. Garribba, M. Turnbull, B. Machura, C.-L. Hsu, W.-T. Chang, A. Pevec, *Polyhedron* **2012**, *44*, 77–87.
- [34] J. Werner, M. Rams, Z. Tomkowicz, C. Näther, *Dalton Trans.* **2014**, *43*, 17333–17342.
- [35] J. Werner, Z. Tomkowicz, M. Rams, S. G. Ebbinghaus, T. Neumann, C. Näther, *Dalton Trans.* **2015**, *44*, 14149–14158.
- [36] S. Wöhlert, T. Fic, Z. Tomkowicz, S. G. Ebbinghaus, M. Rams, W. Haase, C. Näther, *Inorg. Chem.* **2013**, *52*, 12947–12957.
- [37] S. Wöhlert, Z. Tomkowicz, M. Rams, S. G. Ebbinghaus, L. Fink, M. U. Schmidt, C. Näther, *Inorg. Chem.* **2014**, *53*, 8298–8310.
- [38] A. Jochim, M. Rams, T. Neumann, C. Wellm, H. Reinsch, G. M. Wójtowicz, C. Näther, *Eur. J. Inorg. Chem.* **2018**, *2018*, 4779–4789.
- [39] A. Jochim, M. Rams, M. Böhme, T. Lohmiller, M. Ceglarska, A. Schnegg, W. Plass, C. Näther, *Inorg. Chem.* **2020**, *59*, 8971–8982.
- [40] I. N. B. Machura, K. Michalik, *Polyhedron* **2011**, *Vol. 30*, 2619–2626.
- [41] A. Tahli, J. K. Maclaren, I. Boldog, C. Janiak, *Inorg. Chim. Acta* **2011**, *374*, 506–513.
- [42] Ql. Ma, M. Zhu, C. Yuan, S. Feng, L. Lu, Q. Wang, *Cryst. Growth Des.* **2009**, *Vol. 10*, 1706–1714.
- [43] X. Zhu, X.-Y. Wang, B.-L. Li, J. Wang, S. Gao, *Polyhedron* **2012**, *31*, 77–81.
- [44] M. Rams, Z. Tomkowicz, M. Böhme, W. Plass, S. Suckert, J. Werner, I. Jess, C. Näther, *Phys. Chem. Chem. Phys.* **2017**, *19*, 3232–3243.
- [45] S. Suckert, M. Rams, M. M. Rams, C. Näther, *Inorg. Chem.* **2017**, *56*, 8007–8017.
- [46] M. Böhme, A. Jochim, M. Rams, T. Lohmiller, S. Suckert, A. Schnegg, W. Plass, C. Näther, *Inorg. Chem.* **2020**, *59*, 5325–5338.
- [47] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr.* **2016**, *B72*, 171–179.
- [48] J. V. Handy, G. Ayala, R. D. Pike, *Inorg. Chim. Acta* **2017**, *456*, 64–75.
- [49] K. M. Miller, S. M. McCullough, E. A. Lepekhina, I. J. Thibau, R. D. Pike, X. Li, J. P. Killarney, H. H. Patterson, *Inorg. Chem.* **2011**, *50*, 7239–7249.
- [50] S. Wöhlert, I. Jess, C. Näther, *Inorg. Chim. Acta* **2013**, *407*, 243–251.
- [51] A. D. Nicholas, B. M. Otten, G. Ayala, J. Hutchinson, L. Wojtas, M. A. Omary, R. D. Pike, H. H. Patterson, *J. Phys. Chem. C* **2017**, *121*, 25430–25439.
- [52] K. Robinson, G. V. Gibbs, P. H. Ribbe, *Science* **1971**, *172*, 567–570.
- [53] T. K. Maji, I. R. Laskar, G. Mostafa, A. J. Welch, P. S. Mukherjee, N. R. Chaudhuri, *Polyhedron* **2001**, *20*, 651–655.
- [54] M. H. Moore, L. R. Nassimbeni, M. L. Niven, *Inorg. Chim. Acta* **1987**, *131*, 45–52.
- [55] T. Neumann, M. Ceglarska, M. Rams, L. S. Germann, R. E. Dinnebier, S. Suckert, I. Jess, C. Näther, *Inorg. Chem.* **2018**, *57*, 3305–3314.
- [56] Stoe&Cie (2008), *X-AREA* (Version 1.44). STOE & CIE GmbH, Darmstadt (Germany).
- [57] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3–8.
- [58] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3–8.

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