Synthesis, Structures, and Properties of Transition Metal Thiocyanato Coordination Compounds with 4-(4-Chlorobenzyl)pyridine as Ligand

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Dedicated to Professor Martin Jansen on the Occasion of His 70th Birthday

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Abstract. Reactions of transition metal thiocyanates with 4-(4-chlorobenzyl)pyridine (Clbp) lead to the formation of compounds of composition M(NCS)₂(4-(4-chlorobenzyl)pyridine)₄ (Mn-1, Fe-1/I, Fe-1/ II, Ni-1, and Cd-1) and M(NCS)₂(4-(4-chlorobenzyl)pyridine)₂ (Mn-2, Ni-2, and Cd-2). In the crystal structures of compounds M-1 the metal cations are octahedrally coordinated by two terminal N-bonded thiocvanato anions and four Clbp ligands, whereas in compounds M-2 the metal cations are linked by μ -1,3-bridging anionic ligands. IR spectroscopic investigations show that the value of the asymmetric C-N stretching vibration depends on the coordination mode of the

Introduction

Investigations on the synthesis, structure, and properties of new coordination compounds are still an active field in coordination chemistry. The major goal in this area includes the development of strategies for a more rational synthesis of compounds with definite structures and desired physical properties.^[1-11] This also includes investigations on compounds that show cooperative magnetic phenomena and therefore, a large number of compounds based on small ligands like e.g. azides, oxalates and others were recently reported.^[12-18] In this context also coordination compounds based on thio- or selenocyanates are of interest and some representative examples are given in the reference list.^[19–34]

In our own research, we are also interested in the magnetic properties of thio- and selenocyanato coordination polymers, with focus on compounds, in which the central metal atoms are linked by μ -1,3-bridging anionic ligands.^[35] In the course of this project we have investigated several of such compounds, predominantly based on Mn^{II}, Fe^{II}, Co^{II}, and Ni^{II} that as function of the metal cations and the neutral N-donor coligand show different magnetic properties.^[36-44] Within this

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thiocyanato ligand and the nature of the metal cations. The thermal properties were investigated by simultaneous differential thermoanalysis and thermogravimetry as well as temperature dependent X-ray powder diffraction. On heating compound Ni-1 looses half of the Clbp ligands and transforms into Ni-2. Clbp deficient intermediates were also detected on thermal decomposition of Mn-1 and Fe-1/I but the samples are of low crystallinity and therefore, their structures cannot be determined. Magnetic investigations reveal that Ni-2 show only Curie-Weiss paramagnetism without any magnetic anomaly.

project we are especially interested in compounds, in which the central metal atoms are coordinated only by monodentate ligands and are linked by pairs of thio- or selenocyanato anions into chains, which are not further connected into layers by the co-ligands. Unfortunately, the compounds with bridging ligands are sometimes difficult to prepare in solution and therefore, we use an alternative solid state route, in which suitable precursor compounds with terminal bonded anionic ligands are thermally decomposed.^[45-47] The synthesis of coordination compounds via typical solid state methods is not uncommon and also other strategies were reported.^[48-51] However, one disadvantage of thermal decomposition reactions is the fact that only crystalline powders and sometimes different modifications are obtained and therefore, structural information is difficult to retrieve.^[52] In some cases the coordination mode of the anionic ligands might be determined by IR spectroscopy.^[53,54] Moreover, structural information can also be extracted by preparing the corresponding compounds with cadmium or zinc, because in several cases they are isotypic to the paramagnetic analogs.^[55,56] Therefore, systematic investigations on the synthesis, the crystal structures as well as the thermal and spectroscopic properties of thio- and selenocyanato coordination compounds are of extraordinary importance for our project.

In the course of our investigations we decided to study the influence of larger monodentate N-donor co-ligands on the thermal reactivity in more detail and for the present study Clbp was selected, for which no coordination compounds are reported in the Cambridge Structural Database.^[57] Within these

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bridging thiocyanato anions are present (see below).

ARTICLE

investigations we prepared several new compounds based on Mn^{II}, Fe^{II}, Ni^{II}, and Cd^{II}, in which the central metal atoms are coordinated by terminal N-bonded anions and which might be useful as precursors for the preparation of the desired compounds with a bridging coordination. Herein we report on our results.

Results and Discussion

Synthetic Investigations

To investigate, which compounds are available in solution different ratios of $M(NCS)_2$ (M = Mn, Fe, Ni, Cd) and 4-(4-chlorobenzyl)pyridine) (Clbp) were reacted in different solvents at room temperature and the residues obtained were filtered of and investigated by elemental analysis and X-ray powder diffraction (XRPD). Elemental analyses showed that compounds of composition $M(NCS)_2(4-(4-chlorobenzyl)pyridine)_4$ (**Mn-1, Fe-1/I, Ni-1**, and **Cd-1**) and of composition $M(NCS)_2$ -(4-(4-chlorobenzyl)pyridine)_2 (**Mn-2, Ni-2**, and **Cd-2**) were formed (Table S1, Supporting Information). For **Mn-2** some deviations from the calculated values are found, indicating that this compound contains some contamination.

XRPD investigations indicate that **Mn-1**, **Fe-1/I**, and **Cd-1** are isotypic and that **Ni-1** crystallizes differently (Figure 1). Moreover, the residue obtained with iron at ratio 1:4 shows a different powder pattern, indicating that a second modification is obtained (**Fe-1/II**) that might be contaminated with **Fe-1/I** (Figure 1). It is noted, that the powder pattern of **Fe-1/II** is similar to that of **Ni-1** (Figure 1). IR spectroscopic investigations indicate that the C–N stretching vibrations of compounds **M-1** are in the range expected for terminally N-bonded thiocyanato anions (see below).



Figure 1. Experimental XRPD pattern of Mn-1, Fe-1/I, Fe-1/II, Ni-1, and Cd-1.

For the *M*-2 compounds XRPD investigations indicate that **Mn-2** and **Ni-2** are isotypic, that **Cd-2** exhibits a different structure and that **Mn-2** is contaminated with large amounts of **Mn-1** (Figure 2). Based on the value of the asymmetric C–N



stretching vibration it can be assumed that in compounds M-2

Figure 2. Experimental XRPD pattern of Mn-2, Ni-2, and Cd-2.

Solvent mediated conversion experiments of a mixture of **Fe-1/I** and **Fe-1/II** prove, that in water **Fe-1/II** transforms into **Fe-1/I** and therefore, that **Fe-1/I** represent the thermodynamic stable modification at room temperature (Figure S1 in the Supporting Information).

In further work crystallization experiments were performed at room temperature and under solvothermal conditions, which lead to the formation of single crystals of Mn-1, Fe-1/I, Ni-1, Cd-1 as well as of Mn-2, Ni-2 and Cd-2. Comparison of the experimental powder patterns of compounds *M*-1 and *M*-2 with that calculated from single crystal data proves that Mn-1, Fe-1/I, Ni-1, Cd-1, and Ni-2 are obtained as pure phases, whereas Mn-2 is contaminated with Mn-1 and Cd-2 with a small amount of an additional phase, that cannot be identified (Figures S2–S8, Supporting Information).

Crystal Structures

The compounds $M(NCS)_2(4-(4-chlorobenzyl)pyridine)_4$ [M = Mn (**Mn-1**), Fe (**Fe-1/I**), and Cd (**Cd-1**)] are isotypic and crystallize in the monoclinic centrosymmetric space group C2/c with four formula units in the unit cell. The asymmetric unit consists of one crystallographically independent discrete complex, which is located on a center of inversion, as well as of one thiocyanato anion and two 4-(4-chlorobenzyl)pyridine ligands in general position (Figure 3). Ni(NCS)₂(4-(4-chlorobenzyl)pyridine)₄ (**Ni-1**) crystallizes monoclinic in space group $P2_1$ with two formula units in the unit cell and all atoms in general positions.

In the crystal structures of compounds M-1 the metal cations are coordinated by two nitrogen atoms of two terminal thiocyanato anions and four nitrogen atoms of terminal bonded 4-(4chlorobenzyl)pyridine ligands within a slightly distorted octahedral coordination arrangement. The angles around the metal cations range between 88.33(17) and 91.39(8)° and the metal-

Pages: 9



Figure 3. Crystal structure of Mn-1 as a representative with atom labeling (Ortep plots of Mn-1, Fe-1/I, Ni-1 and Cd-1 are shown in Figures S9–S12 in the Supporting Information).

nitrogen distances range between 2.040(3) and 2.381(2) Å. (Tables S2–S5, Supporting Information).

The compounds $[M(NCS)_2(4-(4-\text{chlorobenzyl})\text{pyridine})_2]_n$ (M = Mn, Ni) crystallize in the triclinic centrosymmetric space group $P\bar{1}$ with two formula units in the unit cell. The asymmetric unit consists of two metal cations, which are situated on a center of inversion as well as two 4-(4-chlorobenzyl)pyridine and two thiocyanato ligands in general positions (Figure 4). $[Cd(NCS)_2(4-(4-\text{chlorobenzyl})\text{pyridine})_2]_n$ crystallizes monoclinic in space group $P2_1/c$ with two formula unit in the unit cell. The asymmetric unit consists of two metal cations, three thiocyanato anions and three 4-(4-chlorobenzyl)pyridine ligands. One metal cation is located on center of inversion; all other atoms are located in general positions.

In their crystal structures the metal cations are coordinated by two N-bonded Clbp ligands and two N-bonded μ -1,3 bridging thiocyanato anions as well as two adjacent S-bonded μ -1,3 bridging thiocyanato anions. The cations are linked into chains by pairs of μ -1,3 bridging thiocyanato anions. The metal–nitrogen distances range between 2.027(2) and 2.335(3) Å as well as the metal–sulfur distances range between 2.5151(6) and 2.7438(10) Å (Tables S6–S8, Supporting Information).

Thermoanalytical Investigations

To check if Clpb deficient compounds are accessible, the precursor compounds $M(NCS)_2(4-(4-chlorobenzyl) pyridine)_4$ (M = Mn, Fe, Ni, Cd) were investigated by simultaneous differential thermoanalysis and thermogravimetry (DTA-TG). On heating all *M***-1** compounds show one mass step at about 200 °C, which, as function of the metal cation is differently resolved (Figure 5).

For **Mn-1** the mass loss of the first step does not correspond to that calculated for the removal of two Clbp ligands and if



Figure 4. Crystal structure of compound Mn-2 as a representative with atom labeling (Ortep plots of Mn-2, Ni-2, and Cd-2 are shown in Figures S13–S15 in the Supporting Information).



Figure 5. TG curves for the compounds Mn-1, Fe-1/I, Ni-1, and Cd-1. Heating rate = $1 \, {}^{\circ}C \cdot \min^{-1}$.

the residue formed in the first step is investigated by XRPD it is obvious that a mixture of **Mn-1** and **Mn-2** is obtained (Figure S20, Supporting Information). For **Fe-1/I** and **Cd-1** similar observations were made and there are no indications for additional intermediates. This does not change if all compounds are investigated by heating rate dependent measurements, which show that the best resolution is obtained with 1 °C· min⁻¹ (Figures S16–19, Supporting Information). In contrast, **Ni-1** shows two good resolved mass steps and the experimental mass loss of 39.7% in the first and 39.0% in the second TG 6:29

Pages: 9

ARTICLE

step is in moderate agreement with the calculated mass loss for the removal of two 4-(4-chlorobenzyl)pyridine ligands ($\Delta m_{\text{calcd.}} = -41.2\%$). If the residue formed after the first mass step is investigated by XRPD it is proven that **Ni-2** has formed as a pure phase (Figure 6).



Figure 6. Experimental XRPD pattern of the residue obtained after the first mass step in thermal decomposition of compound Ni-1 (A), experimental XRPD pattern for Ni-2 obtained from solution (B) and calculated XRPD for compound Ni-2 (C).

Further investigations using temperature dependent XRPD measurements on **Mn-1**, **Fe-1/I**, and **Cd-1** indicate that even for these compounds new Clbp deficient intermediates are formed, which are of low crystallinity (Figures S21–23, Supporting Information). The powder patterns of these samples do not correspond to that of compounds *M-2* or their mixtures with compounds **M-1** but indexing failed because of their poor quality. Summarizing, we have found no access to pure samples of **Mn-2**.

IR Spectroscopy

To investigate how the value of the C–N stretching vibration depends on the coordination mode of the ligand and the nature of the metal cation all compounds were measured by IR spectroscopy (Figures S24–31, Supporting Information). These investigations show that for all compounds with terminal N-bonded anions; v_{as} (CN) is observed between 2051 and 2071 cm⁻¹ and increases from Mn to Ni (Table 1). A similar trend is observed for the bridging compounds, for which values between 2094 and 2117 cm⁻¹ are observed (Table 1). There is a clear gap between the *M*-1 and *M*-2 compounds, which in this case definitely allows differing between a terminal and a bridging coordination. If these values are compared with those for the corresponding compounds with pyridine as reference a small influence of the co-ligand becomes obvious, because most values are shifted by several wave numbers.^[38,40]

Table 1. Values of the asymmetric C–N stretching vibration for compounds *M*-1 and *M*-2 as well as for the corresponding compounds with pyridine retrieved from literature.^[38,40]

Compound	$\nu_{as}(CN) \ /cm^{-1}$	Compound	$v_{as}(CN)$ /cm ⁻
Cd-1	2054	Cd-2	2107
Mn-1	2051	Mn-2	2094
Fe-1/I	2056	Fe-2	_
Ni-1	2071	Ni-2	2117
$Cd(NCS)_2(Pyr)_4$	2050	$Mn(NCS)_2(Pyr)_2$	2097
$Mn(NCS)_2(Pyr)_4$	2060	$Mn(NCS)_2(Pyr)_2$	2090
Fe(NCS) ₂ (Pyr) ₄	2066	$Mn(NCS)_2(Pyr)_2$	2093
Ni(NCS) ₂ (Pyr) ₄	2082	$Mn(NCS)_2(Pyr)_2$	2110

This clearly shows that an assignment of the coordination mode for different compounds only on the basis of IR spectroscopic data might be sometimes difficult to achieve.

Magnetic Investigations

Compound Ni-2, in which the central metal atoms are linked by pairs of μ -1,3 bridging thiocyanato anions was investigated for its magnetic properties. It is noted that compounds *M*-1 consist of discrete complexes and therefore, only Curie or Curie-Weiss behavior is expected as observed for related compounds reported recently.^[38,40] As shown above, compound **Mn-2** is contaminated with **Mn-1** and therefore, were not investigated.

The temperature dependence of the susceptibility χ was measured as function of temperature for Ni-2 and only paramagnetic behavior is observed. The experimental magnetic moment at room-temperature retrieved from the $(8\chi T)^{1/2}$ curve of about 2.8 μ_B is in perfect agreement with that calculated for Ni^{II} in high-spin configuration (2.82 μ_B). Analyzing the magnetic data using an Curie-Weiss fit, leads to an effective magnetic moment of 2.89 μ_B and a positive Weiss constant of 16.5 K On cooling the χT product increases indicating dominating ferromagnetic interactions between the Ni cations and afterwards the susceptibility curve passes a maximum (Figure 7).



Figure 7. χ and $(8\chi T)^{1/2}$ as function of temperature for Ni-2 measured at $H_{dc} = 1$ kOe.

Pages: 9



This is in agreement with results for compounds with similar Ni(NCS)₂ chains like, e.g. in the two modifications of Ni(NCS)₂(4-ethylpyridine)₂, for which paramagnetic behavior dominating ferromagnetic interactions are observed and for which the χT vs. *T* curves looks similar.^[52] It is noted, that the corresponding compound with pyridine is a metamagnet with an antiferromagnetic ground state.^[40] Therefore, it cannot be excluded that antiferromagnetic ordering will occur at lower temperatures for Ni-2.

Transition Metal Thiocyanato Coordination Compounds

Conclusions

In the presented contribution new thiocyanato coordination compounds with 4ö-(4-chlorobenzyl)pyridine as co-ligand were prepared and investigated for their properties. For the paramagnetic compounds it was found that the compounds with terminal bonded thiocyanato anions can easily be prepared in solution, whereas not all of the corresponding compounds with bridging anionic ligands are accessible from solution. The bridging compounds with Mn and Fe can also not be prepared by thermal decomposition and this might be traced back to the relatively large co-ligand because similar compounds with smaller co-ligands are easily accessible by this route. IR spectroscopic investigations reveal that one can easily differ between the different coordination modes and that only a small shift is observed for the different cations. Magnetic measurements on Ni-2 reveal that only paramagnetic behavior without any magnetic anomaly is observed and this is in agreement with our findings for compounds of same composition but with slightly different co-ligands. If there is any correlation between the size of the co-ligand and the thermal reactivity of the corresponding coordination compounds will be the subject of further investigations.

Experimental Section

Synthesis: MnSO₄·H₂O, NiSO₄·6H₂O, CdSO₄·8/3H₂O, KNCS, and FeCl₂·4H₂O were obtained from Merck, Ba(NCS)₂·3H₂O and 4-(4-chlorobenzyl)pyridine were obtained from Alfa Aesar. Solvents were used without further purification. Crystalline powders of all compounds were prepared by stirring the reactants in open vessels in the respective solvents at room temperature. The residues were filtered off and washed with appropriate solvents and dried in air. The purity of all compounds was checked by X-ray powder diffraction and elemental analysis

Cd(NCS)₂: Ba(NCS)₂·3H₂O (3.076 g, 10 mmol) and CdSO₄·8/3H₂O (2.566 g, 10 mmol) were stirred in water (100 mL). The white precipitate of BaSO₄ was filtered off and the water was removed from the filtrate by heating. The final product was dried by 80 °C. The homogeneity of the product was investigated by Xray powder diffraction and elemental analysis.

 $Mn(NCS)_2$: Ba(NCS)₂·3H₂O (17.9 g, 58.44 mmol) and MnSO₄·6H₂O (9.9 g, 58.44 mmol) were stirred in water (400 mL). The white precipitate of BaSO₄ was filtered off and the water evaporated using a rotary evaporator. The homogeneity of the product was investigated by Xray powder diffraction and elemental analysis.

Ni(NCS)₂: Ba(NCS)₂·3H₂O (17.5 g, 57 mmol) and NiSO₄·6H₂O (15.0 g, 57 mmol) were stirred in water (400 mL). The white precipitate of BaSO₄ was filtered off and the water evaporated using a rotary evaporator. The homogeneity of the product was investigated by Xray powder diffraction and elemental analysis

Synthesis of Cd-1: Single crystals suitable for single-crystal X-ray diffraction were prepared by the reaction of Cd(NCS)₂ (0.15 mmol, 34.3 mg) and 4-(4-chlorobenzyl)pyridine (0.15 mmol, 26.4 μ L) in ethanol (1.5 mL). Colorless crystals were obtained after several days. A colorless crystalline powder on a larger scale was prepared by stirring Cd(NCS)₂ (114.3 mg, 0.50 mmol), and 4-(4-chlorobenzyl)pyridine (877.9 μ L, 5.00 mmol) in ethanol (5 mL) for 3 d. Yield: 90.7%. C₅₀H₄₀N₆Cl₄S₂Cd (1043.25 g·mol⁻¹): calcd. C 57.57, H 3.86, N 8.06, S 6.15%; found C 57.22, H 3.81, N 8.10, S 6.06%. **IR** (ATR): \tilde{v}_{max} = 3063 (w), 3038 (w), 2054 (s), 1614 (m), 1558 (w), 1490 (m), 1423 (m), 1222 (m), 1091 (m), 1069 (m), 1015 (s), 856 (m), 804 (s), 788 (s), 592 (s), 487 (s) cm⁻¹.

Synthesis of Mn-1: Single crystals suitable for single-crystal X-ray diffraction were obtained by a reaction of $Mn(NCS)_2$ (0.3 mmol, 51.3 mg) and 4-(4-chlorobenzyl)pyridine (0.15 mmol, 26.4 µL) in methanol (1.5 mL). Yellow colored block-shaped crystals were obtained after several days. A white crystalline powder on a larger scale was obtained by stirring $Mn(NCS)_2$ (171.1 mg, 1.00 mmol), and 4-(4-chlorobenzyl)pyridine (702.3 µL, 4.00 mmol) in ethanol (5 mL) for 3 d. Yield: 95.2%. C₅₀H₄₀N₆Cl₄S₂Mn (985.79): calcd. C 60.92, H 4.09, N 8.51; S 6.51%; found C60.82, H 3.97, N 8.55, S 6.39%. **IR** (ATR): $\tilde{v}_{max} = 3066$ (w), 3036 (w), 2051 (s), 1615 (m), 1557 (w), 1488 (m), 1422 (m), 1348 (w), 1223 (m), 1014 (s), 855 (m), 804 (s), 788 (s), 591 (s), 488 (s) cm⁻¹.

Synthesis of Fe-1: Single crystals suitable for single-crystal X-ray diffraction were obtained by a reaction of FeCl₂·4H₂O (0.15 mmol, 29.8 mg), KNCS (0.3 mmol, 29.2 mg) and 4-(4-chlorobenzyl)pyridine (0.6 mmol, 105.4 μ L) in acetonitrile (1.5 mL). Red colored block-shaped crystals were obtained after several days. A red-brown crystal-line powder on a larger scale was obtained by stirring FeCl₂·4H₂O (198.8 mg, 1.00 mmol), KNCS (194.4 mg, 2.00 mmol) and 4-(4-chlorobenzyl)pyridine (1629.3 μ L, 4.00 mmol) in H₂O (5 mL) and EtOH (3 mL) for 4 d. Yield: 92.7 %. C₅₀H₄₀Cl₄FeN₆S₂ (986.70): calcd. C 60.86, H 4.09, N 8.52; S 6.50%, found C 60.84, H 4.04, N 8.36, S 5.68 %. **IR** (ATR): $\tilde{v}_{max} = 3070$ (w), 3039 (w), 2915 (w), 2056 (s), 2015 (m), 1613 (s), 1557 (m), 1488 (s), 1422 (s), 1406 (m), 1222 (m), 1091 (m), 1013 (s), 855 (m), 804 (s), 788 (s), 591 (s), 489 (s) cm⁻¹.

Synthesis of Ni-1: Single crystals suitable for single-crystal X-ray diffraction were prepared by Ni(NCS)₂ (0.15 mmol, 26.3 mg) and 4-(4-chlorobenzyl)pyridine (0.6 mmol, 105.4 µL). After few days, lightblue well-shaped single crystals were obtained. A light-green crystalline powder on a larger scale was obtained by stirring Ni(NCS)₂ (174.9 mg, 0.50 mmol), and 4-(4-chlorobenzyl)pyridine (1222 µL, 6.00 mmol) in ethanol (5 mL) for 3 d. Yield: 97.6%. C₅₀H₄₀N₆Cl₄S₂Ni (989.54): calcd. C 60.69, H 4.07, N 8.49, S 6.48%; found C 60.35, H 4.06, N 8.64, S 6.24%. **IR** (ATR): $\tilde{v}_{max} = 3074$ (w), 3031 (w), 2086 (m), 2069 (s), 1610 (m), 1558 (m), 1489 (s), 1423 (s), 1222 (m), 1090 (m), 1016, 917 (w), 788 (s), 650 (w), 592 (s), 485 (s) cm⁻¹.

Synthesis of Mn-2: Single crystals suitable for single-crystal X-ray diffraction were prepared by slow evaporation of the filtrate of the reaction of $Mn(NCS)_2$ (3.0 mmol, 511.0 mg), and 4-(4-chlorobenzyl) pyridine (0.75 mmol, 131.8 µL) in 4 mL acetonitrile.

Pages: 9

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ARTICLE

Synthesis of Ni-2: Single crystals suitable for single-crystal X-ray diffraction were obtained by a reaction of Ni(NCS)₂ (0.15 mmol, 26.3 mg) and 4-(4-chlorobenzyl)pyridine (0.3 mmol, 52.7 µL) in water (1.5 mL) at 105 °C in a closed 10 mL glass culture tube. Light-blue colored crystals were obtained after several days. A light-blue crystalline powder on a larger scale was obtained by stirring Ni(NCS)2 (349.7 mg, 4.00 mmol), and 4-(4-chlorobenzyl)pyridine (176 µL, 1.00 mmol) in ethanol (5 mL) for 10 d. Yield: 93.7 %. C₂₆H₂₀N₄Cl₂S₂Ni (582.20): calcd. C 53.64, H 3.46, N 9.62, S 11.02 %; found C 53.45, H 3.42, N 9.88, S 11.03 %. IR (ATR): \tilde{v}_{max} = 2910 (w), 2118 (s), 1613 (m), 1559 (w), 1489 (m), 1423 (m), 1223 (w), 1094 (m), 1067 (m), 1014 (m), 919 (w), 852 (m), 807 (m), 787 (s), 656 (w), 597 (s), 492 (s) cm⁻¹.

Synthesis of Cd-2: Single crystals suitable for single-crystal X-ray diffraction were obtained by a reaction of Cd(NCS)₂ (0.30 mmol, 68.6 mg) and 4-(4-chlorobenzyl)pyridine (0.15 mmol, 26.3 µL) in acetonitrile (1.5 mL) at room temperature. Colorless crystals were obtained after several days. A colorless crystalline powder on a larger scale was obtained by stirring Cd(NCS)₂ (114.3 mg, 0.50 mmol), and 4-(4-chlorobenzyl)pyridine (93.8 µL, 0.50 mmol) in ethanol (2 mL) and H₂O (1 mL) for 3 d. Yield: 75.2%. C₂₆H₂₀CdCl₂N₄S₂ (635.91): calcd. C 49.11, H 3.17, N 8.81, S 10.09%; found C 49.12, H 3.09, N 8.93, S 10.22 %. **IR** (ATR): \tilde{v}_{max} = 2108 (s), 1665 (m), 1609 (m), 1558 (w), 1491 (m), 1425 (m), 1286 (w), 1225 (m), 1092 (m), 1070 (m), 1017 (s), 918 (w), 855 (m), 786 (s), 669 (w), 594 (s), 482 (s) cm⁻¹.

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

Elemental Analysis of the Residue Obtained in the Thermal Decomposition: Isolated in the first heating step (see thermoanalytical investigations) of compound Ni-1. Calculated for the ligand-deficient compound Ni-2: C₂₆H₂₀N₄Cl₂S₂Ni (582.20): calcd. C 53.64, H 3.46, N 9.62; S 11.02%; found C 53.53, H 3.39, N 9.50, S 11.03%.

Differential Thermal Analysis and Thermogravimetry: The DTA-TG measurements were performed in a dynamic nitrogen atmosphere (purity: 5.0) in Al₂O₃ crucibles with a STA-409CD thermobalance from Netzsch. All measurements were performed with a flow rate of 75 mL min⁻¹ and were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

Single-Crystal Structure Analysis: The investigations were performed with the imaging plate diffraction system (IPDS-1 for Cd-1; IPDS-2 for Mn-1, Fe-1, Ni-1, Mn-2, Ni-2) with Mo-K_α-radiation from STOE & CIE. The structure solution was performed with direct methods using SHELXS-97 and structure refinements were performed against F² using SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters $[U_{iso}(H) = 1.2 \cdot U_{eq}(C_{aromatic})$ using a riding model. For compounds Mn-1, Fe-1, and Cd-1 the Cl atom is disordered over two sites and was refined using a split model. The crystal of compound Ni-1 is racemically twinned and therefore, a twin refinement was performed (BASF parameter: 0.28401).

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-1021251 (Mn-1), CCDC-1021533 (Fe-1), CCDC-

Table 2. Selected crystal data and details on the structure determinations for compounds M-1 (M = Cd, Mn, Fe, Ni) and M-2 (M = Cd, Mn, Ni).

	Cd-1	Mn-1	Fe-1	Ni-1	Cd-2	Mn-2	Ni-2
Formula	C ₅₀ H ₄₀ CdN ₆ Cl ₄ S ₂	C ₅₀ H ₄₀ Cl ₄ MnN ₆ S ₂	C ₅₀ H ₄₀ Cl ₄ FeN ₆ S ₂	C50H40Cl4N6NiS2	C ₇₈ H ₆₀ Cd ₃ Cl ₆ N ₁₂ S ₆	C ₂₆ H ₂₀ Cl ₂ MnN ₄ S ₂	C ₂₆ H ₂₀ Cl ₂ N ₄ NiS ₂
MW /g·mol ⁻¹	1043.20	985.74	986.65	989.51	1907.64	578.42	582.19
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	C2/c	C2/c	C2/c	P2 ₁	$P2_{1/c}$	PĪ	ΡĪ
a /Å	18.9719(13)	19.0051(8)	18.8321(6)	13.199(3)	17.4730(6)	9.0790(10)	9.0222(4)
b /Å	9.7143(5)	9.6769(4)	9.5826(2)	13.613(3)	8.2738(4)	11.0140(15)	10.7966(5)
<i>c</i> /Å	27.6679(19)	27.8212(9)	27.6478(10)	13.454(3)	29.5128(13)	14.898(3)	14.9511(7)
a /°	90.000	90.00	90.00	90.000	90.000	73.854(13)	73.166(4)
β /°	106.855(8)	106.656(3)	106.794(3)	95.54(3)	107.970(3)°	82.870(13)	83.501(4)
γ /°	90.000	90.000	90.00	90.000	90.000	68.830(9)	67.963(4)
$V/Å^3$	4880.1(5)	4901.9(3)	4776.5(3)	2406.1(8)	4058.5(3)	1333.9(3)	1292.11(10)
<i>T /</i> K	293	293	293	293	200	200	200
Ζ	4	4	4	2	2	2	2
$D_{\rm calc}$ /g·cm ⁻³	1.420	1.336	1.372	1.366	1.561	1.440	1.496
μ /mm ⁻¹	0.793	0.613	0.669	0.753	1.181	0.874	1.142
$\theta_{\rm max}$ /°	28.06	26.00	27.53	26.00	25.45	26.99	27.00
Measured refl.	20586	19496	29617	17043	36322	15000	18683
R _{int}	0.0768	0.0251	0.0338	0.0380	0.0460	0.0471	0.0413
Unique reflns.	5805	4793	5454	9281	7435	5789	5641
Refl. $[F_{o} >$	4002	2011	1575	6976	6140	4407	4200
$4\sigma(F_{\rm o})$]	4223	3844	4373	0820	0148	4497	4398
Parameters	296	295	296	569	541	319	320
$R_1 [F_0 > 4\sigma(F_0)]$	0.0438	0.0489	0.0491	0.0575	0.0417	0.0333	0.0421
wR_2 [all data]	0.1035	0.1232	0.1074	0.1140	0.0793	0.0870	0.0939
GOF	1.026	1.058	1.075	1.108	1.092	1.026	1.047
$\Delta ho_{ m max/min}$ /e·Å ⁻³	0.500/ -0.526	0.418/ -0.366	0.417/ -0.337	0.270/ -0.177	0.706/ -0.654	0.310/ -0.375	0.349/ -0.427

Pages: 9



1021252 (Ni-1), CCDC-1021250 (Cd-1), CCDC-1021248 (Mn-2), CCDC-1021249 (Ni-2) and CCDC-1021247 (Cd-2) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

X-ray Powder Diffraction (XRPD): XRPD experiments were performed with a Stoe Transmission Powder Diffraction System (STADI P) with Cu- K_{α} -radiation ($\lambda = 1.5406$ Å) that is equipped with a linear position-sensitive detector (Delta 2 $\theta = 6.5-7^{\circ}$ simultaneous; scan range overall = 2–130°) from STOE & CIE and an Image Plate Detector (scan range overall = 0–127°) and a PANalytical X'Pert Pro MPD reflection powder diffraction system with Cu- K_{α} radiation ($\lambda =$ 154.0598 pm) equipped with a PIXcel semiconductor detector from PANanlytical. Crystallographic data and structure refinement results are summarized in Table 2.

Temperature dependent XRPD measurements were performed with a high temperature chamber HTK 1200N with He atmosphere from Anton Paar (heating rate 3 °C-min^{-1} in a temperature rate from 25–300 °C).

Magnetic Measurements: All magnetic measurements were performed with a Physical Property Measuring System (PPMS) from Quantum Design, which is equipped with a 9 T magnet. The data were corrected for Core diamagnetism using Pascal constants.^[58]

Supporting Information (see footnote on the first page of this article): Calculated XRPD patterns, Ortep plots, tables with bond lengths and angles, TG curves, temperature dependent XRPD measurements, and selected magnetic curves.

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Pages: 9

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Pages: 9

Transition Metal Thiocyanato Coordination Compounds

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Synthesis, Structures, and Properties of Transition Metal Thiocyanato Coordination Compounds with 4-(4-Chlorobenzyl) pyridine as Ligand

