Synthesis, Crystal Structures, and Thermal and Spectroscopic Properties of Thiocyanato Coordination Compounds with 3-Acetylpyridine as a Ligand

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

The reaction of transition metal thiocyanates with 3-acetylpyridine (3-AcPy) leads to the formation of compounds of compositions $M$(NCS)$_2$(3-AcPy)$_4$ ($M_1; M = Mn, Fe, Ni$) and $M$(NCS)$_2$(3-AcPy)$_2$(H$_2$O)$_2$ ($M_2; M = Mn, Fe, Ni$). Thermogravimetric investigations show that in the first step some of these compounds transform into the new coordination polymers $M$(NCS)$_2$(3-AcPy)$_2$ ($M_3$ with $M = Mn, Fe$ and Ni), that decompose into the new compounds $M$(NCS)$_2$(3-AcPy) ($M_4$ with $M = Mn$ and Ni) in the second step. Unfortunately, the powder patterns of compounds $M_3$ and $M_4$ cannot be indexed, and there are strong indications that these compounds are contaminated with a small amount of the precursor or unknown crystalline phases. IR spectroscopic investigations indicate that in compounds $M_3$ the metal cations are linked by $\mu$-1,3-bridging thiocyanato anions into 1D or 2D coordination polymers that are further linked by the 3-AcPy ligands in compounds $M_4$.

Key words: Synthesis, Thiocyanato Coordination Compounds, Crystal Structures, Thermoanalytical Measurements, IR Spectroscopy

Introduction

Investigations on the synthesis, structures and properties of transition metal coordination polymers is still an important field in inorganic chemistry [1 – 12]. One interesting aspect of this class of compounds is that their network dimensionality and their network topology can be influenced to some extend based on some basic knowledge on the coordination properties of the metal cations, the anionic ligands and the neutral co-ligands [1 – 8]. In most cases such compounds are prepared in solution, in which different species might exist in equilibria and therefore, on crystallization mixtures of different compounds are sometimes obtained [13]. In some cases, these problems can be overcome if typical solid-state methods are used, and some selected examples are given in the reference list [14 – 19].

In this context we have reported on thermal decomposition reactions for the preparation of new copper(I) halide coordination polymers [20 – 22]. Later on we became interested in the synthesis of magnetic materials based on transition metal thiocyanates. For such compounds interesting properties like, e.g., spin crossover or cooperative magnetic phenomena have been reported [23 – 41]. The latter are especially observed in cases, where the metal cations are linked by $\mu$-1,3-bridging ligands. However, in contrast to compounds in which the thiocyanato anions are only terminally bonded, the corresponding species with bridging anionic ligands are less stable and thus, sometimes more difficult to prepare. This is the reason why we have developed an alternative approach that is based on the thermal decomposition of precursors with terminally bonded thio- and selenocyanato anions [42 – 45]. Within this project we have reported a number of compounds that show different magnetic properties including a slow relaxation of the magnetization [46 – 55]. Unfortunately, upon thermal decomposition usually crystalline powders are obtained that hinder a struc-
ture determination. First information on the coordination mode of the anionic ligands can be retrieved from IR spectroscopy, but – because these values are based on relatively old work – in some cases no definite decision can be made [56 – 58]. This is one of the reasons why we are also interested in the spectroscopic properties of such compounds. However, structural information can also be obtained by preparing the corresponding cadmium compounds. In several cases they are isotypic to the paramagnetic compounds, which allows the determination of their structures using Rietveld refinements [59 – 61].

In the course of our project we have also investigated the influence of the neutral N-donor co-ligand on the thermal, spectroscopic and magnetic properties of such compounds, and in this contribution we report on new coordination compounds based on Mn, Fe and Ni thiocyanates with 3-acetylpyridine as a co-ligand.

Results and Discussion

Synthetic investigations

Different molar ratios of $M$(NCS)$_2$ ($M$ = Mn, Fe, Ni) and 3-acetylpyridine (3-Acpy) were stirred in water, ethanol, methanol, and acetonitrile, and the resulting crystalline powders were investigated by powder X-ray diffraction. These experiments indicated the presence of three different crystalline phases, and elemental analyses revealed that the compositions of these phases are $M$(NCS)$_2$(3-Acpy)$_4$ ($M$ = Mn, Fe, Ni) (M1) and $M$(NCS)$_2$(3-Acpy)$_2$(H$_2$O)$_2$ ($M$ = Mn, Fe, Ni) (M2). IR-spectroscopic measurements suggested that the thiocyanato anions are terminally bonded. The compounds Mn1 and Fe1 are isotypic, whereas Ni1 crystallizes in a different modification, and according to PXRD investigations all compounds M2 are isotypic.

Crystallization experiments led to single crystals of Mn1, Fe1, Mn2, Fe2, and Ni2, which were investigated by single-crystal X-ray diffraction (see below). Based on these results the powder X-ray patterns were calculated and compared with the experimental patterns (Figs. 1 and 2). The results confirmed that the hydrates M2 ($M$ = Mn, Fe, Ni) are isotypic, Mn1 and Fe1 are also isotypic, whereas Ni1 crystallizes in a different modification and that all compounds were obtained as pure phases (Figs. 1 and 2). The fact that the structures of such coordination compounds with Mn and Fe are isotypic, whereas those with Ni are different has also been found in related compounds with different co-ligands [55].

Crystal structures of Fe1 and Ni1

Fe(NCS)$_2$(3-acetylpyridine)$_4$ (Fe1) and Mn(NCS)$_2$(3-acetylpyridine)$_4$ (Mn1) crystallize in the triclinic centrosymmetric space group $P\overline{1}$ with two formula
units in the unit cell. The asymmetric unit consists of two crystallographically independent metal cations which are located on centers of inversion and of two thiocyanato anions and four 3-Acpy ligands the atoms of which occupy general positions (Fig. 3).

Ni(NCS)$_2$(3-acetylpyridine)$_4$ (Ni1) crystallizes in the monoclinic space group $C_2/c$ with 8 formula units in the unit cell. The asymmetric unit consists of two crystallographically independent nickel cations each of them located on a twofold rotation axis, as well as of four thiocyanato anions and four 3-Acpy ligands with atoms on general positions. In the crystal structures of all compounds the metal cations are coordinated by two terminal $N$-bonded thiocyanato anions and four 3-Acpy ligands with a slightly distorted octahedral geometry.

Bond lengths and angles in the two independent complexes of Fe1 are comparable but large differences are found in the conformation of the 3-Acpy ligands (Table 1, Fig. 4). As expected the $M$–N distances to the thiocyanato anions are shorter than those to the neutral co-ligands, and all these values are shorter for Ni1 compared to Mn1 (Table 1).

**Crystal structures of Mn2, Fe2 and Ni2**

The compounds $M$(NCS)$_2$(3-acetylpyridine)$_2$ ($M$: Mn, Fe, Ni) are isotypic and

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**Table 1.** Selected bond lengths (Å) and angles (deg) for Fe1 and Ni1. Symmetry codes: A: $-x$, $-y+1$, $-z+1$, B: $-x+1$, $-y$, $-z$.

<table>
<thead>
<tr>
<th></th>
<th>Fe1</th>
<th>Ni1</th>
<th>Fe1</th>
<th>Ni1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$(1)–N(1)</td>
<td>2.0849(14)</td>
<td>2.0452(17)</td>
<td>N(1)–M(1)–N(21A)</td>
<td>89.44(5)</td>
</tr>
<tr>
<td>$M$(2)–N(2)</td>
<td>2.0697(14)</td>
<td>2.042(2)</td>
<td>N(2)–M(2)–N(31)</td>
<td>90.78(5)</td>
</tr>
<tr>
<td>$M$(1)–N(11)</td>
<td>2.2372(14)</td>
<td>2.129(16)</td>
<td>N(11)–M(1)–N(21)</td>
<td>93.54(5)</td>
</tr>
<tr>
<td>$M$(1)–N(21)</td>
<td>2.2578(12)</td>
<td>2.1317(16)</td>
<td>N(11)–M(1)–N(21A)</td>
<td>86.46(5)</td>
</tr>
<tr>
<td>$M$(2)–N(31)</td>
<td>2.2293(13)</td>
<td>2.1265(18)</td>
<td>N(2)–M(2)–N(31B)</td>
<td>89.22(5)</td>
</tr>
<tr>
<td>$M$(2)–N(41)</td>
<td>2.3019(13)</td>
<td>2.1438(17)</td>
<td>N(2)–M(2)–N(41B)</td>
<td>91.18(5)</td>
</tr>
<tr>
<td>N(1)–M(1)–N(11)</td>
<td>91.10(5)</td>
<td>91.52(7)</td>
<td>N(2)–M(2)–N(41)</td>
<td>89.82(5)</td>
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<tr>
<td>N(1)–M(1)–N(11A)</td>
<td>88.90(5)</td>
<td>89.48(7)</td>
<td>N(31)–M(2)–N(41B)</td>
<td>87.31(5)</td>
</tr>
<tr>
<td>N(1)–M(1)–N(21)</td>
<td>90.36(5)</td>
<td>88.69(7)</td>
<td>N(31)–M(2)–N(41)</td>
<td>92.69(5)</td>
</tr>
</tbody>
</table>
crystallize in the triclinic space group $P\overline{1}$ with one formula unit in the unit cell. The asymmetric unit consists of one metal cation, which is located on a center of inversion and one thiocyanato anion, one 3-Acpy ligand and one water molecule in general positions (Fig. 5). The metal cations are coordinated by two terminally bonded thiocyanato anions, two $N$-bonded 3-Acpy ligands and two water molecules within a slightly distorted octahedral geometry (Table 2). As expected, the $M$–$N$ and $M$–$O$ bond lengths decrease with decreasing cation radii, and the $M$–$N$ bond lengths to the negatively charged 3-Acpy ligands are significantly shorter than those to the neutral 3-Acpy ligands.

Table 2. Selected bond lengths (Å) and angles (deg) for Mn2, Fe2 and Ni2. Symmetry code: $A: -x, -y, -z$.

<table>
<thead>
<tr>
<th></th>
<th>Mn2</th>
<th>Fe2</th>
<th>Ni2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$(1)–N(1)</td>
<td>2.1753(15)</td>
<td>2.1222(13)</td>
<td>2.0456(14)</td>
</tr>
<tr>
<td>$M$(1)–N(11)</td>
<td>2.3135(14)</td>
<td>2.2403(13)</td>
<td>2.1293(15)</td>
</tr>
<tr>
<td>$M$(1)–O(1)</td>
<td>2.1922(13)</td>
<td>2.1217(11)</td>
<td>2.0845(12)</td>
</tr>
<tr>
<td>N(1)–$M$(1)–O(1)</td>
<td>92.11(6)</td>
<td>91.54(5)</td>
<td>90.91(6)</td>
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<tr>
<td>N(1)–$M$(1)–N(11)</td>
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<td>91.64(5)</td>
<td>91.05(6)</td>
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<tr>
<td>N(1)–$M$(1)–N(11A)</td>
<td>88.54(6)</td>
<td>88.36(5)</td>
<td>88.95(6)</td>
</tr>
</tbody>
</table>

In the crystal structure the individual complexes are linked by intermolecular O–H···O hydrogen bonds into chains that elongate in the direction of the crystallographic $c$ axis (Fig. 6). These chains are further linked by intermolecular O–H···S hydrogen bonds into layers that are located in the $a$-$c$ plane (Fig. 6). The intermolecular O···O and O···S distances of 2.740 and 3.226 Å and the O–H···O and O–H···S angles of 172.4° and 167.4°, respectively, indicate strong interactions.

Thermoanalytical investigations on compounds M1 and M2

To investigate if the 3-Acpy-rich compounds are suitable precursors for the preparation of new compounds with bridging thiocyanato anions the thermal properties were investigated using simultaneous differential thermoanalysis and thermogravimetry. Upon heating compounds Mn1 and Fe1 show a continuous mass loss up to 450 °C, which clearly proves that no intermediate compounds can be obtained. By contrast, Ni1 shows three distinct mass losses, indicating that the 3-Acpy ligands are stepwise removed. The experimental mass loss of $\Delta m_{\text{exp}} = 36\%$ in the first and $\Delta m_{\text{exp}} = 35\%$ in the second TG step is in rough agreement with the loss of two 3-Acpy ligands in each step ($\Delta m_{\text{calc.}} = 37\%$) (Fig. 7).
Fig. 7. TG curves for compounds Mn₁, Fe₁ and Ni₁ (top), and for compounds Mn₂, Fe₂ and Ni₂ (bottom).

Upon heating of compounds M₂ all compounds show three mass steps up to 450 °C, most of them are well resolved. The experimental mass loss of the first step is in good agreement with the one calculated for the removal of two water molecules (Table 3). On further heating compounds Mn₂ and Ni₂ show a second mass loss of ∆mₜₐₚ = 24% for Mn₂ and ∆mₜₐₚ = 26% for Ni₂, which are in reasonable agreement with the removal of one 3-Acpy ligand (Table 3). For Fe₂ the second step is not well resolved. Finally, on further heating the remaining 3-Acpy ligands are removed, and the transition metal thiocyanates are formed.

To further characterize the intermediates formed upon thermal decomposition additional TG measurements were performed and stopped after the respective mass loss. Afterwards the residues were investigated by elemental analysis and powder X-ray diffraction.

Elemental analysis of the product formed in the first TG step of Ni₁ yields a composition of Ni(NCS)₂(3-Acpy)₂ (Ni₃), and PXRD investigations show a completely different pattern, in which a small amount of the precursor seems to be present (Fig. 8 A). Similar investigations on Mn₂, Fe₂ and Ni₂ always lead to the formation of intermediates of the composition [M(NCS)₂(3-Acpy)₂]ₙ (M₄) after the first TG step. Comparison of their experimental XRPD patterns indicates that Ni₃ and Fe₃ are isotypic but both of them contain reflections of an unknown crystalline phase (Fig. 8). Therefore, all attempts to index these powder patterns failed.

If the experimental pattern of Mn₃ is compared with that calculated for the corresponding Cd compound Cd(NCS)₂(3-Acpy)₂ reported recently, it becomes obvious that these compounds are isotypic (Fig. 8) [62]. However, an additional peak of an unknown phase proves that also this compound is not obtained as a pure crystalline phase. We carried out several different TG measurements using different heating rates and we also tried to obtain pure samples by isothermal annealing but all attempts remained unsuccessful. Therefore, the magnetic properties of these compounds were not investigated.

Additional TG measurements of compounds Mn₂ and Ni₂ were also performed and stopped after the second mass loss, in which compounds of the composition M(NCS)₂(3-Acpy) (M = Mn and Ni) (M₄) were obtained. The XRPD patterns of Mn₄ and Ni₄ are completely different, which proves that compounds with different structures are obtained (Fig. 9). Unfortunately, none of these patterns could be indexed, indicating the obtained samples are not phase-pure. Surprisingly, none of these PXRD patterns is similar to that of [Cd(NCS)₂(3-Acpy)]ₙ reported recently [62].

<table>
<thead>
<tr>
<th>Table 3. Experimental and calculated mass losses for compounds M₂.</th>
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<td><strong>First step:</strong> Mn₂  Fe₂  Ni₂  <strong>Second step:</strong> Mn₂  Ni₂</td>
</tr>
<tr>
<td>Calculated (%)</td>
</tr>
<tr>
<td>Experimental (%)</td>
</tr>
</tbody>
</table>
IR spectroscopic investigations

In order to get information on the coordination mode in the 3-Acpy-deficient phases IR spectroscopic investigations were performed. For comparison the precursors M1 and M2 were also measured. For compounds in which the thiocyanato anions are terminally N-bonded the asymmetric CN stretching vibration is located at about 2050 cm$^{-1}$, whereas it is shifted to about 2100 cm$^{-1}$ in compounds, in which they act as µ-1,3-bridging ligands [56, 58].

For compounds M1 the CN stretching vibrations are detected between 2041 and 2078 cm$^{-1}$, which is in agreement with terminally N-bonded anions already found in the crystal structures (Table 4). In compounds M2 this vibration is significantly shifted to values between 2067 and 2092 cm$^{-1}$. This shows that the coordinating water molecules lead to a shift of the CN vibration to higher values. However, in Mn3 the CN stretching vibration is shifted above 2100 cm$^{-1}$, which clearly proves that the metal cations are linked by µ-1,3-bridging thiocyanato anions. This has already been found in Cd(NCS)$_2$(3-Acpy)$_2$, which is isotypic to Mn3, and in which the metal cations are linked into chains by pairs of thiocyanato anions [62]. Similar values are also found for Fe3 and Ni3 and thus, these compounds should also contain bridging anionic ligands. Moreover, the CO stretching vibration of the acetyl O atom is similar to that in compounds M1 and M2, which indicates that the 3-Acpy ligand is still terminally bonded.

For compounds M4 the CN stretching vibrations are observed at about 2100 cm$^{-1}$ and above, which again indicates the presence of µ-1,3-bridging thiocyanato anions (Table 4). In Mn4 the CO stretching vibration is

Table 4. Values of the $\nu_{\text{as}}$(CN) stretching vibration of the thiocyanato anion and of the $\nu_{\text{as}}$(CO) stretching vibration of the acetyl group of the 3-Acpy ligand for compounds M1, M2, M3, and M4 as well as for related Cd compounds taken from the literature [62].

<table>
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<th>Compound</th>
<th>$\nu_{\text{as}}$(CN)</th>
<th>$\nu_{\text{as}}$(CO)</th>
<th>Compound</th>
<th>$\nu_{\text{as}}$(CN)</th>
<th>$\nu_{\text{as}}$(CO)</th>
</tr>
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<tbody>
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<td>Mn1</td>
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<td>1686</td>
<td>Mn2</td>
<td>2067</td>
<td>1678</td>
</tr>
<tr>
<td>Fe1</td>
<td>2044</td>
<td>1686</td>
<td>Fe2</td>
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<td>1678</td>
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<tr>
<td>Ni1</td>
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<td>Ni2</td>
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<td>Mn3</td>
<td>2086</td>
<td>1694</td>
<td>Mn4</td>
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<td>1660</td>
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<td>Fe3</td>
<td>2096</td>
<td>1694</td>
<td>Ni4</td>
<td>2142/2108</td>
<td>1688</td>
</tr>
<tr>
<td>Ni3</td>
<td>2114</td>
<td>1691</td>
<td>Cd(NCS)$_2$(3-Acpy)$_2$</td>
<td>2043</td>
<td>1684</td>
</tr>
<tr>
<td>Cd(NCS)$_2$(3-Acpy)$_2$</td>
<td>2092</td>
<td>1694</td>
<td>Cd(NCS)$_2$(3-Acpy)</td>
<td>2096</td>
<td>1671</td>
</tr>
</tbody>
</table>
shifted to 1660 cm\(^{-1}\), suggesting that this ligand also acts as a bridging ligand. This is supported by IR measurement on the corresponding Cd compound, which shows a similar value and in which the metal cations are linked by both, the thiocyanato anions and the 3-Acpy ligands (Table 4) \cite{62}.

The CO stretching vibration of Ni\textit{4} is is similar to that in compounds M3 and M4.

This strongly indicates that in this compound chains are present, in which \(\mu\)-1,3(N,S) bridging thiocyanato anions and \(\mu\)-1,5(N,O) bridging Acpy ligands are present as already observed in the crystal structure of [Cd(NCS)\(_2\)(pyridine)]\(_n\) \cite{63}.

### Conclusion

In the present study new coordination compounds obtained from transition metal thiocyanates and 3-acetylpyridine were prepared and investigated. In solution compounds with two different compositions were obtained, in which the metal cations are only coordinated by terminal N-bonded thiocyanato anions. Upon heating these compounds are transformed into 3-Acpy-deficient phases in the first step, in which the metal cations are linked by the 3-Acpy ligands into 1D or 2D coordination polymers. On further heating additional 3-Acpy ligands are removed leading to compounds with a more condensed coordination network. Unfortunately, none of these new compounds could be obtained in pure form and therefore, no magnetic measurements were performed. This is not unusual for this class of compounds, which upon thermal decomposition frequently form compounds of different stoichiometry including different polymorphic modifications.

### Experimental Section

#### Materials

MnSO\(_4\) \(\cdot\) 6H\(_2\)O, Ni(SO\(_4\))\(_2\) \(\cdot\) 6H\(_2\)O, KCNS and FeCl\(_3\) \(\cdot\) 4H\(_2\)O were obtained from Merck, Ba(NCS)\(_2\):3H\(_2\)O and 3-acetylpyridine were obtained from Alfa Aesar. The chemicals were used without further purification. Mn(NCS)\(_2\) was prepared by the reaction of Ba(NCS)\(_2\):3H\(_2\)O (17.9 g, 58.44 mmol) and MnSO\(_4\) \(\cdot\) 6H\(_2\)O (9.9 g, 58.44 mmol) in water (400 mL). The colorless precipitate of BaSO\(_4\) was filtered off, and the water was removed from the filtrate using a rotary evaporator. The homogeneity of the product was proven by powder X-ray diffraction and elemental analysis. Ni(NCS)\(_2\) was prepared by the reaction of Ba(NCS)\(_2\):3H\(_2\)O (17.5 g, 57 mmol) and NiSO\(_4\) \(\cdot\) 6H\(_2\)O (15.0 g, 57 mmol) in water (400 mL). The colorless precipitate of BaSO\(_4\) was filtered off, and the water was removed from the filtrate using a rotary evaporator. The homogeneity of the product was proven by powder X-ray diffraction and elemental analysis

#### Synthesis of Mn(NCS)\(_2\)(3-acetylpyridine)\(_4\) (Mn1)

A colorless crystalline powder was obtained by stirring 60.8 mg of Mn(NCS)\(_2\) (0.25 mmol) in 436.5 \(\mu\)L of 3-Acpy (4.00 mmol) for 3 days. – C\(_{10}\)H\(_{38}\)MnN\(_6\)O\(_4\)S\(_2\) (655.66 g mol\(^{-1}\)): calcd. C 55.0, H 4.3, N 12.8, S 9.8; found C 54.8, H 4.3, N 12.7, S 9.7. – IR (ATR): \(\nu_{\text{max}} = 3100\) (w), 3073 (w), 3007 (w), 2916 (w), 2844 (s), 1868 (s), 1747 (w), 1420 (m), 1358 (m), 1033 (m), 958 (m), 808 (m), 697 (s), 591 (s) cm\(^{-1}\).

#### Synthesis of Fe(NCS)\(_2\)(3-acetylpyridine)\(_4\) (Fe1)

A yellow crystalline powder was obtained by stirring 49.7 mg of FeCl\(_3\) \(\cdot\) 4H\(_2\)O (0.25 mmol), 48.6 mg of KCNS (0.50 mmol) and 272.8 \(\mu\)L of 3-Acpy (2.50 mmol) in 1.5 mL of H\(_2\)O. The precipitate was filtered off, and the volume of the filtrate was reduced by slow evaporation. After a few days single crystals suitable for X-ray diffraction were obtained. – C\(_{10}\)H\(_{38}\)FeN\(_6\)O\(_4\)S\(_2\) (656.57 g mol\(^{-1}\)): calcd. C 54.9, H 4.3, N 12.8, S 9.8; found C 54.3, H 4.1, N 12.1, S 9.3. – IR (ATR): \(\nu_{\text{max}} = 3103\) (w), 3079 (w), 3007 (w), 2916 (w), 2041 (s), 1868 (s), 1744 (w), 1419 (m), 1358 (m), 1267 (s), 1194 (m), 1034 (m), 1014 (w), 958 (m), 808 (m), 697 (s), 593 (m) cm\(^{-1}\).

#### Synthesis of Ni(NCS)\(_2\)(3-acetylpyridine)\(_4\) (Ni1)

A violet crystalline powder was obtained by stirring 43.7 mg of Ni(NCS)\(_2\) (0.25 mmol) and 163.2 \(\mu\)L of 3-Acpy (1.50 mmol) in 1.5 mL of H\(_2\)O. The precipitate was filtered off, and the volume of the filtrate was reduced by slow evaporation. After three days single crystals suitable for X-ray diffraction were obtained. – C\(_{10}\)H\(_{38}\)NiN\(_6\)O\(_4\)S\(_2\) (659.41 g mol\(^{-1}\)): calcd. C 54.6, H 4.3, N 12.7, S 9.7; found C 54.5, H 4.1, N 12.7, S 9.6. – IR (ATR): \(\nu_{\text{max}} = 3106\) (w), 3081 (w), 3007 (w), 2997 (w), 2916 (w), 2078 (s), 1694 (s), 1599 (m), 1576 (m), 1480 (w), 1426 (m), 1362 (m), 1272 (s), 1195 (m), 1100 (m), 1043 (m), 958 (m), 817 (m), 700 (s), 645 (m), 595 (s) cm\(^{-1}\).

#### Synthesis of Mn(NCS)\(_2\)(3-acetylpyridine)\(_2\)(H\(_2\)O)\(_2\) (Mn2)

A colorless crystalline powder was obtained by stirring 60.8 mg of Mn(NCS)\(_2\) (0.25 mmol) and 54.6 \(\mu\)L of 3-Acpy (0.50 mmol) in 1.5 mL of H\(_2\)O. Single crystals suitable for single-crystal X-ray diffraction were prepared by slow evaporation of the solvent from the filtrate. – C\(_{16}\)H\(_{18}\)MnN\(_6\)O\(_4\)S\(_2\) (449.41 g mol\(^{-1}\)): calcd. C 42.8, H 4.0, N 12.5, S 14.3; found C 42.7, H 4.0, N 12.5, S 14.5. –
IR (ATR): $v_{\text{max}} = 3313$ (b), 3220 (b), 2857 (w), 2067 (s), 1678 (s), 1591 (s), 1557 (m), 1472 (m), 1425 (m), 1357 (m), 1277 (s), 1194 (m), 1128 (m), 1039 (m), 960 (s), 811 (s), 695 (s), 639 (s), 600 (s), 469 (s) cm$^{-1}$.

**Synthesis of Fe(NCS)$_2$(3-acetylpyridine)$_2$(H$_2$O)$_2$ (Fe2)**

A yellow crystalline powder was obtained by stirring of 49.7 mg of FeCl$_3$·4H$_2$O (0.25 mmol), 48.6 mg of KNCS (0.50 mmol) and 54.6 µL of 3-Acyc (0.50 mmol) in 1.5 mL of H$_2$O. Single crystals suitable for single-crystal X-ray diffraction were prepared by slow evaporation of the solvent from the filtrate. – C$_{16}$H$_{18}$Ni$_2$NO$_4$S$_2$ (453.17 g mol$^{-1}$): calcd. C 42.4, H 4.0, N 12.4, S 14.2; found C 42.7, H 4.0, N 12.4, S 14.2. – IR (ATR): $v_{\text{max}} = 3217$ (b), 2861 (w), 2077 (s), 1678 (s), 1592 (s), 1473 (w), 1426 (m), 1357 (m), 1280 (s), 1194 (w), 1131 (w), 1097 (w), 1042 (m), 961 (m), 812 (s), 765 (m), 694 (s), 640 (s), 601 (m), 564 (m), 471 (m) cm$^{-1}$.

**Synthesis of Ni(NCS)$_2$(3-acetylpyridine)$_2$(H$_2$O)$_2$ (Ni2)**

A light-blue crystalline powder was obtained by stirring 43.7 mg of Ni(NCS)$_2$ (0.25 mmol) and 54.6 µL of 3-Acyc (0.50 mmol) in 1.5 mL of H$_2$O. Single crystals suitable for single-crystal X-ray diffraction were prepared under similar conditions without stirring. – C$_{16}$H$_{18}$Ni$_2$NO$_4$S$_2$ (453.17 g mol$^{-1}$): calcd. C 42.4, H 4.0, N 12.4, S 14.2; found C 42.7, H 4.0, N 12.4, S 14.2. – IR (ATR): $v_{\text{max}} = 3217$ (b), 2861 (w), 2077 (s), 1678 (s), 1592 (s), 1473 (w), 1426 (m), 1357 (m), 1280 (s), 1194 (w), 1131 (w), 1097 (w), 1042 (m), 961 (m), 812 (s), 765 (m), 694 (s), 640 (s), 601 (m), 564 (m), 471 (m) cm$^{-1}$.

For the experiments performed using a Stoe Transmission Powder Diffraction System (STADI P. Stoe & Cie, Darmstadt, Germany) with CuK$_\alpha$ radiation ($\lambda = 1.540598$ pm) equipped with a linear position-sensitive detector ($\delta 2\theta = 6.5–7.0$) simultaneous; scan range overall = 2 – 130°.

**Differential thermal analysis and thermogravimetry**

The DTA-TG measurements were performed in nitrogen atmosphere (purity: 5.0) in Al$_2$O$_3$ crucibles using a STA-409CD thermobalance (Netzsch, Selb, Germany). 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.

Spectroscopy

IR spectra were recorded on a Bruker Alpha IR spectrometer equipped with a Platinum ATR QuickSnap™ sampling module between 4000 – 375 cm⁻¹.

Elemental analysis

CHNS analyses were performed using an EURO EA elemental analyzer (Euro Vector Instruments).

Single-crystal structure analyses

Data collection was performed with an imaging plate diffraction system (IPDS-2 for Ni₁, Mn₂ and Ni₂; IPDS-1 for Fe₁) from Stoe & Cie with MoKα radiation. The data were corrected for absorption using X-RED and X-SHAPE from Stoe [64, 65]. Structure solutions were performed with Direct Methods using SHELXS-97, and structure refinements were done against F² using SHELXL-97 [66]. 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 with Uiso(H) = 1.2 Ueq(C) (1.5 for methyl H atoms) using a riding model. The O–H H atoms were located in the Fourier difference map, their bond lengths were set to ideal values, and they were refined isotropically with Ueq(H) = 1.5 · Ueq(O) using a riding model. Details of the structure determination are given in Table 5.

CCDC 1021212 (Fe₁), 1021215 (Ni₁), 1021213 (Mn₂), 1021211 (Fe₂) and 1021214 (Ni₂) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[64] X-RED (version 1.11), Program for Data Reduction and Absorption Correction, Stoe & Cie GmbH, Darmstadt (Germany) 1998.