Synthesis, crystal structure and thermal properties of the dinuclear complex \(\text{bis}(\mu-4\text{-methylpyridine } N\text{-oxide}-\kappa^2\text{O}:\text{O})\text{bis}[(\text{methanol}-\kappa\text{O})(4\text{-methylpyridine } N\text{-oxide}-\kappa\text{O})\text{bis}(\text{thiocyanato}-\kappa\text{N})\text{cobalt(II)}]\)

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Reaction of Co(NCS)\(_2\) with 4-methylpyridine N-oxide in methanol leads to the formation of crystals of the title compound, [Co\(_2\)(NCS)\(_4\)(C\(_6\)H\(_7\)NO)\(_4\)(CH\(_4\)O)\(_2\)] or Co\(_2\)(NCS)\(_4\)(4-methylpyridine N-oxide)\(_4\)(methanol)\(_2\). The asymmetric unit consist of one Co\(^{II}\) cation, two thiocyanate anions, two 4-methylpyridine N-oxide coligands and one methanol molecule in general positions. The H atoms of one of the methyl groups are disordered and were refined using a split model. The Co\(^{II}\) cations octahedrally coordinate two terminal N-bonded thiocyanate anions, three 4-methylpyridine N-oxide coligands and one methanol molecule. Each two Co\(^{II}\) cations are linked by pairs of \(\mu\)-1,1(\(\text{O},\text{O}\))-bridging 4-methylpyridine N-oxide coligands into dinuclear units that are located on centers of inversion. Powder X-ray diffraction (PXRD) investigations prove that the title compound is contaminated with a small amount of Co(NCS)\(_2\)(4-methylpyridine N-oxide)\(_3\). Thermogravimetric investigations reveal that the methanol molecules are removed in the beginning, leading to a compound with the composition Co(NCS)\(_2\)(4-methylpyridine N-oxide), which has been reported in the literature and which is of poor crystallinity.

1. Chemical context

The synthesis of new coordination compounds and polymers is still an important topic in inorganic chemistry because of their versatile structural behavior and their varied physical properties. One important part of these investigations includes the synthesis of compounds with paramagnetic metal cations to prepare materials with promising magnetic behavior. In several cases, the cations are linked by small-sized anionic ligands and in this regard, compounds based on thiocyanate anions are of interest because this anionic ligand can mediate magnetic exchange (Palion-Gazda et al., 2015; Mekumembata et al., 2018; Shurdha et al., 2013; Rams et al., 2017, 2020). Compared to cyanides or azides, this anionic ligand shows many more coordination modes and consequently a more pronounced structural variability, leading to metal thiocyanate substructures that consist of linear and corrugated chains or layered structures of different topology (Wöhlert et al., 2013; Werner et al., 2015; Neumann et al. 2018; Böhme et al., 2020, 2022). However, most paramagnetic metal cations are not very chalcophilic and therefore, the N-terminal coordination mode frequently dominates over the various bridging modes.

However, in recent work we used pyridine N-oxide derivatives as coligands that can be terminally O-bonded or that can bridge two metal cations in the \(\mu\)-1,1(\(O,O\)) bridging mode, leading to an enhanced structural variability. In the beginning, we focused on Co(NCS)\(_2\) compounds because, among other things, this cation is of special interest in terms of its magnetic
properties (Murrie, 2010; Mautner et al., 2018a,b; Rams et al., 2017, 2020). In the course of this project, we became interested in 4-methylpyridine N-oxide as a coligand. With this ligand, two compounds with the composition Co(NCS)$_2$(4-methylpyridine N-oxide) (Refcode: MEOKOJ, Zhang et al., 2006a) and Co(NCS)$_2$(4-methylpyridine N-oxide)(methanol) (Refcode: REKBUF; Shi et al., 2006a) have already been reported in the literature. In the first compound, the Co$^{II}$ cations octahedrally coordinate two N- and two S-bonding thiocyanate anions and two $\mu$-1,1(O,O)-bridging 4-methylpyridine N-oxide ligands, and are connected by pairs of bridging thiocyanate anions into corrugated chains. These chains are further linked into layers by $\mu$-1,1(O,O)-bridging 4-methylpyridine N-oxide ligands (Zhang et al., 2006a). In the second compound, the Co$^{II}$ cations sixfold coordinate two bridging and one terminal thiocyanate anion, two O atoms of two bridging 4-methylpyridine N-oxide ligands and one methanol molecule (Refcode: REKBUF; Shi et al., 2006a). The Co cations are linked by alternating pairs of $\mu$-1,3-bridging thiocyanate anions and $\mu$-1,1(O,O)-bridging 4-methylpyridine N-oxide ligands into chains.

In our own synthetic work, we have added two additional compounds with the composition Co(NCS)$_2$(4-methylpyridine N-oxide)$_3$ and Co(NCS)$_2$(4-methylpyridine N-oxide)$_4$, that form discrete complexes with two different metal coordinations ( Näther & Jess, 2024). In the latter compound, an octahedral coordination is observed, whereas the former shows a trigonal–bipyramidal coordination, which is relatively rare for Co$^{II}$ cations. Surprisingly, this compound can easily be prepared, whereas only a few crystals of the complex with a sixfold coordination were accidentally obtained. Much effort was made to prepare Co(NCS)$_2$(4-methylpyridine N-oxide)$_4$ but without any success. In the course of these investigations, we always found additional reflections in some of the powder patterns of products prepared in methanol that do not correspond to the discrete complexes or to the coordination polymers mentioned above. Therefore, an additional crystalline phase based on Co(NCS)$_2$ and 4-methylpyridine N-oxide must exist. Based on these findings the synthesis conditions were varied, leading to the formation of a new crystalline phase that was characterized by single-crystal X-ray diffraction. This proves that a dinuclear complex with methanol was obtained, that is somehow structurally related to Co(NCS)$_2$(4-methylpyridine N-oxide)(methanol), which has already been reported in the literature (refcode REKBUF; Shi et al., 2006a).

2. Structural commentary

The asymmetric unit of the title compound, Co$_2$(NCS)$_4$(4-methylpyridine N-oxide)$_4$(methanol)$_2$, consists of one cobalt cation, two thiocyanate anions, one methanol molecule and two 4-methylpyridine N-oxide ligands, all of them located in general positions. The Co cations sixfold coordinate two terminal N-bonding thiocyanate anions, one methanol molecule and one terminal as well as two $\mu$-1,1(O,O)-bridging 4-methylpyridine N-oxide ligands (Fig. 1). Bond lengths and angles are similar to those in related compounds (Shi et al., 2006a) and show that the octahedra are slightly distorted.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>N–Co–O (Å)</th>
<th>O–Co–O (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co1–N1</td>
<td>2.0525(18)</td>
<td>Co1–O21</td>
</tr>
<tr>
<td>Co1–N2</td>
<td>2.0840(18)</td>
<td>Co1–O21'</td>
</tr>
<tr>
<td>Co1–O11</td>
<td>2.0543(16)</td>
<td>Co1–O31</td>
</tr>
<tr>
<td>N1–Co1–N2</td>
<td>96.79(7)</td>
<td>O11–Co1–N2</td>
</tr>
<tr>
<td>N1–Co1–O11</td>
<td>96.07(7)</td>
<td>O11–Co1–O21</td>
</tr>
<tr>
<td>N1–Co1–O21'</td>
<td>94.26(7)</td>
<td>O11–Co1–O21'</td>
</tr>
<tr>
<td>N1–Co1–O21</td>
<td>166.79(7)</td>
<td>O21–Co1–O31</td>
</tr>
<tr>
<td>N1–Co1–O31</td>
<td>95.14(7)</td>
<td>O21–Co1–O31</td>
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<tr>
<td>N2–Co1–O21'</td>
<td>167.69(7)</td>
<td>O21'–Co1–O31</td>
</tr>
<tr>
<td>N2–Co1–O21</td>
<td>96.37(7)</td>
<td>Co1–O21–O31</td>
</tr>
<tr>
<td>N2–Co1–O31</td>
<td>86.85(7)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry code: (i) $-x+1,-y,-z+1$.  

Figure 1

The molecular structure of the title compound with atom labelling and displacement ellipsoids drawn at the 50% probability level. The disorder of the H atoms of one of the methyl groups is shown with full and open bonds. [Symmetry code: (i) $-x+1,-y,-z+1$.]
Figure 2
Crystal structure of the title compound in a view along the crystallographic a axis. Intermolecular C—H···S and O—H···O hydrogen bonding is shown as dashed lines

(Table 1). Each two cobalt cations are linked via two μ-1,1(O, O)-bridging 4-methylpyridine N-oxide ligands into dinuclear units, with the Co₃O₂ rings that are the central motif located on centers of inversion (Fig. 1).

Similar Co₃O₂ rings are also observed in the related compound Co(NCS)₂(4-methylpyridine N-oxide)(methanol), in which the Co cations are additionally linked via alternating pairs of μ-1,3-bridging thiocyanate anions and μ-1,1(O,O)-bridging 4-methylpyridine N-oxide ligands into chains (Shi et al., 2006a).

3. Supramolecular features
In the crystal structure of the title compound, the dinuclear units are arranged in columns along the crystallographic a-axis direction (Fig. 2). Several C—H···S, one C—H···O and one C—H···N contacts are observed between the complexes, but only for some of them are the C—H···X angles close to linearity and the H···X distances relatively short, indicating a significant interaction (Fig. 2, Table 2).

4. Database survey
As mentioned above, two Co(NCS)₂ compounds with 4-methylpyridine N-oxide are already reported in the Cambridge Structural Database (Version 5.43, last update March 2023; Groom et al., 2016), including Co(NCS)₂(4-methylpyridine N-oxide)(methanol) (CSD refcode REKBUF; Shi et al., 2006a) and Co(NCS)₂(4-methylpyridine N-oxide) (refcode MEQKOJ; Zhang et al., 2006a). There are also two discrete complexes with the composition Co(NCS)₂(4-methylpyridine N-oxide) and Co(NCS)₂(4-methylpyridine N-oxide)₄ as already mentioned in the Chemical context section (Näther & Jess, 2024).

With Ni²⁺, a discrete complex with the composition Ni(NCS)₂(4-methylpyridine N-oxide)₂(H₂O)₂ has been reported that contains only terminally O-bonded coligands and which crystallizes as a monohydrate (Shi et al., 2005a). With Mn²⁺, a similar discrete complex with the composition Mn(NCS)₂(4-methylpyridine N-oxide)₂(H₂O)₂ has also been reported (Mautner et al., 2018a,b).

Two compounds with the composition M(NCS)₂(4-methylpyridine N-oxide) (with M = Ni, Cd) are also found that are isotypic to its Co analog mentioned in the chemical context section [refcodes PEDSUN (Shi et al., 2006b), PEDSUN01 (Marsh, 2009) and TEQKAC (Shi et al., 2006c)].

With Cu(II), one compound with the composition Cu(NCS)₂(4-methylpyridine N-oxide) is reported in which the Cu(II) cations are octahedrally coordinated by two N and three S-bonding thiocyanate anions and one terminal O-coordinating 4-methylpyridine N-oxide coligand (refcode TEBTAW; Shi et al., 2006d). The Cu(II) cations are connected into linear chains by pairs of bridging thiocyanate anions, that are further linked via Cu₃S₂ rings into double chains.

Finally, three isotypic compounds with the composition M(NCS)₂(acetato)₂(H₂O)₄ (4-methylpyridine N-oxide) (with M = Sm, Eu, Gd) are found [refcodes GHBUV (Zhang & Shi, 2007) and PIJBIU and PIJBOA (Shi et al., 2007a)].

Some Co(NCS)₂ compounds with other pyridine N-oxide derivatives are also known. This includes Co(NCS)₂(pyridine N-oxide)₂(H₂O)₂ and Co(NCS)₂(3-hydroxypyridine N-oxide)₃(H₂O)₂ that consist of discrete octahedral complexes [refcodes FONBIU (Shi et al., 2005b) and IDOYEG (Shi et al., 2006c)]. This also includes Co(NCS)₂(4-methoxypyridine N-oxide) that is isotypic to its 4-methylpyridine N-oxide analog (refcode TERRAK; Zhang et al., 2006b).

Finally, a compound with the composition Co(NCS)₂(4-nitropyridine N-oxide) is also reported in the literature (refcode TILHIG; Shi et al., 2007b).

5. Additional investigations
The title compound was also investigated by powder X-ray diffraction. Comparison of the experimental pattern with that calculated from single-crystal data reveals that this compound is of low crystallinity and that only a poor powder pattern can be obtained (Fig. 3). The low signal-to-noise ratio originates from the fact that only relatively large crystals were obtained, that could not be crushed into smaller crystals because in this case the compound started to decompose. However, it is obvious that no pure crystalline phase was obtained. In this context, it is noted that in those cases where different batches were investigated, the powder patterns always showed some differences. However, comparison of the experimental pattern
with those calculated for the title compound and for Co(NCS)$_2$(4-methylpyridine N-oxide)$_3$ (Näther & Jess, 2024) compounds retrieved from the literature indicate that the title compound is contaminated with a small amount of the discrete complex Co(NCS)$_2$(4-methylpyridine N-oxide)$_3$ (Näther & Jess, 2024). In fact, this is difficult to prove because the powder pattern was measured at room temperature, whereas the patterns calculated for the literature compounds are based in part on structure determinations at lower temperatures.

However, measurements with thermogravimetry and differential thermoanalysis (TG-DTA) show three mass losses, of which the first is accompanied by an endothermic and the second by a strong exothermic signal in the DTA curve (Fig. 4). The first mass loss of 6.4% is a bit lower than that calculated for the removal of the methanol molecules (7.5%), whereas the sum of the second and third mass losses is slightly higher than expected for the removal of all 4-methylpyridine N-oxide coligands (51.2%). However, the strong exothermic signal points to a decomposition of the coligands, as is usually observed for pyridine N-oxide derivatives (Näther & Jess, 2023, 2024). To characterize the compound formed after the first mass loss, it was isolated in a second TG run and investigated by PXRD. The powder pattern proves that a new crystalline phase of low crystallinity had been obtained that obviously contains a large amount of amorphous content (Figure S1). If the experimental pattern of the residue is compared with that calculated for Co(NCS)$_2$(4-methylpyridine N-oxide) reported in the literature (Refcode: MEQKOJ; Zhang et al., 2006a), it is obvious that this compound has formed by methanol removal.

6. Synthesis and crystallization

Co(NCS)$_2$ (99%) was purchased from Sigma Aldrich, 4-methylpyridine N-oxide (97%) from Thermo Scientific and methanol from Fisher Chemical.

**Synthesis:**

The title compound was prepared by the reaction of 0.5 mmol (87 mg) of Co(SCN)$_2$ and 1 mmol (109 mg) of 4-methylpyridine N-oxide in 1 mL of methanol. The reaction mixture was stored overnight, leading to the formation of violet-colored crystals that were always contaminated with Co(NCS)$_2$(4-methylpyridine N-oxide) (Näther & Jess, 2024).

**Experimental details:**

The data collection for single-crystal structure analysis was performed using an XtaLAB Synergy, Dualflex, HyPix diffractometer from Rigaku with Cu $K\alpha$ radiation. The PXRD measurements were either performed with the single-crystal diffractometer mentioned above (Fig. S1) or with a Stoe Transmission Powder Diffraction System STADI P (Fig. 3) equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator using Cu $K\alpha_1$ radiation ($\lambda = 1.540598$ Å). Thermogravimetry and differential thermoanalysis (TG-DTA) measurements were performed in a dynamic nitrogen atmosphere in Al$_2$O$_3$ crucibles using a STA-PT 1000 thermobalance from Linseis. The instrument was calibrated using standard reference materials.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydrogen atoms were positioned with idealized geometry and were refined with $U_{eq}(H) = 1.2U_{eq}(C)$ (1.5 for methyl H atoms) using a riding model. The H atoms of one of the methyl groups are disordered and...
were refined using a split model with two orientations rotated to each other by 60°.

Acknowledgements
This work was supported by the State of Schleswig-Holstein.

References

Table 3

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>Chemical formula</th>
<th>M_r</th>
<th>Crystal system, space group</th>
<th>Temperature (K)</th>
<th>a, b, c (Å)</th>
<th>β (°)</th>
<th>V (Å³)</th>
<th>Z</th>
<th>Radiaton type</th>
<th>μ (mm⁻¹)</th>
<th>Crystal size (mm)</th>
</tr>
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<tbody>
<tr>
<td>[Co₆(NCS)₄(C₂H₅NO)₄(CH₃O)₂]</td>
<td>850.77</td>
<td>Monoclinic, P2₁/n</td>
<td>100</td>
<td>11.46665 (13), 12.37103 (15), 13.58185 (17)</td>
<td>97.0894 (11)</td>
<td>1911.91 (4)</td>
<td>2</td>
<td>Cu Kα</td>
<td>9.27</td>
<td>0.21 x 0.14 x 0.1</td>
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Data collection
Diffractometer
Absorption correction
Multi-scan (CrysAlis PRO; Rigaku OD, 2023)

Table 3

<table>
<thead>
<tr>
<th>No. of measured, independent and observed</th>
<th>R int</th>
<th>R(Δ2 &gt; 2σ(Δ2))</th>
<th>wR(F²)</th>
<th>S</th>
</tr>
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<tbody>
<tr>
<td>4111</td>
<td>0.038</td>
<td>0.103, 1.09</td>
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</table>

No. of reflections | 4111
No. of parameters | 231
H-atoms treatment | H atoms treated by a mixture of independent and constrained refinement

Δρ_max / Δρ_min (e Å⁻³) | 0.67, –0.57

Computer programs: CrysAlis PRO (Rigaku OD, 2023), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2016/6 (Sheldrick, 2015b), DIAMOND (Brandenburg & Putz, 1999), XP in SHELXTL-PC (Sheldrick, 2008) and pubICIF (Westrip, 2010).