

Synthesis, crystal structure and thermal properties of the dinuclear complex bis(μ -4-methylpyridine *N*-oxide- κ^2 O:O)bis[(methanol- κ O)(4-methylpyridine *N*-oxide- κ O)bis(thiocyanato- κ N)cobalt(II)]

Christian Näther* and Inke Jess

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Accepted 10 April 2024Institut für Anorganische Chemie, Universität Kiel, Germany. *Correspondence e-mail: cnather@ac.uni-kiel.de

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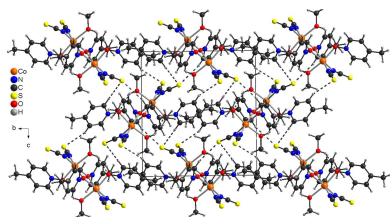
Keywords: synthesis; crystal structure; thermal properties; cobalt thiocyanate coordination compound; 4-methylpyridine *N*-oxide.**CCDC reference:** 2347590**Supporting information:** this article has supporting information at journals.iucr.org/e

Reaction of $\text{Co}(\text{NCS})_2$ with 4-methylpyridine *N*-oxide in methanol leads to the formation of crystals of the title compound, $[\text{Co}_2(\text{NCS})_4(\text{C}_6\text{H}_7\text{NO})_4(\text{CH}_4\text{O})_2]$ or $\text{Co}_2(\text{NCS})_4(4\text{-methylpyridine } N\text{-oxide})_4(\text{methanol})_2$. 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 μ -1,1(*O,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 $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_3$. Thermogravimetric investigations reveal that the methanol molecules are removed in the beginning, leading to a compound with the composition $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})$, which has been reported in the literature and which is of poor crystallinity.

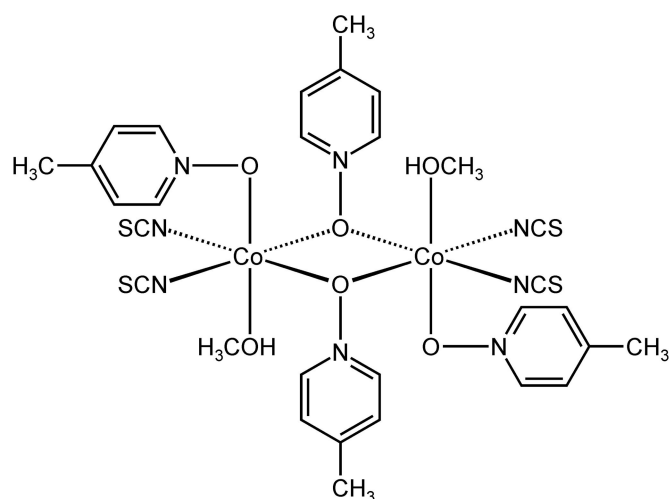
1. Chemical context

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; Mekuimemba *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 μ -1,1(*O,O*) bridging mode, leading to an enhanced structural variability. In the beginning, we focused on $\text{Co}(\text{NCS})_2$ compounds because, among other things, this cation is of special interest in terms of its magnetic



properties (Murrie, 2010; Mautner *et al.*, 2018*a,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 $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})$ (Refcode: MEQKOJ, Zhang *et al.*, 2006*a*) and $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})(\text{methanol})$ (Refcode: REKBUF; Shi *et al.*, 2006*a*) 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 $\mu\text{-}1,1(O,O)$ -bridging 4-methylpyridine *N*-oxide coligands, and are connected by pairs of bridging thiocyanate anions into corrugated chains. These chains are further linked into layers by $\mu\text{-}1,1(O,O)$ -bridging 4-methylpyridine *N*-oxide coligands (Zhang *et al.*, 2006*a*). 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.*, 2006*a*). The Co cations are linked by alternating pairs of $\mu\text{-}1,3$ -bridging thiocyanate anions and $\mu\text{-}1,1(O,O)$ -bridging 4-methylpyridine *N*-oxide coligands into chains.



In our own synthetic work, we have added two additional compounds with the composition $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_3$ and $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_4$, 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 $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_4$ 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 $\text{Co}(\text{NCS})_2$ and 4-methylpyridine *N*-oxide must exist. Based on these findings the synthesis conditions

Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.0525 (18)	Co1—O21	2.1057 (15)
Co1—N2	2.0840 (18)	Co1—O21 ⁱ	2.1043 (15)
Co1—O11	2.0543 (16)	Co1—O31	2.1301 (16)
N1—Co1—N2	96.79 (7)	O11—Co1—N2	96.57 (7)
N1—Co1—O11	96.07 (7)	O11—Co1—O21	83.57 (6)
N1—Co1—O21 ⁱ	94.26 (7)	O11—Co1—O21 ⁱ	87.62 (7)
N1—Co1—O21	166.79 (7)	O11—Co1—O31	167.80 (6)
N1—Co1—O31	95.14 (7)	O21 ⁱ —Co1—O21	72.53 (6)
N2—Co1—O21 ⁱ	167.69 (7)	O21 ⁱ —Co1—O31	86.77 (7)
N2—Co1—O21	96.37 (7)	O21—Co1—O31	84.42 (7)
N2—Co1—O31	86.85 (7)		

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

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 $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})(\text{methanol})$, which has already been reported in the literature (refcode REKBUF; Shi *et al.*, 2006*a*).

2. Structural commentary

The asymmetric unit of the title compound, $\text{Co}_2(\text{NCS})_4(4\text{-methylpyridine } N\text{-oxide})_4(\text{methanol})_2$, consists of one cobalt cation, two thiocyanate anions, one methanol molecule and two 4-methylpyridine *N*-oxide coligands, 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 $\mu\text{-}1,1(O,O)$ -bridging 4-methylpyridine *N*-oxide coligands (Fig. 1). Bond lengths and angles are similar to those in related compounds (Shi *et al.*, 2006*a*) and show that the octahedra are slightly distorted

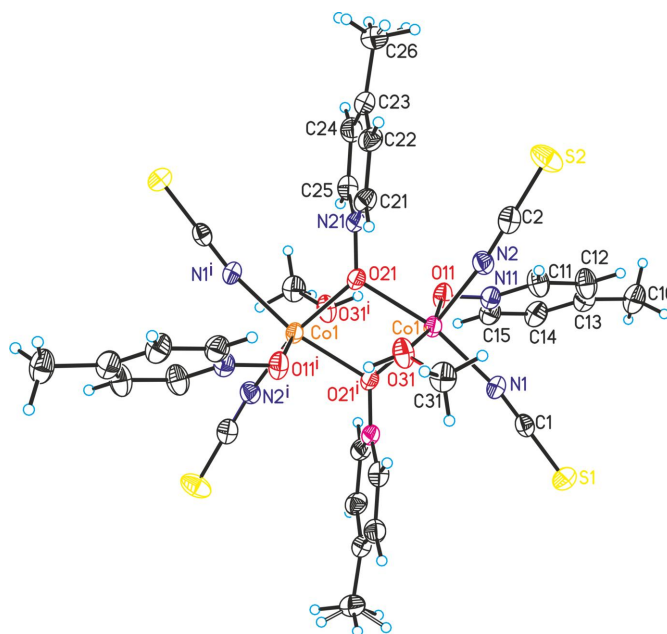
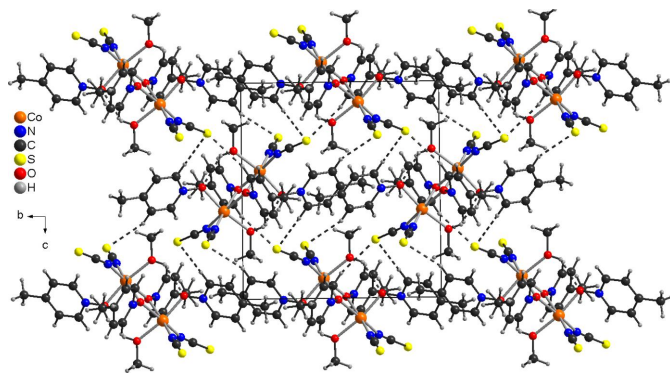


Figure 1
The molecular structure of the title compound with atom labelling and displacement ellipsoids drawn at the 50% probability level. The disorder of the H atoms of one of the methyl groups is shown with full and open bonds. [Symmetry code: (i) $-x + 1, -y, -z + 1$.]


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 coligands into dinuclear units, with the Co₂O₂ rings that are the central motif located on centers of inversion (Fig. 1).

Similar Co₂O₂ 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 coligands into chains (Shi *et al.*, 2006*a*).

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.*, 2006*a*) and Co(NCS)₂(4-methylpyridine *N*-oxide) (refcode MEQKOJ; Zhang *et al.*, 2006*a*). There are also two discrete complexes with the composition Co(NCS)₂(4-methylpyridine *N*-oxide)₃ and Co(NCS)₂(4-methylpyridine *N*-oxide)₄, as already mentioned in the *Chemical context* section (Näther & Jess, 2024).

With Ni^{II}, 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.*, 2005*a*). With Mn^{II}, a similar discrete complex with the composition Mn(NCS)₂(4-

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C11—H11···N2	0.95	2.40	3.225 (3)	145
C12—H12···S1 ⁱⁱ	0.95	2.79	3.688 (3)	158
C15—H15···S2 ⁱⁱⁱ	0.95	2.68	3.609 (3)	167
C21—H21···S2 ^{iv}	0.95	3.03	3.917 (2)	156
C22—H22···S1 ^v	0.95	2.98	3.821 (2)	148
O31—H31···S1 ^{vi}	0.84	2.97	3.6106 (18)	134
O31—H31···O11 ⁱ	0.84	2.31	3.003 (2)	141
C31—H31B···S2 ^{iv}	0.98	2.83	3.575 (3)	133

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $x - 1, y, z$; (vi) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

methylpyridine *N*-oxide)₂(H₂O)₂ has also been reported (Mautner *et al.*, 2018*a,b*).

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

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.*, 2006*d*). The Cu(II) cations are connected into linear chains by pairs of bridging thiocyanate anions, that are further linked *via* Cu₂S₂ rings into double chains.

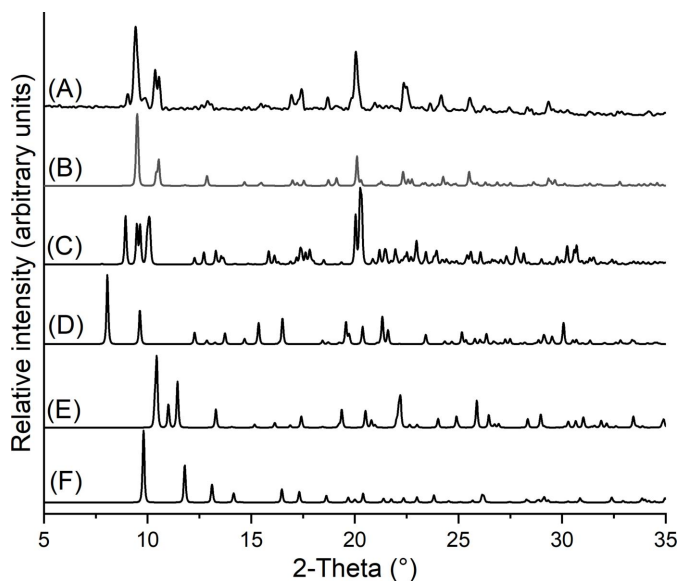
Finally, three isotopic compounds with the composition *M*(NCS)₂(acetato)₂(H₂O)₃(4-methylpyridine *N*-oxide) (with *M* = Sm, Eu, Gd) are found [refcodes GIHBUV (Zhang & Shi, 2007) and PIJBIU and PIJBOA (Shi *et al.*, 2007*a*)].

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)₂(H₂O)₂ that consist of discrete octahedral complexes [refcodes FONBIU (Shi *et al.*, 2005*b*) and IDOYEG (Shi *et al.*, 2006*e*)]. This also includes Co(NCS)₂(4-methoxypyridine *N*-oxide) that is isotopic to its 4-methylpyridine *N*-oxide analog (refcode TERRAK; Zhang *et al.*, 2006*b*).

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

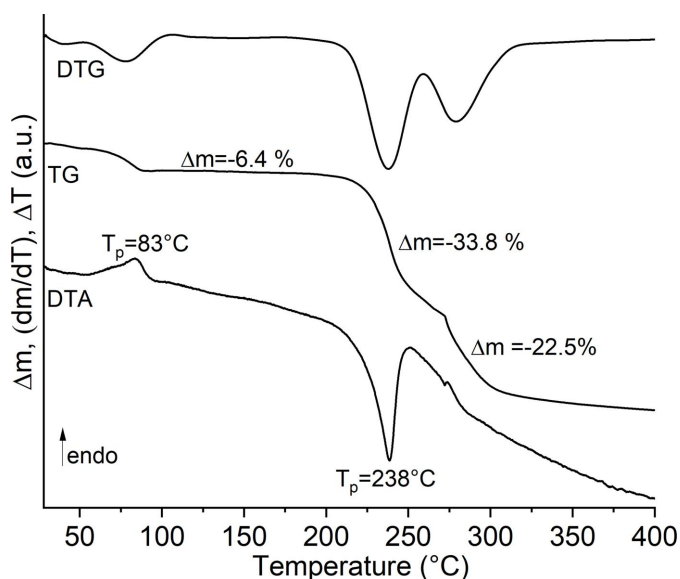
5. Additional investigations

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


Figure 3

Experimental powder pattern of the title compound (A) together with the calculated pattern for the title compound (B), $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_3$ (C, Näther & Jess, 2024), $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_4$ (D, Näther & Jess, 2024), $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})(\text{methanol})$ (E, Refcode: REKBUF; Shi *et al.*, 2006a) and $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})$ (F, Refcode: MEQKOJ; Zhang *et al.*, 2006a).

with those calculated for the title compound and for $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})$ compounds retrieved from the literature indicate that the title compound is contaminated with a small amount of the discrete complex $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_3$ (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.


Figure 4

TG-DTA curve of the title compound measured at 8°C min^{-1} .

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 $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})$ 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

$\text{Co}(\text{NCS})_2$ (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 $\text{Co}(\text{SCN})_2$ 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 $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_3$ (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 $\text{Cu } K\alpha$ 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 $\text{Ge}(111)$ monochromator using $\text{Cu } K\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$). Thermogravimetry and differential thermoanalysis (TG-DTA) measurements were performed in a dynamic nitrogen atmosphere in Al_2O_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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (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

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Table 3

Experimental details.

Crystal data	
Chemical formula	[Co ₂ (NCS) ₄ (C ₆ H ₇ NO) ₄ (CH ₄ O) ₂]
<i>M_r</i>	850.77
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.46665 (13), 12.37103 (15), 13.58185 (17)
β (°)	97.0894 (11)
<i>V</i> (Å ³)	1911.91 (4)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	9.27
Crystal size (mm)	0.21 × 0.14 × 0.1
Data collection	
Diffraction	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2023)
<i>T</i> _{min} , <i>T</i> _{max}	0.529, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	13370, 4111, 3945
<i>R</i> _{int}	0.024
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.640
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.038, 0.103, 1.09
No. of reflections	4111
No. of parameters	231
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (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 *pubCIF* (Westrip, 2010).

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