Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

# Synthesis and crystal structure of diisothiocyanatotetrakis(4-methylpyridine *N*-oxide)cobalt(II) and diisothiocyanatotris(4-methylpyridine *N*-oxide)cobalt(II) showing two different metal coordination polyhedra

**Christian Näther* and Inke Jess**

Institut für Anorganische Chemie, Universität Kiel, Germany. *Correspondence e-mail: cnaether@ac.uni-kiel.de

Received 10 January 2024
Accepted 12 January 2024

Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

**Keywords:** synthesis; coordination compound; cobalt thiocyanate; 4-methylpyridine *N*-oxide; crystal structure.

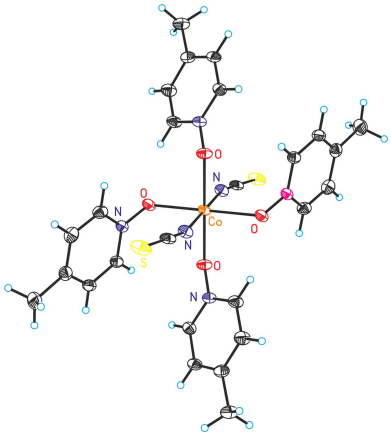
**CCDC references:** 2325197; 2325196

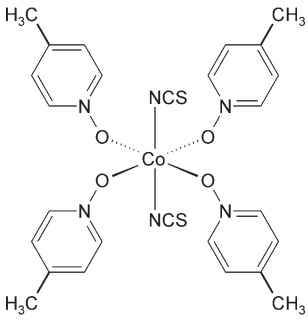
**Supporting information:** this article has supporting information at journals.iucr.org/e

The reaction of $Co(NCS)_2$ with 4-methylpyridine *N*-oxide ($C_6H_7NO$) leads to the formation of two compounds, namely, tetrakis(4-methylpyridine *N*-oxide-$\kappa O$)bis(thiocyanato-$\kappa N$)cobalt(II), $[Co(NCS)_2(C_6H_7NO)_4]$ (**1**), and tris(4-methylpyridine *N*-oxide-$\kappa O$)bis(thiocyanato-$\kappa N$)cobalt(II), $[Co(NCS)_2(C_6H_7NO)_3]$ (**2**). The asymmetric unit of **1** consists of one $Co^{II}$ cation located on a centre of inversion, as well as one thiocyanate anion and two 4-methylpyridine *N*-oxide coligands in general positions. The $Co^{II}$ cations are octahedrally coordinated by two terminal *N*-bonding thiocyanate anions in *trans* positions and four 4-methylpyridine *N*-oxide ligands. In the extended structure, these complexes are linked by C—H···O and C—H···S interactions. In compound **2**, two crystallographically independent complexes are present, which occupy general positions. In each of these complexes, the $Co^{II}$ cations are coordinated in a trigonal–bipyramidal manner by two terminal *N*-bonding thiocyanate anions in axial positions and by three 4-methylpyridine *N*-oxide ligands in equatorial positions. In the crystal, these complex molecules are linked by C—H···S interactions. For compound **2**, a nonmerohedral twin refinement was performed. Powder X-ray diffraction (PXRD) reveals that **2** was nearly obtained as a pure phase, which is not possible for compound **1**. Differential thermoanalysis and thermogravimetry data (DTA–TG) show that compound **2** start to decompose at about 518 K.

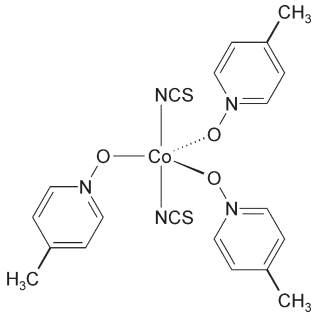
## 1. Chemical context

Complexes based on transition-metal thiocyanates are an important class of compounds in coordination chemistry. Because of their versatile coordination behaviour they show a variety of coordination modes and a large structural variability, which can lead to networks of different dimensionality (Buckingham, 1994; Kabešová *et al.*, 1995; Barnett *et al.*, 2002; Werner *et al.*, 2014; Neumann *et al.*, 2018). In this context, compounds based on paramagnetic metal cations are of special interest, because they show very versatile magnetic behaviour. We have been interested in the structural, thermal and magnetic behaviour of thiocyanate compounds with 3*d*-metal cations for several years. In terms of magnetic properties, compounds based on $Co^{II}$, in which the cations are linked into chains, are of special interest, because they show a variety of magnetic properties, including ferro- or single-chain magnetism (Mautner *et al.*, 2018*b*; Rams *et al.*, 2017, 2020, 2023; Wöhlert *et al.*, 2013).






1




2

Concerning the coordination behaviour of cobalt thiocyanates, in the majority of compounds the $Co^{II}$ cations are sixfold coordinated within a slightly distorted octahedral geometry and more than 1000 such structures can be found in the Cambridge Structural Database (CSD; Version 5.43, last update March 2023; Groom *et al.*, 2016). Depending on the nature of the coligand, in some cases, the $Co^{II}$ cations are tetrahedrally coordinated and about 280 of such structures are reported in the CSD. In very rare cases, a compound with an octahedral coordination and another compound with a tetrahedral coordination were obtained in a synthesis using the same coligand (Mautner *et al.*, 2018*b*). In contrast, $Co(NCS)_2$ compounds with a fivefold coordination are uncommon and only about 60 structures have been reported. In this context, it is noted that we have reported the first $Co^{II}$ chain compound, in which the $Co^{II}$ cations shows an alternating five- and sixfold coordination (Böhme *et al.*, 2022).

In our recent work, however, we exclusively used *N*-donor coligands, such as pyridine derivatives, for the synthesis of new thiocyanate coordination polymers, but in the course of our systematic work we started to use also *O*- or *S*-donor coligands (Jochim *et al.*, 2020). For *O*-donor coligands, pyridine *N*-oxide derivatives might be suitable, for which only 11 compounds with cobalt are reported in the CSD (see *Database survey* section). In this context, it is noted that we recently reported on new compounds with the composition $Co(NCS)_2$(2-methylpyridine *N*-oxide) and $Co(NCS)_2$(3-cyanopyridine *N*-oxide)$_4$. In the first compound, the cations are octahedrally coordinated by two *O*-bonding 2-methylpyridine *N*-oxide ligands, as well as by two thiocyanate anions, and are connected by $\mu$-1,3(*N*,*S*)-bridging thiocyanate anions into chains that are further linked into layers by pairs of $\mu$-1,1(*O*,*O*) bridging coligands (Näther & Jess, 2024). In contrast, the second compound consists of discrete octahedral complexes (Näther & Jess, 2023). In continuation of this work, we tried to prepare similar compounds with 4-methylpyridine *N*-oxide ($C_6H_7NO$), for which only one compound with the composition $Co(NCS)_2(C_6H_7NO)$(methanol) is reported, in which the $Co^{II}$ cations are also sixfold coordinated by two O atoms of the coligand, one methanol molecule, as well as by one terminal and two bridging thiocyanate anions, and linked into chains by alternating pairs of thiocyanate anions and 4-methylpyridine *N*-oxide coligands (CSD refcode REKBUF; Shi *et al.*, 2006*a*). Within our synthetic work, crystals of two different crystalline phases were obtained. Single-crystal structure analysis shows that discrete complexes had formed, in which the $Co^{II}$ cations shows either a sixfold or a fivefold coordination. We note that some transition-metal thiocyanate compounds with pyridine *N*-oxide derivatives are reported in the literature that also form discrete complexes, but in none of them are the cations fivefold coordinated (see *Database survey* section).

## 2. Structural commentary

The reactions of different molar ratios of $Co(NCS)_2$ and 4-methylpyridine *N*-oxide leads to the formation of crystals of two compounds with the compositions $Co(NCS)_2(C_6H_7NO)_4$ (**1**) and $Co(NCS)_2(C_6H_7NO)_3$ (**2**). Compound **2** can be prepared in larger amounts, whereas a few crystals of compound **1** were accidently obtained in only one batch (see *Synthesis and crystallization* section). The asymmetric unit of compound **1** consists of one $Co^{II}$ cation located on a crystallographic centre of inversion, as well as one thiocyanate anion and two 4-methylpyridine *N*-oxide coligands in general positions (Fig. 1). The cations are sixfold coordinated by two terminal *N*-bonded thiocyanate anions in *trans* positions and by four O atoms of the 4-methylpyridine *N*-oxide coligands. From the bond lengths and angles it is apparent that the *trans*-$CoN_2O_4$ octahedra are slightly distorted (Table 1). It is noted that numerous similar complexes with a distorted octahedral coordination are reported in the literature.

In compound **2**, all the atoms are in general positions and two crystallographically independent discrete complexes are present (Fig. 2). In each of them, the $Co^{II}$ cations are fivefold coordinated by two terminal *N*-bonded thiocyanate anions and three 4-methylpyridine *N*-oxide coligands, and the coor-

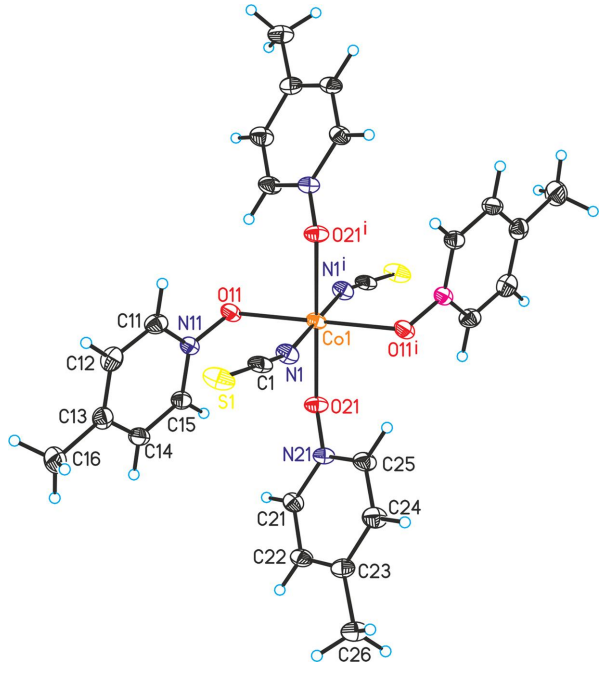



**Figure 1**
Crystal structure of compound **1**, with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x+1, -y, -z+1$.]

**Table 1**
Selected geometric parameters (Å, °) for (**1**).

| | | | |
|---|---|---|---|
| Co1—N1 | 2.0910 (14) | Co1—O21 | 2.1266 (11) |
| Co1—O11 | 2.1005 (12) | | |
| | | | |
| $N1^{i}$—Co1—$O11^{i}$ | 92.39 (5) | $O11^{i}$—Co1—$O21^{i}$ | 87.15 (5) |
| N1—Co1—$O11^{i}$ | 87.61 (5) | $O11^{i}$—Co1—O21 | 92.85 (5) |
| N1—Co1—$O21^{i}$ | 87.56 (5) | Co1—N1—C1 | 165.56 (14) |
| $N1^{i}$—Co1—$O21^{i}$ | 92.44 (5) | | |

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

**Table 2**
Selected geometric parameters (Å, °) for (**2**).

| | | | |
|---|---|---|---|
| Co1—N1 | 2.0767 (16) | Co2—N3 | 2.0804 (16) |
| Co1—N2 | 2.0895 (15) | Co2—N4 | 2.0844 (16) |
| Co1—O11 | 1.9949 (13) | Co2—O41 | 1.9999 (13) |
| Co1—O21 | 1.9989 (14) | Co2—O51 | 1.9880 (14) |
| Co1—O31 | 2.0045 (14) | Co2—O61 | 1.9941 (14) |
| | | | |
| N1—Co1—N2 | 179.11 (7) | O41—Co2—N3 | 93.31 (6) |
| O11—Co1—N1 | 93.86 (6) | O41—Co2—N4 | 88.08 (6) |
| O11—Co1—N2 | 86.87 (6) | O51—Co2—N3 | 86.15 (6) |
| O11—Co1—O21 | 122.93 (6) | O51—Co2—N4 | 92.14 (6) |
| O11—Co1—O31 | 121.98 (6) | O51—Co2—O41 | 122.04 (6) |
| O21—Co1—N1 | 87.05 (6) | O51—Co2—O61 | 115.95 (6) |
| O21—Co1—N2 | 92.13 (6) | O61—Co2—N3 | 87.50 (6) |
| O21—Co1—O31 | 115.07 (6) | O61—Co2—N4 | 92.75 (6) |
| O31—Co1—N1 | 87.43 (6) | O61—Co2—O41 | 121.94 (6) |
| O31—Co1—N2 | 92.62 (6) | Co2—N3—Co3 | 168.81 (15) |
| Co1—N1—Co | 167.85 (16) | | |

dination polyhedra around the Co centres can be described as slightly distorted trigonal pyramids with the anionic ligands in the axial and the coligands in the equatorial positions (Fig. 2 and Table 2). Within each complex, two of the coligands point 'up' (roughly parallel to the axis of the Co—NCS grouping) and one points 'down'. Bond lengths and angles are comparable in both complexes (Table 2). As mentioned above, $Co(NCS)_2$ complexes with a fivefold coordination are relatively rare and, therefore, it is surprising that compound **2** can be prepared easily, which is not the case for **1** with an octahedral coordination (see *Synthesis and crystallization* section).

## 3. Supramolecular features

In the extended structure of **1**, the discrete complex molecules are arranged into columns that proceed along the *a*-axis direction (Fig. 3). Between the complexes, weak intermolecular C—H···O and C—H···S interactions are observed (Table 3). In compound **2**, numerous C—H···O, C—H···N and C—H···S interactions are observed, but in most of them, the *X*···H distances are long and the angles vary far from linearity, indicating that these are very weak interactions (Table 4). Some C—H···S contacts seems to be stronger, and if they are considered, the discrete complexes are linked into chains (Fig. 4).

## 4. Database survey

A CSD search for cobalt thiocyanate compounds with pyridine *N*-oxide derivatives revealed that only a few structures have been reported. These include discrete complexes with the composition $Co(NCS)_2$(pyridine *N*-oxide)$_2(H_2O)_2$ (FONBIU; Shi *et al.*, 2005*b*) and $Co(NCS)_2$(3-hydroxypyridine *N*-oxide)$_2$-

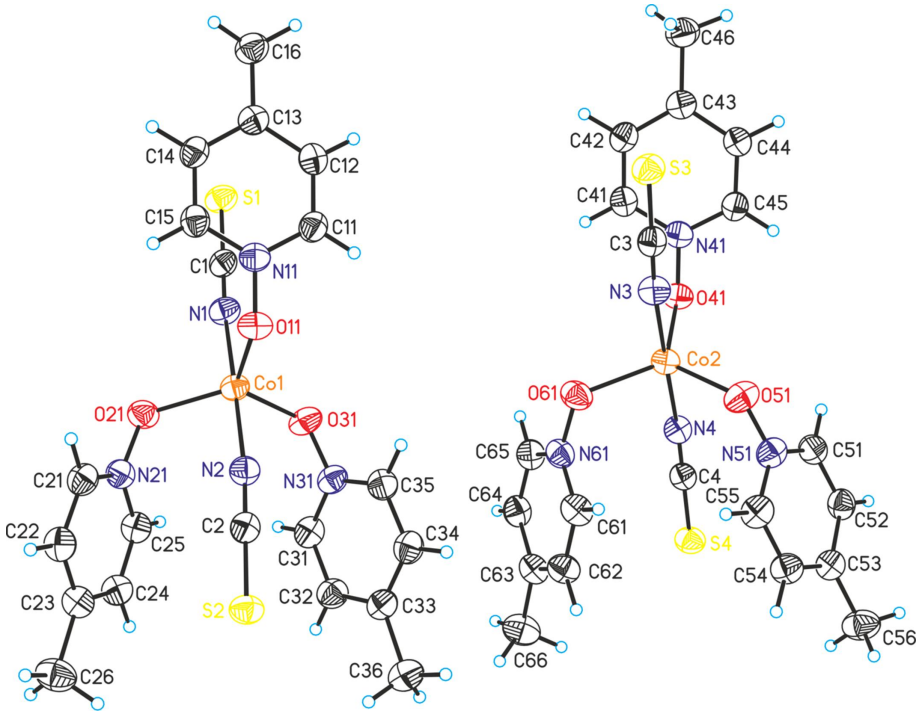



**Figure 2**
Crystal structure of the two crystallographically independent complexes molecules in compound **2**, with displacement ellipsoids drawn at the 50% probability level.

**Table 3**
Hydrogen-bond geometry (Å, °) for (**1**).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C14—H14···S1$^{ii}$ | 0.95 | 2.83 | 3.7271 (17) | 157 |
| C15—H15···O21$^{iii}$ | 0.95 | 2.40 | 3.295 (2) | 157 |
| C21—H21···O21$^{iii}$ | 0.95 | 2.62 | 3.520 (2) | 158 |
| C24—H24···S1$^{iv}$ | 0.95 | 2.87 | 3.7591 (18) | 156 |
| C25—H25···O11$^{i}$ | 0.95 | 2.25 | 3.090 (2) | 147 |

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x-1, y, z$; (iii) $-x, -y, -z+1$; (iv) $-x+1, -y, -z$.

**Table 4**
Hydrogen-bond geometry (Å, °) for (**2**).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C11—H11···S4$^{i}$ | 0.95 | 2.88 | 3.8088 (19) | 166 |
| C21—H21···S2$^{ii}$ | 0.95 | 2.87 | 3.739 (2) | 153 |
| C24—H24···S1$^{iii}$ | 0.95 | 2.90 | 3.841 (2) | 169 |
| C25—H25···O31$^{iii}$ | 0.95 | 2.63 | 3.259 (2) | 124 |
| C31—H31···O21$^{iii}$ | 0.95 | 2.44 | 3.277 (2) | 146 |
| C34—H34···S3 | 0.95 | 2.99 | 3.754 (2) | 138 |
| C41—H41···S3$^{iv}$ | 0.95 | 2.97 | 3.6966 (19) | 134 |
| C45—H45···S2 | 0.95 | 2.89 | 3.6082 (19) | 133 |
| C55—H55···O61$^{v}$ | 0.95 | 2.46 | 3.184 (2) | 133 |
| C61—H61···O51$^{v}$ | 0.95 | 2.48 | 3.233 (2) | 136 |
| C62—H62···S3$^{v}$ | 0.95 | 2.98 | 3.900 (2) | 162 |
| C64—H64···N4$^{vi}$ | 0.95 | 2.64 | 3.484 (2) | 148 |
| C65—H65···S4$^{vi}$ | 0.95 | 3.00 | 3.870 (2) | 154 |

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

$(H_2O)_2$ (IDOYEG; Shi *et al.*, 2006*e*), in which the Co cations are octahedrally coordinated by two thiocyanate anions, two water molecules and two terminal 3-hydroxypyridine *N*-oxide ligands. Discrete dinuclear complexes are observed in $Co(NCS)_2$(2-pyridinecarboxaldehyde-1-oxido 2′-pyridinylhydrazone), in which the thiocyanate anions are only terminally *N*-bonded and two $Co^{II}$ cations are linked by two $\mu$-1,1-bridging O atoms of the coligands (VAZDAB; Craig *et al.*, 1989).

In $Co(NCS)_2$[*N*,*N*′-ethane-1,2-diylbis(pyridine-4-carboxamide) 1,1-dioxide]$(H_2O)_2$ dihydrate (FATJAN; Cao *et al.*, 2012) and in $Co(NCS)_2$[*N*,*N*′-hexane-1,6-diylbis(pyridine-4-carboxamide) 1,1′-dioxide]$(H_2O)_2$ (FATJER; Cao *et al.*, 2012), the Co cations are also octahedrally coordinated but linked into chains by the pyridine *N*-oxide coligands.

In $Co(NCS)_2$(4-nitropyridine *N*-oxide)$_2$, the $Co^{II}$ cations are octahedrally coordinated by four bridging thiocyanate anions and two terminal *O*-bonded 4-nitropyridine *N*-oxide coligands and linked by pairs of thiocyanate anions into chains (TILHIG; Shi *et al.*, 2007). Chains are also observed in $Co(NCS)_2$(4-methylpyridine *N*-oxide)(methanol) (REKBUF; Shi *et al.*, 2006*a*).

A layered structure is observed in $Co(NCS)_2$(4-methoxypyridine)$_2$ (TERRAK; Zhang *et al.*, 2006*a*). In this structure, the $Co^{II}$ cations are octahedrally coordinated by four bridging anionic ligands and two coligands. As in $Co(NCS)_2$(2-methylpyridine *N*-oxide)(methanol), the cations are connected into chains by alternating pairs of thiocyanate anions and 2-methylpyridine *N*-oxide coligands, and the chains are are further linked into layers by additional pairs of thiocyanate anions. A further layered structure is found in $Co(NCS)_2$(4-methylpyridine *N*-oxide), in which the $Co^{II}$ cations are octahedrally coordinated by two *N*- and two *S*-bonding thiocyanate anions, and two bridging 4-methylpyridine *N*-oxide coligand (MEQKOJ; Zhang *et al.*, 2006*b*). The cations are connected by pairs of bridging thiocyanate anions into corrugated chains, that are further linked into layers by bridging 4-methylpyridine *N*-oxide coligands.

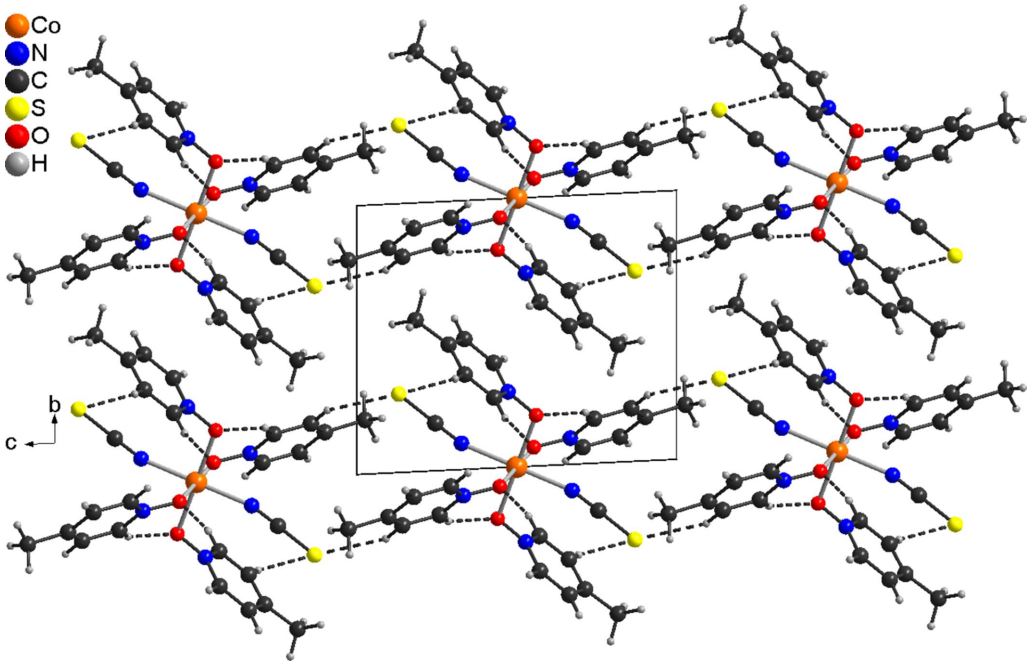



**Figure 3**
Crystal structure of compound **1**, viewed along the crystallographic *a* axis. Intermolecular C—H···S and C—H···O contacts are shown as dashed lines.

In $Co(NCS)_2$(1,3-bis(4-pyridyl)propane *N*,*N*′-dioxide)-$(H_2O)_2$, each two $Co^{II}$ cations are further linked by $\mu$-1,1-bridging atoms of the *N*-oxide ligands into dinuclear units that are futher connected into layers by the 1,3-bis(4-pyridyl) propane *N*,*N*′-dioxide coligands (UMAVAF; Zhang *et al.*, 2003). Layers are also observed in $Co(NCS)_2$(1,3-bis(4-pyridyl)propane *N*,*N*′-dioxide)$_2$, in which the $Co^{II}$ cations are also linked by the *N*-oxide coligands (UMAVUZ; Zhang *et al.*, 2003).

Finally we note that some compounds with 4-methylpyridine *N*-oxide and other transition-metal cations are reported in the CSD. These include discrete octahedral complexes with the composition $M(NCS)_2$(4-methylpyridine *N*-oxide)$_2(H_2O)_2$, with *M* = Mn (KESSEJ; Mautner *et al.*, 2018*a*) and Ni (GAMDOO; Shi *et al.*, 2005*a*). These also include $Ni(NCS)_2$(4-methylpyridine *N*-oxide) [PEDSUN (Shi *et al.*, 2006*c*) and PETSUN01 (Marsh, 2009)]. There is also one Cu compound with the composition Cu(NCS)2(4-methylpyridine) (TEBTAW; Shi *et al.*, 2006*d*) and one Cd compound with the composition $Cd(NCS)_2$(4-methylpyridine) (TEQKAC; Shi *et al.*, 2006*b*), in which the cations are linked into chains.

## 5. Additional investigations

Based on the single-crystal data, a powder pattern was calculated and compared with the experimental pattern, which revealed that compound **2** was nearly obtained as a pure phase (Fig. S1 in the supporting information). There are a few additional reflections of very low intensity that cannot be assigned to a known phase.

The thermal behaviour of compound **2** was investigated by thermogravimetry and differential thermoanalysis (TG–DTA) measurements. Upon heating at a rate of 8 K $min^{-1}$, one mass loss is observed, accompanied by an exothermic event in the DTA curve (Fig. S2). The experimental mass loss of 68.1% is in reasonable agreement with that calculated for the removal of all three 4-methylpyridine *N*-oxide coligands of 65.2%. The exothermic signal, however, indicates that the coligand decompose as already observed for compounds with other pyridine *N*-oxide derivatives (Näther & Jess, 2023). There is one endothermic signal at 438 K, where the sample mass does not change, which might originate from a melting of the complex before decomposition is observed.

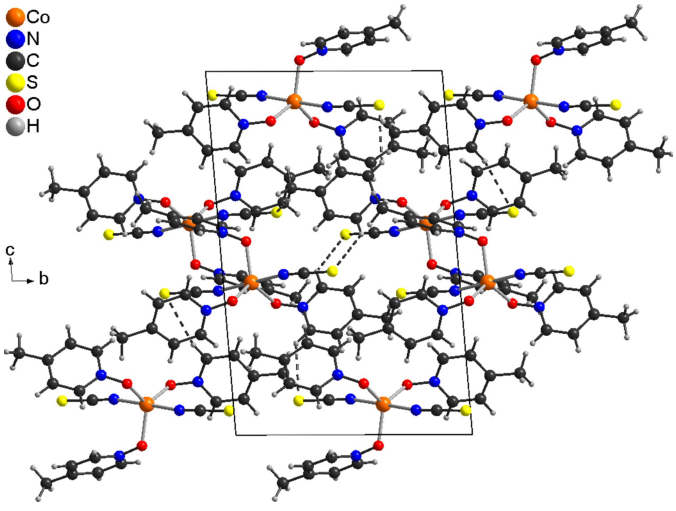



**Figure 4**
Crystal structure of compound **2**, viewed along the crystallographic *a* axis. Intermolecular C—H···S contacts are shown as dashed lines.

## 6. Synthesis and crystallization

$Co(NCS)_2$ (99%) was purchased from Sigma–Aldrich and 4-methylpyridine *N*-oxide (98%) from Fisher Chemical. Single crystals of compound **2** were obtained by the reaction of $Co(SCN)_2$ (0.500 mmol, 87.5 mg) and 4-methylpyridine *N*-oxide (1.500 mmol, 163.7 mg) in methanol (1 ml). Within 2 d, crystals suitable for structure analysis were obtained. If the same reaction conditions are used and the batch is stirred for 1 d, a microcrystalline powder of **2** is obtained.

For compound **1**, a few crystals were obtained accidentally in a mixture with **2**, using the same conditions as described above. It is noted that **2** is also obtained if $Co(NCS)_2$ is reacted with 4-methylpyridine *N*-oxide in a 1:4 ratio. We also used larger ratios and other solvents, *e.g.* ethanol or *n*-butanol, but in none of these batches was compound **1** obtained as a pure phase. It seems that compound **2**, with a fivefold coordination, is more stable. Finally, it is noted that in some batches where methanol and ethanol was used as solvent, powder X-ray diffraction (PXRD) measurements prove that additional and unknown crystalline phases were obtained.

The PXRD data were collected using an XtaLAB Synergy, Dualflex, Thermogravimetry and differential thermoanalysis (TG–DTA) measurements were performed under a dynamic nitrogen atmosphere in $Al_2O_3$ crucibles using an STA-PT 1000 thermobalance from Linseis. The instrument was calibrated using standard reference materials.

## 7. Refinement

The H atoms were positioned with idealized geometry (C—H = 0.95–0.98 Å) and were refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C).

The crystal of **2** chosen for data collection was found to be twinned. Both components were indexed separately (Fig. S3) and afterwards a twin-refinement with data in HKLF-5 format using the twin matrix −0.9998 0.0004 −0.0001/−0.0006 −1.0001 −0.0006/0.2122 0.2564 1.0002 was performed. Therefore, no internal *R* value is reported. The ratio between domains refined to 0.8273 (7):0.1727 (7). Crystal data, data collection and structure refinement details are summarized in Table 5.

## Acknowledgements

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

**Table 5**
Experimental details.

For both structures: triclinic, $P\overline{1}$. Experiments were carried out at 100 K with Cu $K\alpha$ radiation using a Rigaku XtaLAB Synergy Dualflex diffractometer with a HyPix detector. Absorption was corrected for by multi-scan methods, (*CrysAlis PRO*; Rigaku OD, 2021). H-atom parameters were constrained.

| | **1** | **2** |
|---|---|---|
| Crystal data | | |
| Chemical formula | $[Co(NCS)_2(C_6H_7NO)_4]$ | $[Co(NCS)_2(C_6H_7NO)_3]$ |
| $M_r$ | 611.59 | 502.47 |
| $a$, $b$, $c$ (Å) | 7.0709 (3), 9.6651 (5), 11.0401 (4) | 11.70330 (8), 12.55284 (9), 17.5256 (2) |
| $\alpha$, $\beta$, $\gamma$ (°) | 90.609 (3), 96.346 (3), 108.090 (4) | 93.5044 (8), 91.8625 (8), 115.0705 (7) |
| $V$ (Å$^3$) | 712.00 (6) | 2322.89 (4) |
| $Z$ | 1 | 4 |
| $\mu$ (mm$^{-1}$) | 6.45 | 7.74 |
| Crystal size (mm) | 0.12 × 0.08 × 0.04 | 0.2 × 0.18 × 0.1 |
| Data collection | | |
| $T_{min}$, $T_{max}$ | 0.859, 1.000 | 0.024, 0.116 |
| No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections | 7433, 2950, 2935 | 11225, 11225, 10980 |
| $R_{int}$ | 0.017 | See *Refinement* section |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.639 | 0.639 |
| Refinement | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.029, 0.081, 1.11 | 0.029, 0.081, 1.07 |
| No. of reflections | 2950 | 11225 |
| No. of parameters | 181 | 566 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.34, −0.48 | 0.33, −0.25 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT2014* (Sheldrick, 2015*b*), *SHELXL2016* (Sheldrick, 2015*a*), *DIAMOND* (Brandenburg & Putz, 1999) and *publCIF* (Westrip, 2010).

## References


Barnett, S. A., Blake, A. J., Champness, N. R. & Wilson, C. (2002). *Chem. Commun.* pp. 1640–1641.

Böhme, M., Rams, M., Krebs, C., Mangelsen, S., Jess, I., Plass, W. & Näther, C. (2022). *Inorg. Chem.* **61**, 16841–16855.

Brandenburg, K. & Putz, H. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Buckingham, D. A. C. (1994). *Coord. Chem. Rev.* **135–136**, 587–621.

Cao, W., Sun, H. L. & Li, Z. (2012). *Inorg. Chem. Commun.* **19**, 19–22.

Craig, D. C., Phillips, D. J. & Kaifi, F. M. Z. (1989). *Inorg. Chim. Acta*, **161**, 247–251.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Jochim, A., Lohmiller, T., Rams, M., Böhme, M., Ceglarska, M., Schnegg, A., Plass, W. & Näther, C. (2020). *Inorg. Chem.* **59**, 8971–8982.

Kabešová, M., Boča, R., Melník, M., Valigura, D. & Dunaj-Jurčo, M. (1995). *Coord. Chem. Rev.* **140**, 115–135.

Marsh, R. E. (2009). *Acta Cryst.* B**65**, 782–783.

Mautner, F. A., Berger, C., Fischer, R. C., Massoud, S. S. & Vicente, R. (2018*a*). *Polyhedron*, **141**, 17–24.

Mautner, F. A., Traber, M., Fischer, R. C., Torvisco, A., Reichmann, K., Speed, S., Vicente, R. & Massoud, S. S. (2018*b*). *Polyhedron*, **154**, 436–442.

Näther, C. & Jess, I. (2023). *Acta Cryst.* E**79**, 867–871.

Näther, C. & Jess, I. (2024). *Acta Cryst.* E**80**, 67–71.

Neumann, T., Ceglarska, M., Germann, L. S., Rams, M., Dinnebier, R. E., Suckert, S., Jess, I. & Näther, C. (2018). *Inorg. Chem.* **57**, 3305–3314.

Rams, M., Böhme, M., Kataev, V., Krupskaya, Y., Büchner, B., Plass, W., Neumann, T., Tomkowicz, Z. & Näther, C. (2017). *Phys. Chem. Chem. Phys.* **19**, 24534–24544.

Rams, M., Jochim, A., Böhme, M., Lohmiller, T., Ceglarska, M., Rams, M. M., Schnegg, A., Plass, W. & Näther, C. (2020). *Chem. Eur. J.* **26**, 2837–2851.

Rams, M., Lohmiller, T., Böhme, M., Jochim, A., Foltyn, M., Schnegg, A., Plass, W. & Näther, C. (2023). *Inorg. Chem.* **62**, 10420–10430.

Rigaku OD (2021). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Shi, J. M., Liu, Z., Lu, J. J. & Liu, L. D. (2005*a*). *Acta Cryst.* E**61**, m1133–m1134.

Shi, J. M., Liu, Z., Lu, J. J. & Liu, L. D. (2005*b*). *Acta Cryst.* E**61**, m871–m872.

Shi, J. M., Liu, Z., Sun, Y. M., Yi, L. & Liu, L. D. (2006*a*). *Chem. Phys.* **325**, 237–242.

Shi, J. M., Liu, Z., Wu, C. J., Xu, H. Y. & Liu, L. D. (2006*b*). *J. Coord. Chem.* **59**, 1883–1889.

Shi, J. M., Liu, Z., Xu, H. K., Wu, C. J. & Liu, L. D. (2007). *J. Coord. Chem.* **60**, 1637–1644.

Shi, J. M., Sun, Y. M., Liu, Z. & Liu, L. D. (2006*c*). *Chem. Phys. Lett.* **418**, 84–89.

Shi, J. M., Sun, Y. M., Liu, Z., Liu, L. D., Shi, W. & Cheng, P. (2006*d*). *Dalton Trans.* pp. 376–380.

Shi, J.-M., Xu, H.-Y. & Liu, L.-D. (2006e). *Acta Cryst.* E**62**, m1577–m1578.

Werner, J., Rams, M., Tomkowicz, Z. & Näther, C. (2014). *Dalton Trans.* **43**, 17333–17342.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Wöhlert, S., Fic, T., Tomkowicz, Z., Ebbinghaus, S. G., Rams, M., Haase, W. & Näther, C. (2013). *Inorg. Chem.* **52**, 12947–12957.

Zhang, L. P., Lu, W. J. & Mak, T. C. W. (2003). *Chem. Commun.* pp. 2830–2831.

Zhang, S.-G., Li, W.-N. & Shi, J.-M. (2006*a*). *Acta Cryst.* E**62**, m3398–m3400.

Zhang, S.-G., Li, W.-N. & Shi, J.-M. (2006*b*). *Acta Cryst.* E**62**, m3506–m3608.

# supporting information

*Acta Cryst.* (2024). E**80**, 174-179 [https://doi.org/10.1107/S2056989024000471]

# Synthesis and crystal structure of diisothiocyanatotetrakis(4-methylpyridine *N*-oxide)cobalt(II) and diisothiocyanatotris(4-methylpyridine *N*-oxide)cobalt(II) showing two different metal coordination polyhedra

**Christian Näther and Inke Jess**

## Computing details

### Tetrakis(4-methylpyridine *N*-oxide-κ*O*)bis(thiocyanato-κ*N*)cobalt(II) (1)

*Crystal data*

$[Co(NCS)_2(C_6H_7NO)_4]$
$M_r$ = 611.59
Triclinic, $P\overline{1}$
$a$ = 7.0709 (3) Å
$b$ = 9.6651 (5) Å
$c$ = 11.0401 (4) Å
$\alpha$ = 90.609 (3)°
$\beta$ = 96.346 (3)°
$\gamma$ = 108.090 (4)°
$V$ = 712.00 (6) Å$^3$
$Z$ = 1
$F(000)$ = 317
$D_x$ = 1.426 Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda$ = 1.54184 Å
Cell parameters from 5312 reflections
$\theta$ = 4.0–78.4°
$\mu$ = 6.45 mm$^{-1}$
$T$ = 100 K
Block, violet
0.12 × 0.08 × 0.04 mm

*Data collection*

Rigaku XtaLAB Synergy Dualflex diffractometer with a HyPix detector
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2021)
$T_{min}$ = 0.859, $T_{max}$ = 1.000
7433 measured reflections
2950 independent reflections
2935 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.017
$\theta_{max}$ = 79.9°, $\theta_{min}$ = 4.0°
$h$ = −8→6
$k$ = −12→12
$l$ = −13→14

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.081
$S$ = 1.11
2950 reflections
181 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.3098P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.47 e Å$^{-3}$
Extinction correction: SHELXL2016 (Sheldrick, 2015a), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0030 (6)

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Co1 | 0.500000 | 0.000000 | 0.500000 | 0.01633 (12) |
| N1 | 0.4838 (2) | −0.09719 (16) | 0.32743 (12) | 0.0207 (3) |
| C1 | 0.4728 (2) | −0.17698 (19) | 0.24550 (14) | 0.0205 (3) |
| S1 | 0.45856 (6) | −0.29171 (5) | 0.13159 (4) | 0.02849 (13) |
| O11 | 0.29908 (17) | −0.18891 (13) | 0.55992 (10) | 0.0207 (2) |
| N11 | 0.1767 (2) | −0.28091 (15) | 0.47249 (12) | 0.0177 (3) |
| C11 | 0.2312 (3) | −0.39113 (19) | 0.42796 (16) | 0.0232 (3) |
| H11 | 0.354482 | −0.404151 | 0.460193 | 0.028* |
| C12 | 0.1101 (3) | −0.48501 (19) | 0.33621 (16) | 0.0252 (4) |
| H12 | 0.149798 | −0.562764 | 0.305869 | 0.030* |
| C13 | −0.0708 (3) | −0.46695 (19) | 0.28735 (15) | 0.0231 (3) |
| C14 | −0.1231 (2) | −0.35312 (19) | 0.33727 (15) | 0.0216 (3) |
| H14 | −0.246404 | −0.338563 | 0.307292 | 0.026* |
| C15 | 0.0012 (2) | −0.26130 (18) | 0.42952 (15) | 0.0193 (3) |
| H15 | −0.036625 | −0.184181 | 0.462878 | 0.023* |
| C16 | −0.2018 (3) | −0.5642 (2) | 0.18404 (18) | 0.0328 (4) |
| H16A | −0.130107 | −0.552506 | 0.111847 | 0.049* |
| H16B | −0.324611 | −0.537857 | 0.165466 | 0.049* |
| H16C | −0.236267 | −0.665831 | 0.207245 | 0.049* |
| O21 | 0.24737 (17) | 0.07014 (13) | 0.44699 (10) | 0.0207 (2) |
| N21 | 0.1883 (2) | 0.09747 (15) | 0.33301 (12) | 0.0186 (3) |
| C21 | −0.0100 (2) | 0.06152 (18) | 0.29449 (15) | 0.0202 (3) |
| H21 | −0.104965 | 0.014060 | 0.347311 | 0.024* |
| C22 | −0.0750 (2) | 0.09351 (19) | 0.17864 (15) | 0.0217 (3) |
| H22 | −0.214644 | 0.067556 | 0.152642 | 0.026* |
| C23 | 0.0608 (3) | 0.16314 (19) | 0.09945 (15) | 0.0226 (3) |
| C24 | 0.2635 (3) | 0.1974 (2) | 0.14277 (16) | 0.0258 (4) |
| H24 | 0.360977 | 0.244184 | 0.091201 | 0.031* |
| C25 | 0.3255 (2) | 0.1652 (2) | 0.25860 (16) | 0.0236 (4) |
| H25 | 0.464495 | 0.190292 | 0.286400 | 0.028* |
| C26 | −0.0054 (3) | 0.2016 (2) | −0.02611 (16) | 0.0284 (4) |
| H26A | −0.131570 | 0.128174 | −0.058861 | 0.043* |
| H26B | 0.097434 | 0.204362 | −0.079528 | 0.043* |
| H26C | −0.025290 | 0.297392 | −0.021875 | 0.043* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Co1 | 0.01222 (18) | 0.0232 (2) | 0.01451 (18) | 0.00671 (14) | 0.00198 (12) | 0.00032 (13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N1 | 0.0185 (7) | 0.0275 (7) | 0.0160 (6) | 0.0071 (5) | 0.0021 (5) | −0.0012 (5) |
| C1 | 0.0131 (7) | 0.0322 (9) | 0.0179 (7) | 0.0095 (6) | 0.0013 (6) | 0.0045 (6) |
| S1 | 0.0247 (2) | 0.0448 (3) | 0.0193 (2) | 0.01733 (19) | −0.00083 (15) | −0.00852 (17) |
| O11 | 0.0159 (5) | 0.0261 (6) | 0.0171 (5) | 0.0032 (4) | −0.0003 (4) | 0.0014 (4) |
| N11 | 0.0152 (6) | 0.0216 (7) | 0.0152 (6) | 0.0042 (5) | 0.0022 (5) | 0.0016 (5) |
| C11 | 0.0197 (8) | 0.0276 (9) | 0.0261 (8) | 0.0118 (7) | 0.0054 (6) | 0.0047 (7) |
| C12 | 0.0284 (9) | 0.0233 (8) | 0.0269 (8) | 0.0107 (7) | 0.0085 (7) | 0.0015 (7) |
| C13 | 0.0263 (9) | 0.0223 (8) | 0.0193 (8) | 0.0050 (7) | 0.0039 (6) | 0.0026 (6) |
| C14 | 0.0190 (8) | 0.0250 (8) | 0.0206 (8) | 0.0076 (6) | −0.0004 (6) | 0.0026 (6) |
| C15 | 0.0178 (7) | 0.0227 (8) | 0.0187 (7) | 0.0080 (6) | 0.0026 (6) | 0.0012 (6) |
| C16 | 0.0377 (11) | 0.0256 (9) | 0.0305 (9) | 0.0055 (8) | −0.0017 (8) | −0.0054 (7) |
| O21 | 0.0191 (5) | 0.0319 (6) | 0.0146 (5) | 0.0127 (5) | 0.0026 (4) | 0.0039 (4) |
| N21 | 0.0172 (6) | 0.0250 (7) | 0.0160 (6) | 0.0101 (5) | 0.0011 (5) | 0.0017 (5) |
| C21 | 0.0145 (7) | 0.0241 (8) | 0.0240 (8) | 0.0085 (6) | 0.0040 (6) | −0.0004 (6) |
| C22 | 0.0174 (8) | 0.0263 (8) | 0.0236 (8) | 0.0115 (6) | −0.0006 (6) | −0.0008 (6) |
| C23 | 0.0224 (8) | 0.0269 (9) | 0.0222 (8) | 0.0133 (7) | 0.0016 (6) | 0.0014 (6) |
| C24 | 0.0197 (8) | 0.0359 (10) | 0.0229 (8) | 0.0096 (7) | 0.0052 (6) | 0.0060 (7) |
| C25 | 0.0148 (7) | 0.0334 (9) | 0.0233 (8) | 0.0081 (7) | 0.0036 (6) | 0.0063 (7) |
| C26 | 0.0269 (9) | 0.0390 (10) | 0.0228 (8) | 0.0157 (8) | 0.0008 (7) | 0.0055 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Co1—N1 | 2.0910 (14) | C15—H15 | 0.9500 |
| Co1—N1$^{i}$ | 2.0910 (14) | C16—H16A | 0.9800 |
| Co1—O11 | 2.1005 (12) | C16—H16B | 0.9800 |
| Co1—O11$^{i}$ | 2.1005 (12) | C16—H16C | 0.9800 |
| Co1—O21$^{i}$ | 2.1266 (11) | O21—N21 | 1.3369 (17) |
| Co1—O21 | 2.1266 (11) | N21—C21 | 1.352 (2) |
| N1—C1 | 1.163 (2) | N21—C25 | 1.356 (2) |
| C1—S1 | 1.6414 (18) | C21—H21 | 0.9500 |
| O11—N11 | 1.3381 (17) | C21—C22 | 1.382 (2) |
| N11—C11 | 1.346 (2) | C22—H22 | 0.9500 |
| N11—C15 | 1.348 (2) | C22—C23 | 1.391 (2) |
| C11—H11 | 0.9500 | C23—C24 | 1.393 (2) |
| C11—C12 | 1.374 (3) | C23—C26 | 1.501 (2) |
| C12—H12 | 0.9500 | C24—H24 | 0.9500 |
| C12—C13 | 1.394 (3) | C24—C25 | 1.376 (2) |
| C13—C14 | 1.392 (3) | C25—H25 | 0.9500 |
| C13—C16 | 1.498 (2) | C26—H26A | 0.9800 |
| C14—H14 | 0.9500 | C26—H26B | 0.9800 |
| C14—C15 | 1.377 (2) | C26—H26C | 0.9800 |
| | | | |
| N1—Co1—N1$^{i}$ | 180.00 (8) | N11—C15—H15 | 120.0 |
| N1$^{i}$—Co1—O11$^{i}$ | 92.39 (5) | C14—C15—H15 | 120.0 |
| N1—Co1—O11$^{i}$ | 87.61 (5) | C13—C16—H16A | 109.5 |
| N1$^{i}$—Co1—O11 | 87.61 (5) | C13—C16—H16B | 109.5 |
| N1—Co1—O11 | 92.39 (5) | C13—C16—H16C | 109.5 |
| N1—Co1—O21$^{i}$ | 87.56 (5) | H16A—C16—H16B | 109.5 |

| | | | |
|---|---|---|---|
| N1$^{i}$—Co1—O21$^{i}$ | 92.44 (5) | H16A—C16—H16C | 109.5 |
| N1$^{i}$—Co1—O21 | 87.56 (5) | H16B—C16—H16C | 109.5 |
| N1—Co1—O21 | 92.44 (5) | N21—O21—Co1 | 125.03 (9) |
| O11—Co1—O11$^{i}$ | 180.00 (5) | O21—N21—C21 | 119.16 (13) |
| O11$^{i}$—Co1—O21$^{i}$ | 87.15 (5) | O21—N21—C25 | 120.30 (13) |
| O11—Co1—O21 | 87.15 (5) | C21—N21—C25 | 120.50 (14) |
| O11$^{i}$—Co1—O21 | 92.85 (5) | N21—C21—H21 | 119.9 |
| O11—Co1—O21$^{i}$ | 92.85 (5) | N21—C21—C22 | 120.29 (15) |
| O21$^{i}$—Co1—O21 | 180.0 | C22—C21—H21 | 119.9 |
| Co1—N1—C1 | 165.56 (14) | C21—C22—H22 | 119.5 |
| N1—C1—S1 | 178.94 (16) | C21—C22—C23 | 121.07 (15) |
| N11—O11—Co1 | 115.97 (9) | C23—C22—H22 | 119.5 |
| O11—N11—C11 | 119.50 (14) | C22—C23—C24 | 116.66 (15) |
| O11—N11—C15 | 119.60 (14) | C22—C23—C26 | 122.24 (16) |
| C11—N11—C15 | 120.90 (14) | C24—C23—C26 | 121.09 (16) |
| N11—C11—H11 | 119.7 | C23—C24—H24 | 119.3 |
| N11—C11—C12 | 120.53 (16) | C25—C24—C23 | 121.49 (16) |
| C12—C11—H11 | 119.7 | C25—C24—H24 | 119.3 |
| C11—C12—H12 | 119.8 | N21—C25—C24 | 119.99 (15) |
| C11—C12—C13 | 120.48 (16) | N21—C25—H25 | 120.0 |
| C13—C12—H12 | 119.8 | C24—C25—H25 | 120.0 |
| C12—C13—C16 | 121.54 (17) | C23—C26—H26A | 109.5 |
| C14—C13—C12 | 117.17 (16) | C23—C26—H26B | 109.5 |
| C14—C13—C16 | 121.28 (16) | C23—C26—H26C | 109.5 |
| C13—C14—H14 | 119.5 | H26A—C26—H26B | 109.5 |
| C15—C14—C13 | 120.93 (16) | H26A—C26—H26C | 109.5 |
| C15—C14—H14 | 119.5 | H26B—C26—H26C | 109.5 |
| N11—C15—C14 | 119.97 (15) | | |

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C14—H14···S1$^{ii}$ | 0.95 | 2.83 | 3.7271 (17) | 157 |
| C15—H15···O21$^{iii}$ | 0.95 | 2.40 | 3.295 (2) | 157 |
| C21—H21···O21$^{iii}$ | 0.95 | 2.62 | 3.520 (2) | 158 |
| C24—H24···S1$^{iv}$ | 0.95 | 2.87 | 3.7591 (18) | 156 |
| C25—H25···O11$^{i}$ | 0.95 | 2.25 | 3.090 (2) | 147 |

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) −*x*, −*y*, −*z*+1; (iv) −*x*+1, −*y*, −*z*.

## Tris(4-methylpyridine *N*-oxide-*κO*)bis(thiocyanato-*κN*)cobalt(II) (2)

*Crystal data*

[Co(NCS)$_2$(C$_6$H$_7$NO)$_3$]
$M_r$ = 502.47
Triclinic, $P\overline{1}$
*a* = 11.70330 (8) Å
*b* = 12.55284 (9) Å
*c* = 17.5256 (2) Å
*α* = 93.5044 (8)°
*β* = 91.8625 (8)°
*γ* = 115.0705 (7)°
*V* = 2322.89 (4) Å$^3$

$Z = 4$
$F(000) = 1036$
$D_x = 1.437$ Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 22375 reflections
$\theta = 3.9–79.4°$
$\mu = 7.74$ mm$^{-1}$
$T = 100$ K
Block, violet
0.2 × 0.18 × 0.1 mm

*Data collection*

Rigaku XtaLAB Synergy Dualflex diffractometer with a HyPix detector
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2021)
$T_{min} = 0.024$, $T_{max} = 0.116$
11225 measured reflections
11225 independent reflections
10980 reflections with $I > 2\sigma(I)$
$\theta_{max} = 80.3°$, $\theta_{min} = 2.5°$
$h = -14\rightarrow14$
$k = -15\rightarrow15$
$l = -22\rightarrow22$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.081$
$S = 1.07$
11225 reflections
566 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.8076P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å$^{-3}$
$\Delta\rho_{min} = -0.25$ e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement**. Refined as a 2-component twin.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Co1 | 0.87727 (3) | 0.63471 (2) | 0.08404 (2) | 0.03107 (7) |
| N1 | 1.05248 (15) | 0.77002 (14) | 0.06799 (10) | 0.0364 (3) |
| C1 | 1.14327 (17) | 0.85769 (17) | 0.06745 (11) | 0.0340 (4) |
| S1 | 1.27208 (4) | 0.98014 (4) | 0.06637 (3) | 0.04113 (11) |
| N2 | 0.70108 (14) | 0.49727 (14) | 0.09855 (9) | 0.0336 (3) |
| C2 | 0.61353 (17) | 0.40560 (16) | 0.09628 (10) | 0.0332 (4) |
| S2 | 0.49072 (4) | 0.27783 (4) | 0.09380 (3) | 0.03765 (10) |
| O11 | 0.81378 (12) | 0.74195 (11) | 0.13747 (8) | 0.0370 (3) |
| N11 | 0.89135 (14) | 0.85821 (13) | 0.14616 (9) | 0.0333 (3) |
| C11 | 0.97058 (18) | 0.90240 (17) | 0.20938 (11) | 0.0359 (4) |
| H11 | 0.970160 | 0.851990 | 0.247757 | 0.043* |
| C12 | 1.05192 (18) | 1.02021 (17) | 0.21838 (11) | 0.0367 (4) |
| H12 | 1.107390 | 1.050856 | 0.263117 | 0.044* |
| C13 | 1.05383 (18) | 1.09533 (17) | 0.16239 (11) | 0.0346 (4) |

| | | | | |
|---|---|---|---|---|
| C14 | 0.96919 (18) | 1.04603 (17) | 0.09893 (11) | 0.0350 (4) |
| H14 | 0.966689 | 1.094846 | 0.060173 | 0.042* |
| C15 | 0.88907 (18) | 0.92801 (17) | 0.09118 (11) | 0.0354 (4) |
| H15 | 0.832126 | 0.895551 | 0.047195 | 0.042* |
| C16 | 1.1468 (2) | 1.22268 (18) | 0.16920 (13) | 0.0432 (4) |
| H16A | 1.160465 | 1.253518 | 0.223087 | 0.065* |
| H16B | 1.113463 | 1.267842 | 0.139177 | 0.065* |
| H16C | 1.227112 | 1.229938 | 0.149776 | 0.065* |
| O21 | 0.85790 (12) | 0.59878 (11) | −0.02960 (8) | 0.0387 (3) |
| N21 | 0.75725 (15) | 0.49966 (14) | −0.05742 (9) | 0.0345 (3) |
| C21 | 0.64766 (19) | 0.50453 (18) | −0.07788 (11) | 0.0380 (4) |
| H21 | 0.642351 | 0.578101 | −0.074644 | 0.046* |
| C22 | 0.54344 (19) | 0.40278 (18) | −0.10347 (12) | 0.0393 (4) |
| H22 | 0.466736 | 0.406627 | −0.118740 | 0.047* |
| C23 | 0.54960 (18) | 0.29452 (18) | −0.10714 (11) | 0.0380 (4) |
| C24 | 0.66481 (18) | 0.29383 (17) | −0.08511 (12) | 0.0373 (4) |
| H24 | 0.672089 | 0.221193 | −0.086544 | 0.045* |
| C25 | 0.76740 (18) | 0.39666 (17) | −0.06148 (11) | 0.0365 (4) |
| H25 | 0.846042 | 0.395408 | −0.047894 | 0.044* |
| C26 | 0.4372 (2) | 0.1817 (2) | −0.13225 (15) | 0.0506 (5) |
| H26A | 0.414610 | 0.130513 | −0.089887 | 0.076* |
| H26B | 0.457444 | 0.141697 | −0.175943 | 0.076* |
| H26C | 0.365747 | 0.198853 | −0.147350 | 0.076* |
| O31 | 0.96976 (12) | 0.55822 (12) | 0.14100 (9) | 0.0401 (3) |
| N31 | 0.89880 (15) | 0.45128 (14) | 0.16484 (10) | 0.0355 (3) |
| C31 | 0.88804 (18) | 0.35399 (18) | 0.12180 (12) | 0.0383 (4) |
| H31 | 0.935574 | 0.361629 | 0.077893 | 0.046* |
| C32 | 0.8084 (2) | 0.24428 (18) | 0.14168 (12) | 0.0404 (4) |
| H32 | 0.800278 | 0.176188 | 0.110891 | 0.048* |
| C33 | 0.73886 (19) | 0.23121 (17) | 0.20659 (12) | 0.0387 (4) |
| C34 | 0.75831 (19) | 0.33383 (18) | 0.25114 (12) | 0.0393 (4) |
| H34 | 0.715986 | 0.328356 | 0.297091 | 0.047* |
| C35 | 0.83775 (19) | 0.44285 (17) | 0.22969 (11) | 0.0376 (4) |
| H35 | 0.849641 | 0.512152 | 0.260476 | 0.045* |
| C36 | 0.6449 (2) | 0.1123 (2) | 0.22542 (14) | 0.0521 (5) |
| H36A | 0.576176 | 0.079770 | 0.185175 | 0.078* |
| H36B | 0.610313 | 0.119739 | 0.274605 | 0.078* |
| H36C | 0.686615 | 0.059380 | 0.228816 | 0.078* |
| Co2 | 0.35615 (3) | 0.11924 (2) | 0.41874 (2) | 0.03115 (7) |
| N3 | 0.53440 (15) | 0.25825 (14) | 0.44106 (10) | 0.0361 (3) |
| C3 | 0.62725 (17) | 0.34432 (16) | 0.44440 (10) | 0.0333 (4) |
| S3 | 0.75865 (4) | 0.46580 (4) | 0.44927 (3) | 0.03878 (10) |
| N4 | 0.18025 (14) | −0.02361 (14) | 0.39579 (9) | 0.0343 (3) |
| C4 | 0.09849 (17) | −0.11823 (16) | 0.39280 (10) | 0.0330 (4) |
| S4 | −0.01714 (5) | −0.25075 (4) | 0.38844 (3) | 0.04076 (11) |
| O41 | 0.28977 (12) | 0.21590 (11) | 0.36094 (8) | 0.0358 (3) |
| N41 | 0.37181 (14) | 0.32772 (14) | 0.35101 (9) | 0.0330 (3) |
| C41 | 0.38679 (18) | 0.41538 (17) | 0.40442 (11) | 0.0350 (4) |

| | | | | |
|---|---|---|---|---|
| H41 | 0.338588 | 0.398404 | 0.448341 | 0.042* |
| C42 | 0.47149 (18) | 0.52902 (17) | 0.39546 (11) | 0.0362 (4) |
| H42 | 0.482020 | 0.590067 | 0.433658 | 0.043* |
| C43 | 0.54250 (18) | 0.55631 (17) | 0.33101 (11) | 0.0353 (4) |
| C44 | 0.52331 (18) | 0.46289 (17) | 0.27734 (11) | 0.0361 (4) |
| H44 | 0.569378 | 0.477614 | 0.232525 | 0.043* |
| C45 | 0.43865 (18) | 0.34961 (17) | 0.28823 (11) | 0.0351 (4) |
| H45 | 0.427369 | 0.286708 | 0.251345 | 0.042* |
| C46 | 0.6381 (2) | 0.67946 (18) | 0.32134 (14) | 0.0467 (5) |
| H46A | 0.604421 | 0.735722 | 0.338290 | 0.070* |
| H46B | 0.656353 | 0.687183 | 0.267249 | 0.070* |
| H46C | 0.716030 | 0.695957 | 0.352149 | 0.070* |
| O51 | 0.44472 (13) | 0.03239 (12) | 0.36803 (9) | 0.0428 (3) |
| N51 | 0.37995 (15) | −0.08235 (14) | 0.34244 (10) | 0.0372 (3) |
| C51 | 0.30902 (19) | −0.11292 (18) | 0.27584 (11) | 0.0380 (4) |
| H51 | 0.304767 | −0.053571 | 0.246299 | 0.046* |
| C52 | 0.24278 (19) | −0.22988 (18) | 0.25057 (11) | 0.0382 (4) |
| H52 | 0.192085 | −0.251061 | 0.203803 | 0.046* |
| C53 | 0.24931 (18) | −0.31784 (17) | 0.29300 (11) | 0.0375 (4) |
| C54 | 0.32194 (19) | −0.28153 (18) | 0.36173 (12) | 0.0400 (4) |
| H54 | 0.326632 | −0.339102 | 0.392848 | 0.048* |
| C55 | 0.38710 (19) | −0.16438 (18) | 0.38572 (12) | 0.0407 (4) |
| H55 | 0.437167 | −0.141148 | 0.432762 | 0.049* |
| C56 | 0.1801 (2) | −0.44603 (19) | 0.26705 (14) | 0.0520 (5) |
| H56A | 0.101210 | −0.480407 | 0.293084 | 0.078* |
| H56B | 0.232895 | −0.486601 | 0.279491 | 0.078* |
| H56C | 0.160765 | −0.455140 | 0.211550 | 0.078* |
| O61 | 0.34565 (13) | 0.11125 (12) | 0.53174 (8) | 0.0410 (3) |
| N61 | 0.25378 (15) | 0.01407 (14) | 0.55669 (9) | 0.0355 (3) |
| C61 | 0.27566 (18) | −0.08185 (18) | 0.56382 (11) | 0.0386 (4) |
| H61 | 0.356316 | −0.078782 | 0.554042 | 0.046* |
| C62 | 0.18226 (18) | −0.18381 (18) | 0.58510 (12) | 0.0391 (4) |
| H62 | 0.198213 | −0.251449 | 0.589358 | 0.047* |
| C63 | 0.06403 (18) | −0.18932 (18) | 0.60056 (11) | 0.0375 (4) |
| C64 | 0.04626 (18) | −0.08750 (18) | 0.59427 (11) | 0.0386 (4) |
| H64 | −0.032499 | −0.087445 | 0.605725 | 0.046* |
| C65 | 0.14146 (19) | 0.01333 (18) | 0.57162 (11) | 0.0380 (4) |
| H65 | 0.127867 | 0.082073 | 0.566563 | 0.046* |
| C66 | −0.0390 (2) | −0.3012 (2) | 0.62263 (15) | 0.0505 (5) |
| H66A | −0.068265 | −0.359616 | 0.578254 | 0.076* |
| H66B | −0.109516 | −0.285417 | 0.639936 | 0.076* |
| H66C | −0.006565 | −0.331754 | 0.664154 | 0.076* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Co1 | 0.02863 (14) | 0.02864 (14) | 0.03621 (15) | 0.01222 (11) | 0.00333 (11) | 0.00390 (11) |
| N1 | 0.0305 (8) | 0.0337 (8) | 0.0446 (9) | 0.0128 (6) | 0.0041 (6) | 0.0059 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C1 | 0.0335 (9) | 0.0349 (9) | 0.0376 (9) | 0.0181 (8) | 0.0016 (7) | 0.0061 (7) |
| S1 | 0.0309 (2) | 0.0339 (2) | 0.0544 (3) | 0.00922 (18) | 0.00113 (19) | 0.0089 (2) |
| N2 | 0.0308 (7) | 0.0336 (8) | 0.0355 (8) | 0.0128 (6) | 0.0040 (6) | 0.0033 (6) |
| C2 | 0.0351 (9) | 0.0358 (9) | 0.0326 (9) | 0.0186 (8) | 0.0055 (7) | 0.0031 (7) |
| S2 | 0.0334 (2) | 0.0321 (2) | 0.0426 (2) | 0.00919 (17) | 0.00627 (18) | 0.00218 (18) |
| O11 | 0.0343 (6) | 0.0293 (6) | 0.0458 (7) | 0.0120 (5) | 0.0058 (5) | 0.0012 (5) |
| N11 | 0.0318 (7) | 0.0315 (7) | 0.0372 (8) | 0.0143 (6) | 0.0035 (6) | 0.0018 (6) |
| C11 | 0.0391 (9) | 0.0367 (9) | 0.0347 (9) | 0.0184 (8) | 0.0023 (7) | 0.0063 (7) |
| C12 | 0.0365 (9) | 0.0401 (10) | 0.0336 (9) | 0.0167 (8) | 0.0000 (7) | 0.0021 (7) |
| C13 | 0.0341 (9) | 0.0349 (9) | 0.0370 (9) | 0.0166 (7) | 0.0054 (7) | 0.0037 (7) |
| C14 | 0.0370 (9) | 0.0380 (9) | 0.0351 (9) | 0.0202 (8) | 0.0042 (7) | 0.0076 (7) |
| C15 | 0.0354 (9) | 0.0408 (10) | 0.0335 (9) | 0.0198 (8) | 0.0011 (7) | 0.0030 (7) |
| C16 | 0.0413 (10) | 0.0371 (10) | 0.0482 (11) | 0.0134 (8) | 0.0023 (8) | 0.0073 (8) |
| O21 | 0.0351 (7) | 0.0347 (7) | 0.0387 (7) | 0.0074 (5) | 0.0061 (5) | 0.0018 (5) |
| N21 | 0.0335 (8) | 0.0355 (8) | 0.0328 (7) | 0.0131 (6) | 0.0049 (6) | 0.0022 (6) |
| C21 | 0.0405 (10) | 0.0393 (10) | 0.0389 (10) | 0.0211 (8) | 0.0056 (8) | 0.0062 (8) |
| C22 | 0.0350 (9) | 0.0451 (11) | 0.0418 (10) | 0.0209 (8) | 0.0027 (8) | 0.0040 (8) |
| C23 | 0.0348 (9) | 0.0402 (10) | 0.0399 (10) | 0.0172 (8) | 0.0033 (7) | 0.0012 (8) |
| C24 | 0.0372 (9) | 0.0375 (9) | 0.0405 (10) | 0.0190 (8) | 0.0054 (8) | 0.0029 (8) |
| C25 | 0.0324 (9) | 0.0406 (10) | 0.0396 (10) | 0.0184 (8) | 0.0034 (7) | 0.0038 (8) |
| C26 | 0.0358 (10) | 0.0445 (11) | 0.0670 (15) | 0.0142 (9) | −0.0017 (10) | −0.0034 (10) |
| O31 | 0.0314 (6) | 0.0334 (7) | 0.0546 (8) | 0.0116 (5) | 0.0033 (6) | 0.0134 (6) |
| N31 | 0.0310 (7) | 0.0346 (8) | 0.0424 (8) | 0.0147 (6) | 0.0029 (6) | 0.0089 (6) |
| C31 | 0.0381 (10) | 0.0429 (10) | 0.0399 (10) | 0.0222 (8) | 0.0087 (8) | 0.0069 (8) |
| C32 | 0.0448 (11) | 0.0369 (10) | 0.0430 (10) | 0.0206 (8) | 0.0061 (8) | 0.0038 (8) |
| C33 | 0.0380 (10) | 0.0375 (10) | 0.0411 (10) | 0.0158 (8) | 0.0036 (8) | 0.0077 (8) |
| C34 | 0.0407 (10) | 0.0436 (10) | 0.0368 (9) | 0.0203 (8) | 0.0061 (8) | 0.0067 (8) |
| C35 | 0.0403 (10) | 0.0386 (9) | 0.0377 (9) | 0.0207 (8) | 0.0015 (8) | 0.0019 (7) |
| C36 | 0.0555 (13) | 0.0411 (11) | 0.0532 (13) | 0.0131 (10) | 0.0079 (10) | 0.0102 (9) |
| Co2 | 0.02840 (14) | 0.03116 (15) | 0.03437 (15) | 0.01296 (12) | 0.00080 (11) | 0.00492 (11) |
| N3 | 0.0315 (8) | 0.0350 (8) | 0.0408 (8) | 0.0132 (7) | −0.0009 (6) | 0.0040 (6) |
| C3 | 0.0341 (9) | 0.0363 (9) | 0.0330 (9) | 0.0186 (8) | 0.0012 (7) | 0.0021 (7) |
| S3 | 0.0320 (2) | 0.0347 (2) | 0.0445 (2) | 0.00978 (17) | 0.00310 (18) | −0.00029 (18) |
| N4 | 0.0303 (7) | 0.0372 (8) | 0.0359 (8) | 0.0149 (6) | 0.0018 (6) | 0.0033 (6) |
| C4 | 0.0320 (9) | 0.0371 (9) | 0.0327 (9) | 0.0171 (8) | 0.0017 (7) | 0.0049 (7) |
| S4 | 0.0360 (2) | 0.0351 (2) | 0.0443 (2) | 0.00832 (18) | 0.00144 (19) | 0.00562 (19) |
| O41 | 0.0312 (6) | 0.0328 (6) | 0.0418 (7) | 0.0119 (5) | 0.0004 (5) | 0.0077 (5) |
| N41 | 0.0310 (7) | 0.0338 (8) | 0.0358 (8) | 0.0151 (6) | 0.0001 (6) | 0.0055 (6) |
| C41 | 0.0352 (9) | 0.0416 (10) | 0.0340 (9) | 0.0219 (8) | 0.0018 (7) | 0.0038 (7) |
| C42 | 0.0381 (9) | 0.0379 (9) | 0.0368 (9) | 0.0209 (8) | −0.0022 (7) | −0.0005 (7) |
| C43 | 0.0335 (9) | 0.0359 (9) | 0.0381 (9) | 0.0164 (7) | −0.0017 (7) | 0.0037 (7) |
| C44 | 0.0355 (9) | 0.0382 (10) | 0.0350 (9) | 0.0160 (8) | 0.0034 (7) | 0.0040 (7) |
| C45 | 0.0376 (9) | 0.0371 (9) | 0.0327 (9) | 0.0184 (8) | 0.0014 (7) | 0.0009 (7) |
| C46 | 0.0456 (11) | 0.0375 (10) | 0.0518 (12) | 0.0129 (9) | 0.0024 (9) | 0.0023 (9) |
| O51 | 0.0306 (6) | 0.0349 (7) | 0.0607 (9) | 0.0129 (5) | 0.0022 (6) | −0.0025 (6) |
| N51 | 0.0306 (8) | 0.0367 (8) | 0.0462 (9) | 0.0164 (6) | 0.0036 (6) | 0.0006 (7) |
| C51 | 0.0393 (10) | 0.0420 (10) | 0.0380 (10) | 0.0219 (8) | 0.0055 (8) | 0.0071 (8) |
| C52 | 0.0406 (10) | 0.0448 (10) | 0.0332 (9) | 0.0222 (8) | 0.0004 (7) | 0.0023 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C53 | 0.0357 (9) | 0.0384 (10) | 0.0388 (10) | 0.0165 (8) | 0.0007 (7) | 0.0017 (8) |
| C54 | 0.0395 (10) | 0.0411 (10) | 0.0425 (10) | 0.0205 (8) | −0.0027 (8) | 0.0046 (8) |
| C55 | 0.0373 (10) | 0.0439 (11) | 0.0432 (10) | 0.0204 (8) | −0.0056 (8) | 0.0002 (8) |
| C56 | 0.0575 (13) | 0.0397 (11) | 0.0535 (13) | 0.0169 (10) | −0.0128 (10) | 0.0027 (9) |
| O61 | 0.0366 (7) | 0.0384 (7) | 0.0380 (7) | 0.0060 (6) | 0.0000 (5) | 0.0072 (6) |
| N61 | 0.0331 (8) | 0.0383 (8) | 0.0327 (7) | 0.0127 (6) | 0.0013 (6) | 0.0054 (6) |
| C61 | 0.0314 (9) | 0.0472 (11) | 0.0416 (10) | 0.0201 (8) | 0.0037 (7) | 0.0100 (8) |
| C62 | 0.0358 (10) | 0.0427 (10) | 0.0443 (10) | 0.0209 (8) | 0.0030 (8) | 0.0104 (8) |
| C63 | 0.0331 (9) | 0.0444 (10) | 0.0359 (9) | 0.0168 (8) | 0.0028 (7) | 0.0077 (8) |
| C64 | 0.0345 (9) | 0.0484 (11) | 0.0379 (10) | 0.0221 (8) | 0.0049 (7) | 0.0043 (8) |
| C65 | 0.0388 (10) | 0.0430 (10) | 0.0360 (9) | 0.0213 (8) | 0.0016 (8) | 0.0029 (8) |
| C66 | 0.0348 (10) | 0.0507 (12) | 0.0633 (14) | 0.0140 (9) | 0.0064 (9) | 0.0161 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Co1—N1 | 2.0767 (16) | Co2—N3 | 2.0804 (16) |
| Co1—N2 | 2.0895 (15) | Co2—N4 | 2.0844 (16) |
| Co1—O11 | 1.9949 (13) | Co2—O41 | 1.9999 (13) |
| Co1—O21 | 1.9989 (14) | Co2—O51 | 1.9880 (14) |
| Co1—O31 | 2.0045 (14) | Co2—O61 | 1.9941 (14) |
| N1—C1 | 1.162 (2) | N3—C3 | 1.160 (2) |
| C1—S1 | 1.6362 (19) | C3—S3 | 1.6388 (19) |
| N2—C2 | 1.170 (2) | N4—C4 | 1.164 (2) |
| C2—S2 | 1.6352 (19) | C4—S4 | 1.6353 (19) |
| O11—N11 | 1.348 (2) | O41—N41 | 1.3494 (19) |
| N11—C11 | 1.348 (2) | N41—C41 | 1.348 (2) |
| N11—C15 | 1.348 (2) | N41—C45 | 1.345 (2) |
| C11—H11 | 0.9500 | C41—H41 | 0.9500 |
| C11—C12 | 1.374 (3) | C41—C42 | 1.372 (3) |
| C12—H12 | 0.9500 | C42—H42 | 0.9500 |
| C12—C13 | 1.396 (3) | C42—C43 | 1.397 (3) |
| C13—C14 | 1.388 (3) | C43—C44 | 1.392 (3) |
| C13—C16 | 1.499 (3) | C43—C46 | 1.500 (3) |
| C14—H14 | 0.9500 | C44—H44 | 0.9500 |
| C14—C15 | 1.372 (3) | C44—C45 | 1.375 (3) |
| C15—H15 | 0.9500 | C45—H45 | 0.9500 |
| C16—H16A | 0.9800 | C46—H46A | 0.9800 |
| C16—H16B | 0.9800 | C46—H46B | 0.9800 |
| C16—H16C | 0.9800 | C46—H46C | 0.9800 |
| O21—N21 | 1.349 (2) | O51—N51 | 1.351 (2) |
| N21—C21 | 1.348 (2) | N51—C51 | 1.346 (3) |
| N21—C25 | 1.345 (3) | N51—C55 | 1.344 (3) |
| C21—H21 | 0.9500 | C51—H51 | 0.9500 |
| C21—C22 | 1.376 (3) | C51—C52 | 1.373 (3) |
| C22—H22 | 0.9500 | C52—H52 | 0.9500 |
| C22—C23 | 1.389 (3) | C52—C53 | 1.395 (3) |
| C23—C24 | 1.394 (3) | C53—C54 | 1.385 (3) |
| C23—C26 | 1.496 (3) | C53—C56 | 1.495 (3) |

| | | | |
|---|---|---|---|
| C24—H24 | 0.9500 | C54—H54 | 0.9500 |
| C24—C25 | 1.367 (3) | C54—C55 | 1.369 (3) |
| C25—H25 | 0.9500 | C55—H55 | 0.9500 |
| C26—H26A | 0.9800 | C56—H56A | 0.9800 |
| C26—H26B | 0.9800 | C56—H56B | 0.9800 |
| C26—H26C | 0.9800 | C56—H56C | 0.9800 |
| O31—N31 | 1.346 (2) | O61—N61 | 1.349 (2) |
| N31—C31 | 1.352 (3) | N61—C61 | 1.345 (3) |
| N31—C35 | 1.348 (3) | N61—C65 | 1.345 (2) |
| C31—H31 | 0.9500 | C61—H61 | 0.9500 |
| C31—C32 | 1.371 (3) | C61—C62 | 1.368 (3) |
| C32—H32 | 0.9500 | C62—H62 | 0.9500 |
| C32—C33 | 1.397 (3) | C62—C63 | 1.392 (3) |
| C33—C34 | 1.392 (3) | C63—C64 | 1.389 (3) |
| C33—C36 | 1.497 (3) | C63—C66 | 1.495 (3) |
| C34—H34 | 0.9500 | C64—H64 | 0.9500 |
| C34—C35 | 1.373 (3) | C64—C65 | 1.377 (3) |
| C35—H35 | 0.9500 | C65—H65 | 0.9500 |
| C36—H36A | 0.9800 | C66—H66A | 0.9800 |
| C36—H36B | 0.9800 | C66—H66B | 0.9800 |
| C36—H36C | 0.9800 | C66—H66C | 0.9800 |

| | | | |
|---|---|---|---|
| N1—Co1—N2 | 179.11 (7) | N3—Co2—N4 | 178.20 (6) |
| O11—Co1—N1 | 93.86 (6) | O41—Co2—N3 | 93.31 (6) |
| O11—Co1—N2 | 86.87 (6) | O41—Co2—N4 | 88.08 (6) |
| O11—Co1—O21 | 122.93 (6) | O51—Co2—N3 | 86.15 (6) |
| O11—Co1—O31 | 121.98 (6) | O51—Co2—N4 | 92.14 (6) |
| O21—Co1—N1 | 87.05 (6) | O51—Co2—O41 | 122.04 (6) |
| O21—Co1—N2 | 92.13 (6) | O51—Co2—O61 | 115.95 (6) |
| O21—Co1—O31 | 115.07 (6) | O61—Co2—N3 | 87.50 (6) |
| O31—Co1—N1 | 87.43 (6) | O61—Co2—N4 | 92.75 (6) |
| O31—Co1—N2 | 92.62 (6) | O61—Co2—O41 | 121.94 (6) |
| Co1—N1—Co | 167.85 (16) | Co2—N3—Co3 | 168.81 (15) |
| N1—C1—S1 | 179.28 (19) | N3—C3—S3 | 179.8 (2) |
| C2—N2—Co1 | 164.31 (15) | C4—N4—Co2 | 161.93 (15) |
| N2—C2—S2 | 179.49 (19) | N4—C4—S4 | 179.57 (19) |
| N11—O11—Co1 | 117.79 (10) | N41—O41—Co2 | 117.09 (10) |
| C11—N11—O11 | 119.39 (15) | C41—N41—O41 | 119.69 (16) |
| C11—N11—C15 | 121.18 (16) | C45—N41—O41 | 119.27 (15) |
| C15—N11—O11 | 119.44 (15) | C45—N41—C41 | 121.03 (16) |
| N11—C11—H11 | 120.0 | N41—C41—H41 | 119.9 |
| N11—C11—C12 | 120.10 (17) | N41—C41—C42 | 120.12 (18) |
| C12—C11—H11 | 120.0 | C42—C41—H41 | 119.9 |
| C11—C12—H12 | 119.7 | C41—C42—H42 | 119.5 |
| C11—C12—C13 | 120.61 (18) | C41—C42—C43 | 120.98 (18) |
| C13—C12—H12 | 119.7 | C43—C42—H42 | 119.5 |
| C12—C13—C16 | 121.34 (18) | C42—C43—C46 | 121.69 (18) |
| C14—C13—C12 | 117.13 (17) | C44—C43—C42 | 116.75 (18) |

| | | | |
|---|---|---|---|
| C14—C13—C16 | 121.49 (17) | C44—C43—C46 | 121.53 (18) |
| C13—C14—H14 | 119.4 | C43—C44—H44 | 119.5 |
| C15—C14—C13 | 121.15 (17) | C45—C44—C43 | 120.98 (18) |
| C15—C14—H14 | 119.4 | C45—C44—H44 | 119.5 |
| N11—C15—C14 | 119.83 (17) | N41—C45—C44 | 120.12 (17) |
| N11—C15—H15 | 120.1 | N41—C45—H45 | 119.9 |
| C14—C15—H15 | 120.1 | C44—C45—H45 | 119.9 |
| C13—C16—H16A | 109.5 | C43—C46—H46A | 109.5 |
| C13—C16—H16B | 109.5 | C43—C46—H46B | 109.5 |
| C13—C16—H16C | 109.5 | C43—C46—H46C | 109.5 |
| H16A—C16—H16B | 109.5 | H46A—C46—H46B | 109.5 |
| H16A—C16—H16C | 109.5 | H46A—C46—H46C | 109.5 |
| H16B—C16—H16C | 109.5 | H46B—C46—H46C | 109.5 |
| N21—O21—Co1 | 116.67 (10) | N51—O51—Co2 | 120.20 (11) |
| C21—N21—O21 | 119.83 (16) | C51—N51—O51 | 120.45 (17) |
| C25—N21—O21 | 118.85 (16) | C55—N51—O51 | 118.22 (17) |
| C25—N21—C21 | 121.27 (17) | C55—N51—C51 | 121.32 (17) |
| N21—C21—H21 | 120.0 | N51—C51—H51 | 120.0 |
| N21—C21—C22 | 119.92 (18) | N51—C51—C52 | 120.03 (18) |
| C22—C21—H21 | 120.0 | C52—C51—H51 | 120.0 |
| C21—C22—H22 | 119.8 | C51—C52—H52 | 119.7 |
| C21—C22—C23 | 120.48 (18) | C51—C52—C53 | 120.55 (18) |
| C23—C22—H22 | 119.8 | C53—C52—H52 | 119.7 |
| C22—C23—C24 | 117.52 (18) | C52—C53—C56 | 122.25 (18) |
| C22—C23—C26 | 121.97 (19) | C54—C53—C52 | 117.00 (18) |
| C24—C23—C26 | 120.49 (19) | C54—C53—C56 | 120.74 (18) |
| C23—C24—H24 | 119.7 | C53—C54—H54 | 119.3 |
| C25—C24—C23 | 120.64 (18) | C55—C54—C53 | 121.34 (19) |
| C25—C24—H24 | 119.7 | C55—C54—H54 | 119.3 |
| N21—C25—C24 | 120.14 (18) | N51—C55—C54 | 119.73 (18) |
| N21—C25—H25 | 119.9 | N51—C55—H55 | 120.1 |
| C24—C25—H25 | 119.9 | C54—C55—H55 | 120.1 |
| C23—C26—H26A | 109.5 | C53—C56—H56A | 109.5 |
| C23—C26—H26B | 109.5 | C53—C56—H56B | 109.5 |
| C23—C26—H26C | 109.5 | C53—C56—H56C | 109.5 |
| H26A—C26—H26B | 109.5 | H56A—C56—H56B | 109.5 |
| H26A—C26—H26C | 109.5 | H56A—C56—H56C | 109.5 |
| H26B—C26—H26C | 109.5 | H56B—C56—H56C | 109.5 |
| N31—O31—Co1 | 116.49 (10) | N61—O61—Co2 | 117.27 (11) |
| O31—N31—C31 | 118.85 (16) | C61—N61—O61 | 118.81 (16) |
| O31—N31—C35 | 119.84 (16) | C61—N61—C65 | 121.31 (17) |
| C35—N31—C31 | 121.29 (17) | C65—N61—O61 | 119.85 (16) |
| N31—C31—H31 | 120.1 | N61—C61—H61 | 119.9 |
| N31—C31—C32 | 119.83 (18) | N61—C61—C62 | 120.28 (18) |
| C32—C31—H31 | 120.1 | C62—C61—H61 | 119.9 |
| C31—C32—H32 | 119.5 | C61—C62—H62 | 119.7 |
| C31—C32—C33 | 120.92 (19) | C61—C62—C63 | 120.57 (18) |
| C33—C32—H32 | 119.5 | C63—C62—H62 | 119.7 |

| | | | |
|---|---|---|---|
| C32—C33—C36 | 121.11 (19) | C62—C63—C66 | 120.74 (19) |
| C34—C33—C32 | 116.96 (18) | C64—C63—C62 | 117.33 (18) |
| C34—C33—C36 | 121.90 (19) | C64—C63—C66 | 121.93 (18) |
| C33—C34—H34 | 119.5 | C63—C64—H64 | 119.6 |
| C35—C34—C33 | 121.01 (19) | C65—C64—C63 | 120.77 (18) |
| C35—C34—H34 | 119.5 | C65—C64—H64 | 119.6 |
| N31—C35—C34 | 119.84 (18) | N61—C65—C64 | 119.70 (18) |
| N31—C35—H35 | 120.1 | N61—C65—H65 | 120.1 |
| C34—C35—H35 | 120.1 | C64—C65—H65 | 120.1 |
| C33—C36—H36A | 109.5 | C63—C66—H66A | 109.5 |
| C33—C36—H36B | 109.5 | C63—C66—H66B | 109.5 |
| C33—C36—H36C | 109.5 | C63—C66—H66C | 109.5 |
| H36A—C36—H36B | 109.5 | H66A—C66—H66B | 109.5 |
| H36A—C36—H36C | 109.5 | H66A—C66—H66C | 109.5 |
| H36B—C36—H36C | 109.5 | H66B—C66—H66C | 109.5 |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C11—H11···S4$^{i}$ | 0.95 | 2.88 | 3.8088 (19) | 166 |
| C21—H21···S2$^{ii}$ | 0.95 | 2.87 | 3.739 (2) | 153 |
| C24—H24···S1$^{iii}$ | 0.95 | 2.90 | 3.841 (2) | 169 |
| C25—H25···O31$^{iii}$ | 0.95 | 2.63 | 3.259 (2) | 124 |
| C31—H31···O21$^{iii}$ | 0.95 | 2.44 | 3.277 (2) | 146 |
| C34—H34···S3 | 0.95 | 2.99 | 3.754 (2) | 138 |
| C41—H41···S3$^{iv}$ | 0.95 | 2.97 | 3.6966 (19) | 134 |
| C45—H45···S2 | 0.95 | 2.89 | 3.6082 (19) | 133 |
| C55—H55···O61$^{v}$ | 0.95 | 2.46 | 3.184 (2) | 133 |
| C61—H61···O51$^{v}$ | 0.95 | 2.48 | 3.233 (2) | 136 |
| C62—H62···S3$^{v}$ | 0.95 | 2.98 | 3.900 (2) | 162 |
| C64—H64···N4$^{vi}$ | 0.95 | 2.64 | 3.484 (2) | 148 |
| C65—H65···S4$^{vi}$ | 0.95 | 3.00 | 3.870 (2) | 154 |

Symmetry codes: (i) *x*+1, *y*+1, *z*; (ii) −*x*+1, −*y*+1, −*z*; (iii) −*x*+2, −*y*+1, −*z*; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*+1, −*y*, −*z*+1; (vi) −*x*, −*y*, −*z*+1.