

# Synthesis, crystal structure and thermal behavior of tetrakis(3-cyanopyridine *N*-oxide- $\kappa$ O)bis(thiocyanato- $\kappa$ N)cobalt(II), which shows strong pseudosymmetry

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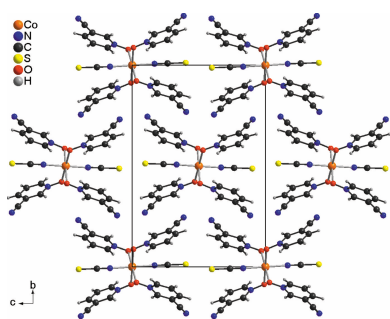
**Keywords:** synthesis; coordination compound; cobalt thiocyanate; 3-cyanopyridine *N*-oxide; crystal structure; pseudosymmetry; thermal properties.

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The title compound,  $[\text{Co}(\text{SCN})_2(\text{C}_6\text{H}_4\text{N}_2\text{O})_4]$ , was prepared by the reaction of cobalt(II)thiocyanate with 3-cyanopyridine *N*-oxide in ethanol. In the crystal, the cobalt(II) cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions and four O-bonded 3-cyanopyridine *N*-oxide coligands, forming discrete complexes that are located on centers of inversion, hence forming *trans*- $\text{CoN}_2\text{O}_4$  octahedra. The structure refinement was performed in the monoclinic space group  $P2_1/n$ , for which a potential lattice translation and new symmetry elements with a fit of 100% is suggested. The structure can easily be refined in the space group  $I2/m$ , where the complexes have  $2/m$  symmetry. However, nearly all of the reflections that violate the centering are observed with significant intensity and the refinement in  $P2_1/n$  leads to significantly lower  $R(F)$  values (0.027 versus 0.033). Moreover, in  $I2/m$  much larger components of the anisotropic displacement parameters are observed and therefore, the crystal structure is presented in the primitive unit cell. IR investigations confirm that the anionic ligands are only terminally bonded and that the cyano group is not involved in the metal coordination. PXRD investigations show that a pure crystalline phase has been obtained and measurements using simultaneously thermogravimetry and differential thermoanalysis reveal that the compound decomposes in an exothermic reaction upon heating, without the formation of a coligand-deficient intermediate phase.

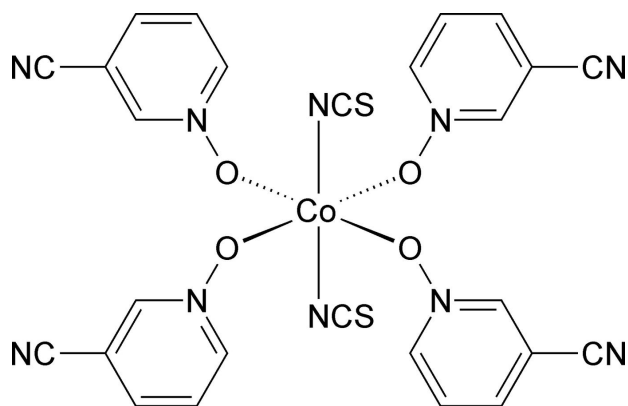
## 1. Chemical context

The synthesis of new coordination compounds is still an important field in chemistry. In most cases, such compounds are prepared in solution but there are alternatives, where they are prepared in the solid state using, for example, molecular milling (Stolar *et al.*, 2017; Darwish *et al.*, 2019), grinding (Adams *et al.*, 2007) or molten-flux synthesis (Höller *et al.*, 2010; Schönfeld *et al.*, 2012). In our own investigations, we frequently use thermal ligand removal of suitable precursor compounds for the solid-state synthesis of new coordination compounds that mostly consist of discrete complexes, in which the anionic ligands are only terminally bonded. Upon heating, these precursors frequently lose their neutral coligands in a stepwise fashion, forming intermediate compounds with condensed networks in which the metal cations are linked by the anionic ligands into one-, two- or three-dimensional networks. In the beginning, our interest focused on transition-metal-halide coordination compounds (Näther *et al.*, 2001; Näther & Jess, 2004), but in recent years we have used this approach for the synthesis of transition-metal thio- and selenocyanates because these anionic ligands mediate reasonable magnetic exchange, which allows the preparation of compounds that show versatile magnetic behavior (Palion-



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Gazda *et al.*, 2015; Mekuimemba, *et al.*, 2018). In this context, of special interest are compounds based on Co<sup>II</sup> in which the cations are linked by pairs of thio- or selenocyanate anions into chains, because they can show three-dimensional but especially one-dimensional magnetic ordering (Werner *et al.*, 2014; Rams *et al.*, 2020). The major advantage of our approach is the fact that the new compounds are obtained in quantitative yield and that frequently metastable polymorphs or isomers can be prepared that often are not available from solution (Werner *et al.*, 2015).



In recent investigations, N-donor coligands have been used that mostly consist of pyridine derivatives (Rams *et al.*, 2017), but to investigate the influence of the coligands on the magnetic anisotropy of Co<sup>II</sup> centers, we also used S-donor coligands, such as ethylenethiourea, that lead to a modified magnetic behavior (Jochim *et al.*, 2020). In a continuation of this work, we became interested in O-donor coligands and we found that only very few Co(NCS)<sub>2</sub> compounds with bridging thiocyanate anions and such coligands have been reported in the literature (see *Database survey*). We also found that only in Co(NCS)<sub>2</sub>(THF)<sub>2</sub> the Co<sup>II</sup> cations are linked by pairs of bridging anionic ligands into linear chains (Cambridge Structural Database refcode QIKQUY; Shurdha *et al.*, 2013). In this context, we became interested in pyridine *N*-oxide derivatives, for which two Co(NCS)<sub>2</sub> compounds with bridging thiocyanate anions are reported in the literature (see *Database survey*). In our first investigations, we used 3-cyanopyridine *N*-oxide (C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>O) as a coligand, which is commercially available and for which no coordination compounds have been reported. However, independent of the amounts of Co(NCS)<sub>2</sub> and 3-cyanopyridine *N*-oxide in the synthesis, the same crystalline phase was always obtained. The CN-stretching vibration of the cyano group is observed at 2241 cm<sup>-1</sup> in the IR spectrum, indicating that this group is not involved in the metal coordination (Fig. S1). The CN-stretching vibration of the thiocyanate anion occurs at 2051 cm<sup>-1</sup>, which proves that the anionic ligand is only terminally coordinated (Fig. S1). To confirm all these assumptions, the new crystalline phase was characterized by single crystal X-ray diffraction (see below).

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

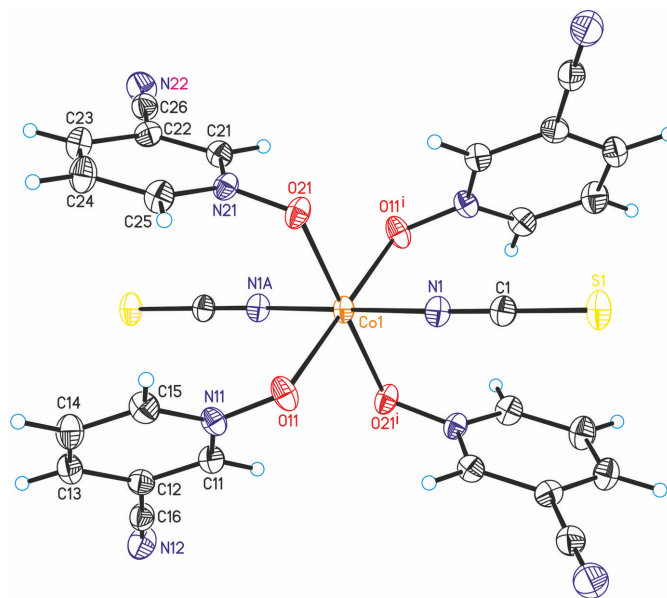
Co1—N1	2.0596 (13)	Co1—O21	2.0985 (9)
Co1—O11	2.1019 (10)		
N1 <sup>i</sup> —Co1—O11	93.52 (4)	N1—Co1—O21 <sup>i</sup>	94.51 (4)
N1—Co1—O11	86.48 (4)	O21—Co1—O11	90.62 (4)
N1—Co1—O21	85.49 (4)	O21—Co1—O11 <sup>i</sup>	89.38 (4)

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

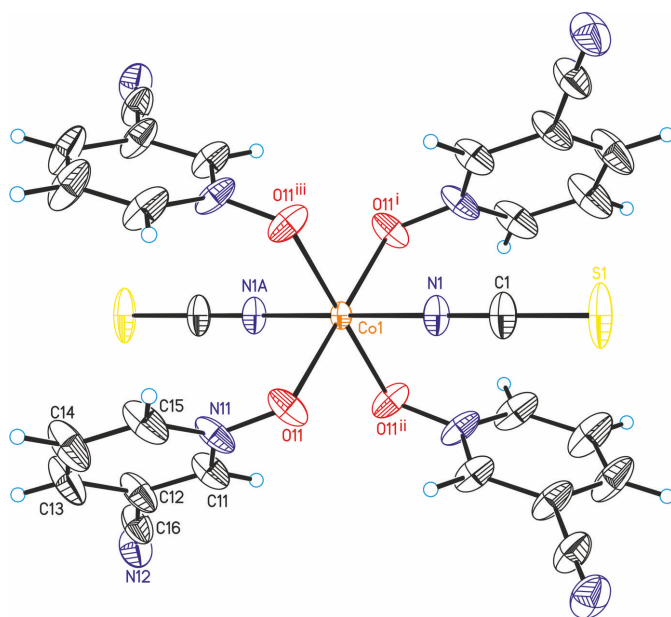
## 2. Structural commentary

The asymmetric unit of the title compound, Co(SCN)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>O)<sub>4</sub>, consists of one crystallographically independent Co<sup>II</sup> cation that is located on a center of inversion, as well as one independent thiocyanate anion and two independent 3-cyanopyridine *N*-oxide coligands in general positions (Fig. 1). The Co<sup>II</sup> cations therefore adopt *trans*-CoN<sub>2</sub>O<sub>4</sub> octahedral geometries (Fig. 1). Bond lengths and angles correspond to literature values and show that the octahedra are slightly distorted (Table 1).

If the structure is checked for higher symmetry using *PLATON* (Spek *et al.*, 2020) or *checkCIF*, a pseudo-translation and space group *I2/m* is suggested with 100% fit. The structure can easily be refined in this space group and the refinement leads to reasonable reliability factors. The refinement in space group *I2/m*, however, leads to significantly higher residuals than in space group *P2<sub>1</sub>/n* [*R*(*F*) for 2829 reflections with  $F_o > 4\sigma(F_o) = 0.027$  in *P2<sub>1</sub>/n* versus 0.033 for 1446 reflections with  $F_o > 4\sigma(F_o)$  in *I2/m* and  $wR(F^2) = 0.083$  for all 2829 independent reflections (*P2<sub>1</sub>/n*) versus 0.092 for all 1446 reflections (*I2/m*)]. In this context, it is noted that nearly all reflections violating the centering are observed. Moreover, from the refinement in *I2/m* it is obvious that significantly



**Figure 1**  
The molecular structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: (i)  $-x, -y + 1, -z + 1$ .

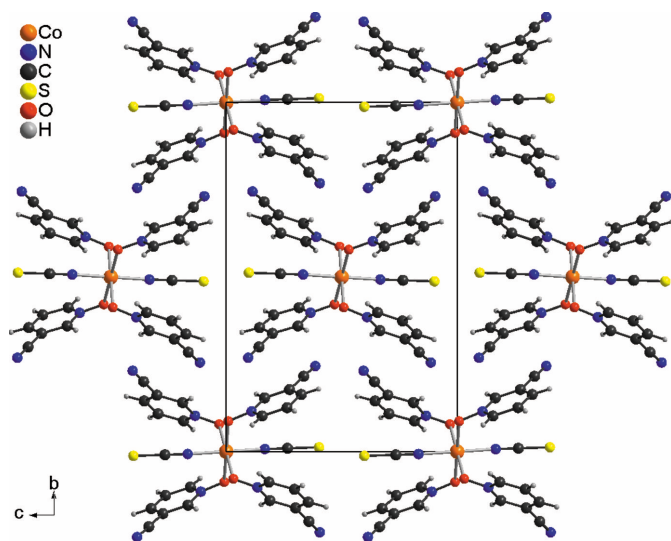


**Figure 2**  
Molecular structure of the title compound refined in space group  $I2/m$  with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (i)  $-x, 1 - y, 1 - z$ , (ii)  $-x, y, 1 - z$ , (iii)  $x, 1 - y, z$ .

enlarged anisotropic displacement parameters are observed, which are much larger than expected for a measurement at 100 K, indicating too high symmetry (Fig. 2). For all these reasons, the crystal structure is presented in the monoclinic primitive space group  $P2_1/n$ .

### 3. Supramolecular features

In the extended structure of the title compound, the complexes are arranged in columns that proceed along the crystallographic  $a$ -axis (Fig. 3). In this direction the translation



**Figure 3**  
The packing of the title compound showing the arrangement of the discrete complexes along the crystallographic  $a$ -axis.

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C11-H11\cdots O21^i$	0.95	2.61	3.3295 (17)	133
$C11-H11\cdots N22^{ii}$	0.95	2.57	3.3902 (19)	145
$C14-H14\cdots S1^{iii}$	0.95	2.91	3.7585 (15)	149
$C15-H15\cdots O21^{iii}$	0.95	2.45	3.2351 (16)	140
$C21-H21\cdots N12^{iv}$	0.95	2.52	3.3233 (19)	142
$C24-H24\cdots S1^{iii}$	0.95	2.96	3.8082 (15)	150
$C25-H25\cdots O11^{iii}$	0.95	2.28	3.1335 (16)	148

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

leading to the pseudo-centering is also obvious. Several  $C-H\cdots O$ ,  $C-H\cdots S$  and  $C-H\cdots N$  contacts are observed between the complexes, but from the distances and angles it is obvious that they do not correspond to strong interactions (Table 2).

### 4. Thermoanalytical investigations

Based on the single-crystal data, an X-ray powder pattern was calculated and compared with the experimental pattern, which proves that the title compound was obtained as a pure phase (Fig. S2). Because in our synthetic investigations no further compounds were detected, it was checked whether a compound with a more condensed network is available by thermal ligand removal. Therefore, the title compound was investigated simultaneously by differential thermoanalysis and thermogravimetry under nitrogen. Upon heating, only one mass loss of 58.8% is observed until  $400^\circ\text{C}$  that does not fit to a stepwise loss of the 3-cyanopyridine  $N$ -oxide ligands (calculated mass loss for each 3-cyanopyridine  $N$ -oxide ligand = 18.3%; Fig. S3). From the DTA curve, the onset of an endothermic event is visible, followed by a strong exothermic event at a peak temperature of  $220^\circ\text{C}$ . This is an unusual observation, because in previous investigations using pyridine derivatives the ligand removal always proceeds in an endothermic reaction. Oxidation of the compound might be excluded because all measurements were performed in a nitrogen atmosphere and therefore one must assume that this ligand is thermally unstable and decomposes upon heating. In agreement with these observations, the residue obtained at  $400^\circ\text{C}$  is amorphous against X-rays (Fig. S4).

### 5. Database survey

A search in the Cambridge Structural Database (version 5.43, last update March 2023; Groom *et al.*, 2016) using ConQuest reveals that no coordination compounds with 3-cyanopyridine  $N$ -oxide as a ligand have been reported. With 4-cyanopyridine, three compounds are known, including 4-cyanopyridine  $N$ -oxide)bis(isothiocyanate)zinc(II) (refcode UKEZIV; Mautner *et al.*, 2016) and the two isotopic compounds bis( $\mu$ -thiocyanato)-diaqua-tetrakis(4-cyanopyridine  $N$ -oxide)bis(isothiocyanato) cadmium(II) (UKIMAE; Mautner *et al.*, 2016) and manganese(II) (KESSIN; Mautner *et al.*, 2018). The Zn compound consists of discrete complexes, in which the  $Zn^{II}$

cations are fivefold coordinated by two terminally N-bonded thiocyanate anions, two 3-cyanopyridine *N*-oxide ligands and one water molecule, whereas the Mn and Cd compounds consist of dinuclear units, in which each metal cation is octahedrally coordinated by one water molecule, one terminal and two bridging thiocyanate anions and two 4-cyanopyridine *N*-oxide ligands, and are linked into dinuclear units by pairs of  $\mu$ -1,3-bridging thiocyanate anions.

Some compounds based on  $\text{Co}(\text{NCS})_2$  and pyridine *N*-oxide derivatives in which the  $\text{Co}^{\text{II}}$  cations are linked by  $\mu$ -1,3-bridging thiocyanate anions are also known. This include the two isotopic compounds (4-methylpyridine *N*-oxide)bisthiocyanate)cobalt(II) (MEQKOJ; Zhang *et al.*, 2006b) (4-methoxy-pyridine *N*-oxide)bisthiocyanate)cobalt(II) (TERRAK; Zhang *et al.*, 2006a), (4-methylpyridine *N*-oxide)(methanol)bisthiocyanate)cobalt(II) (REKBUF; Shi *et al.*, 2006) and bis(4-nitropyridine *N*-oxide)bis(thiocyanate)cobalt(II) (TILHIG; Shi *et al.*, 2007). In the first two compounds, the  $\text{Co}^{\text{II}}$  cations are linked by pairs of thiocyanate anions into corrugated chains that are further connected into layers by  $\mu$ -1,1(*O*, *O*) bridging coligands. In the third compound with methanol, two  $\text{Co}^{\text{II}}$  cations are linked by pairs of anionic ligands into dinuclear units and are further linked by pairs of  $\mu$ -1,1(*O*, *O*) bridging 4-nitropyridine *N*-oxide ligands. In the compound with the 4-nitro substituent, the cations are linked by pairs of bridging thiocyanate anions into chains that are corrugated because of the *cis-cis-trans* configuration at the  $\text{Co}^{\text{II}}$  centers.

## 6. Synthesis and crystallization

$\text{Co}(\text{NCS})_2$  (99%) was purchased from Sigma Aldrich, 3-cyanopyridine *N*-oxide (97%) was purchased from Thermo Scientific and ethanol (99.9%) was purchased from Fisher Chemical.

### Synthesis:

Single crystals were obtained by the reaction of 0.25 mmol (43.5 mg)  $\text{Co}(\text{SCN})_2$  and 1 mmol (120 mg) 3-cyanopyridine *N*-oxide in 1 ml of ethanol. The reaction mixture was stored overnight, which lead to the formation of yellow needle-like crystals.

For the preparation of larger amounts of a microcrystalline powder, the same amount of reactants were stirred in 2 ml of ethanol for 1 d.

### Experimental details:

The PXRD measurements were performed with a Stoe Transmission Powder Diffraction System (STADI P) equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator using  $\text{Cu } K\alpha_1$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ).

The IR spectra were measured using an ATI Mattson Genesis Series FTIR Spectrometer, control software: WINFIRST, from ATI Mattson.

Thermogravimetry and differential thermoanalysis (TG-DTA) measurements were performed in a dynamic nitrogen atmosphere in  $\text{Al}_2\text{O}_3$  crucibles using a STA-PT 1000 thermobalance from Linseis. The instrument was calibrated using standard reference materials.

**Table 3**

Experimental details.

Crystal data	
Chemical formula	$[\text{Co}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2\text{O})_4]$
$M_r$	655.54
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
$a, b, c$ ( $\text{\AA}$ )	6.5899 (1), 17.9658 (2), 11.9444 (1)
$\beta$ ( $^\circ$ )	96.131 (1)
$V$ ( $\text{\AA}^3$ )	1406.04 (3)
$Z$	2
Radiation type	$\text{Cu } K\alpha$
$\mu$ ( $\text{mm}^{-1}$ )	6.63
Crystal size (mm)	$0.28 \times 0.03 \times 0.03$
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2022)
$T_{\text{min}}, T_{\text{max}}$	0.571, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	23719, 2990, 2829
$R_{\text{int}}$	0.028
$(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.635
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.027, 0.083, 1.11
No. of reflections	2990
No. of parameters	197
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	0.24, $-0.34$

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT2014/5* (Sheldrick, 2015b), *SHELXL2016/6* (Sheldrick, 2015a), *DIAMOND* (Brandenburg & Putz, 1999) and *publCIF* (Westrip, 2010).

## 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  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  using a riding model. As mentioned in the *Structural commentary*, the compound shows strong pseudo-symmetry because of a pseudo-lattice translation indicating a centering, but our investigations show that the structure is best described in the primitive space group  $P2_1/n$  instead of  $I2/m$ . This is obvious in the reliability factors obtained by refinements in both space groups, but especially from the large components of the anisotropic displacement parameters if the structure is refined in the body-centered space group. Moreover, nearly all of the reflections that would violate the centering were observed.

## Acknowledgements

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## supporting information

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## Synthesis, crystal structure and thermal behavior of tetrakis(3-cyanopyridine *N*-oxide- $\kappa$ O)bis(thiocyanato- $\kappa$ N)cobalt(II), which shows strong pseudosymmetry

Christian Näther and Inke Jess

### Computing details

Data collection: *CrysAlis PRO* 1.171.42.40a (Rigaku OD, 2022); cell refinement: *CrysAlis PRO* 1.171.42.40a (Rigaku OD, 2022); data reduction: *CrysAlis PRO* 1.171.42.40a (Rigaku OD, 2022); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015b); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015a); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Tetrakis(3-cyanopyridine *N*-oxide- $\kappa$ O)bis(thiocyanato- $\kappa$ N) cobalt(II)

#### Crystal data

$[\text{Co}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2\text{O})_4]$

$M_r = 655.54$

Monoclinic,  $P2_1/n$

$a = 6.5899$  (1) Å

$b = 17.9658$  (2) Å

$c = 11.9444$  (1) Å

$\beta = 96.131$  (1)°

$V = 1406.04$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 666$

$D_x = 1.548$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å

Cell parameters from 16616 reflections

$\theta = 4.5\text{--}76.3^\circ$

$\mu = 6.63$  mm<sup>-1</sup>

$T = 100$  K

Needle, yellow

$0.28 \times 0.03 \times 0.03$  mm

#### Data collection

XtaLAB Synergy, Dualflex, HyPix  
diffractometer

Radiation source: micro-focus sealed X-ray  
tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(*CrysAlisPro*; Rigaku OD, 2022)

$T_{\min} = 0.571$ ,  $T_{\max} = 1.000$

23719 measured reflections

2990 independent reflections

2829 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 78.3^\circ$ ,  $\theta_{\min} = 4.5^\circ$

$h = -8 \rightarrow 7$

$k = -22 \rightarrow 22$

$l = -13 \rightarrow 15$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.083$

$S = 1.11$

2990 reflections

197 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.3714P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup>

$$\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL2016/6*  
 (Sheldrick, 2015a),  
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.0007 (2)

### 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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.000000	0.500000	0.500000	0.01595 (11)
N1	0.1137 (2)	0.50708 (6)	0.66710 (11)	0.0204 (3)
C1	0.1405 (2)	0.50936 (7)	0.76538 (13)	0.0196 (3)
S1	0.17656 (6)	0.51232 (2)	0.90206 (3)	0.02903 (12)
O11	0.22429 (14)	0.57834 (6)	0.46915 (8)	0.0237 (2)
N11	0.23654 (17)	0.60259 (6)	0.36497 (9)	0.0198 (2)
C11	0.0786 (2)	0.64024 (8)	0.31076 (11)	0.0208 (3)
H11	-0.037683	0.652022	0.348001	0.025*
C12	0.0881 (2)	0.66154 (8)	0.19988 (11)	0.0214 (3)
C13	0.2587 (2)	0.64494 (8)	0.14458 (12)	0.0246 (3)
H13	0.264095	0.658366	0.068026	0.030*
C14	0.4198 (2)	0.60828 (9)	0.20484 (13)	0.0270 (3)
H14	0.539395	0.597242	0.170098	0.032*
C15	0.4073 (2)	0.58770 (8)	0.31525 (12)	0.0242 (3)
H15	0.518894	0.563014	0.356478	0.029*
C16	-0.0832 (2)	0.70028 (8)	0.14185 (12)	0.0246 (3)
N12	-0.2185 (2)	0.73137 (8)	0.09481 (11)	0.0324 (3)
O21	0.20988 (14)	0.41291 (6)	0.49113 (8)	0.0221 (2)
C21	0.0785 (2)	0.34632 (7)	0.33413 (12)	0.0206 (3)
H21	-0.041400	0.335659	0.368791	0.025*
C22	0.0971 (2)	0.32231 (8)	0.22576 (12)	0.0218 (3)
C23	0.2739 (2)	0.33654 (8)	0.17478 (12)	0.0263 (3)
H23	0.286155	0.320817	0.099860	0.032*
C24	0.4310 (2)	0.37428 (9)	0.23672 (13)	0.0279 (3)
H24	0.554515	0.383844	0.204898	0.034*
C25	0.4087 (2)	0.39810 (8)	0.34478 (12)	0.0239 (3)
H25	0.517252	0.423673	0.387264	0.029*
C26	-0.0726 (2)	0.28445 (8)	0.16431 (12)	0.0247 (3)
N22	-0.2080 (2)	0.25501 (8)	0.11394 (12)	0.0323 (3)
N21	0.23268 (17)	0.38504 (6)	0.39006 (9)	0.0190 (2)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.01140 (17)	0.02239 (17)	0.01407 (18)	0.00014 (9)	0.00137 (12)	-0.00016 (10)

N1	0.0170 (6)	0.0261 (6)	0.0178 (6)	0.0005 (4)	0.0010 (5)	-0.0008 (4)
C1	0.0135 (6)	0.0248 (6)	0.0207 (7)	-0.0004 (4)	0.0032 (5)	-0.0009 (5)
S1	0.0330 (2)	0.0394 (2)	0.01490 (19)	-0.00001 (15)	0.00368 (14)	-0.00104 (13)
O11	0.0188 (4)	0.0343 (5)	0.0174 (5)	-0.0063 (4)	-0.0012 (3)	0.0061 (4)
N11	0.0162 (5)	0.0236 (5)	0.0193 (5)	-0.0040 (4)	0.0009 (4)	0.0026 (4)
C11	0.0167 (6)	0.0240 (6)	0.0216 (6)	-0.0005 (5)	0.0014 (5)	0.0002 (5)
C12	0.0208 (6)	0.0205 (6)	0.0230 (7)	-0.0007 (5)	0.0016 (5)	0.0004 (5)
C13	0.0256 (7)	0.0284 (7)	0.0203 (6)	-0.0024 (5)	0.0044 (5)	0.0011 (5)
C14	0.0192 (6)	0.0348 (8)	0.0279 (7)	0.0011 (5)	0.0057 (5)	0.0002 (6)
C15	0.0172 (6)	0.0279 (7)	0.0275 (7)	-0.0008 (5)	0.0018 (5)	0.0021 (5)
C16	0.0276 (7)	0.0264 (7)	0.0202 (6)	0.0020 (5)	0.0038 (5)	0.0001 (5)
N12	0.0348 (7)	0.0369 (7)	0.0250 (6)	0.0122 (6)	0.0009 (5)	0.0006 (5)
O21	0.0200 (5)	0.0295 (5)	0.0165 (4)	0.0058 (4)	0.0000 (3)	-0.0042 (4)
C21	0.0165 (6)	0.0222 (6)	0.0230 (6)	-0.0001 (5)	0.0022 (5)	0.0011 (5)
C22	0.0214 (6)	0.0209 (6)	0.0227 (6)	0.0009 (5)	0.0003 (5)	-0.0010 (5)
C23	0.0239 (7)	0.0324 (7)	0.0232 (7)	0.0005 (6)	0.0053 (5)	-0.0035 (6)
C24	0.0197 (6)	0.0380 (8)	0.0268 (7)	-0.0013 (6)	0.0057 (5)	-0.0031 (6)
C25	0.0158 (6)	0.0294 (7)	0.0261 (7)	-0.0005 (5)	0.0010 (5)	-0.0022 (5)
C26	0.0273 (7)	0.0244 (7)	0.0226 (7)	-0.0020 (5)	0.0030 (5)	-0.0002 (5)
N22	0.0343 (7)	0.0333 (7)	0.0286 (6)	-0.0102 (6)	0.0001 (5)	-0.0022 (5)
N21	0.0168 (5)	0.0219 (5)	0.0181 (5)	0.0034 (4)	0.0010 (4)	-0.0020 (4)

*Geometric parameters (Å, °)*

Co1—N1 <sup>i</sup>	2.0596 (13)	C14—H14	0.9500
Co1—N1	2.0596 (13)	C14—C15	1.381 (2)
Co1—O11	2.1019 (10)	C15—H15	0.9500
Co1—O11 <sup>i</sup>	2.1019 (10)	C16—N12	1.147 (2)
Co1—O21 <sup>i</sup>	2.0985 (9)	O21—N21	1.3302 (14)
Co1—O21	2.0985 (9)	C21—H21	0.9500
N1—C1	1.169 (2)	C21—C22	1.382 (2)
C1—S1	1.6254 (16)	C21—N21	1.3480 (17)
O11—N11	1.3290 (14)	C22—C23	1.395 (2)
N11—C11	1.3478 (17)	C22—C26	1.4410 (19)
N11—C15	1.3540 (18)	C23—H23	0.9500
C11—H11	0.9500	C23—C24	1.384 (2)
C11—C12	1.3864 (18)	C24—H24	0.9500
C12—C13	1.3956 (19)	C24—C25	1.382 (2)
C12—C16	1.4398 (19)	C25—H25	0.9500
C13—H13	0.9500	C25—N21	1.3519 (18)
C13—C14	1.384 (2)	C26—N22	1.150 (2)
N1 <sup>i</sup> —Co1—N1	180.0	C14—C13—H13	121.1
N1 <sup>i</sup> —Co1—O11 <sup>i</sup>	86.48 (4)	C13—C14—H14	119.9
N1 <sup>i</sup> —Co1—O11	93.52 (4)	C15—C14—C13	120.24 (13)
N1—Co1—O11	86.48 (4)	C15—C14—H14	119.9
N1—Co1—O11 <sup>i</sup>	93.52 (4)	N11—C15—C14	120.21 (13)
N1 <sup>i</sup> —Co1—O21 <sup>i</sup>	85.49 (4)	N11—C15—H15	119.9



N1—Co1—O21	85.49 (4)	C14—C15—H15	119.9
N1 <sup>i</sup> —Co1—O21	94.51 (4)	N12—C16—C12	179.29 (17)
N1—Co1—O21 <sup>i</sup>	94.51 (4)	N21—O21—Co1	117.74 (7)
O11 <sup>i</sup> —Co1—O11	180.00 (3)	C22—C21—H21	120.4
O21—Co1—O11	90.62 (4)	N21—C21—H21	120.4
O21—Co1—O11 <sup>i</sup>	89.38 (4)	N21—C21—C22	119.20 (12)
O21 <sup>i</sup> —Co1—O11 <sup>i</sup>	90.62 (4)	C21—C22—C23	120.87 (13)
O21 <sup>i</sup> —Co1—O11	89.38 (4)	C21—C22—C26	118.88 (13)
O21 <sup>i</sup> —Co1—O21	180.0	C23—C22—C26	120.21 (13)
C1—N1—Co1	167.31 (12)	C22—C23—H23	121.0
N1—C1—S1	179.70 (15)	C24—C23—C22	117.94 (13)
N11—O11—Co1	119.86 (7)	C24—C23—H23	121.0
O11—N11—C11	119.56 (11)	C23—C24—H24	119.9
O11—N11—C15	118.84 (11)	C25—C24—C23	120.19 (13)
C11—N11—C15	121.60 (12)	C25—C24—H24	119.9
N11—C11—H11	120.5	C24—C25—H25	120.0
N11—C11—C12	119.07 (12)	N21—C25—C24	120.07 (13)
C12—C11—H11	120.5	N21—C25—H25	120.0
C11—C12—C13	120.94 (13)	N22—C26—C22	178.95 (16)
C11—C12—C16	118.69 (12)	O21—N21—C21	119.46 (11)
C13—C12—C16	120.36 (12)	O21—N21—C25	118.86 (11)
C12—C13—H13	121.1	C21—N21—C25	121.66 (12)
C14—C13—C12	117.87 (13)		

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

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C11—H11 $\cdots$ O21 <sup>i</sup>	0.95	2.61	3.3295 (17)	133
C11—H11 $\cdots$ N22 <sup>ii</sup>	0.95	2.57	3.3902 (19)	145
C14—H14 $\cdots$ S1 <sup>iii</sup>	0.95	2.91	3.7585 (15)	149
C15—H15 $\cdots$ O21 <sup>iii</sup>	0.95	2.45	3.2351 (16)	140
C21—H21 $\cdots$ N12 <sup>iv</sup>	0.95	2.52	3.3233 (19)	142
C24—H24 $\cdots$ S1 <sup>iii</sup>	0.95	2.96	3.8082 (15)	150
C25—H25 $\cdots$ O11 <sup>iii</sup>	0.95	2.28	3.1335 (16)	148

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