

# Synthesis and crystal structure of poly[ethanol( $\mu$ -4-methylpyridine *N*-oxide)di- $\mu$ -thiocyanato-cobalt(II)]

Christian Näther\* and Inke Jess

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

Received 4 September 2024

Accepted 16 September 2024

Edited by S. Parkin, University of Kentucky, USA

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

**CCDC reference:** 2384436

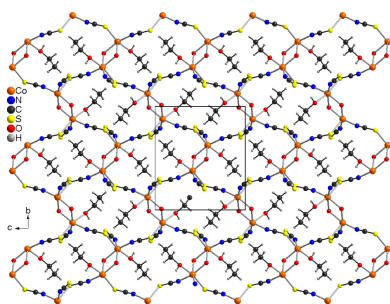
**Supporting information:** this article has supporting information at journals.iucr.org/e

Reaction of 4-methylpyridine *N*-oxide and  $\text{Co}(\text{NCS})_2$  in ethanol as solvent accidentally leads to the formation of single crystals of  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})(\text{ethanol})$  or  $[\text{Co}(\text{NCS})_2(\text{C}_6\text{H}_7\text{NO})(\text{C}_2\text{H}_6\text{O})]_n$ . The asymmetric unit of the title compound consists of one  $\text{Co}^{\text{II}}$  cation, two crystallographically independent thiocyanate anions, one 4-methylpyridine *N*-oxide coligand and one ethanol molecule on general positions. The cobalt cations are sixfold coordinated by one terminal and two bridging thiocyanate anions, two bridging 4-methylpyridine *N*-oxide coligands and one ethanol molecule, with a slightly distorted octahedral geometry. The cobalt cations are linked by single  $\mu$ -1,3(*N,S*)-bridging thiocyanate anions into corrugated chains, that are further connected into layers by pairs of  $\mu$ -1,1(*O,O*)-bridging 4-methylpyridine *N*-oxide coligands. The layers are parallel to the *bc* plane and are separated by the methyl groups of the 4-methylpyridine *N*-oxide coligands. Within the layers, intralayer hydrogen bonding is observed.

## 1. Chemical context

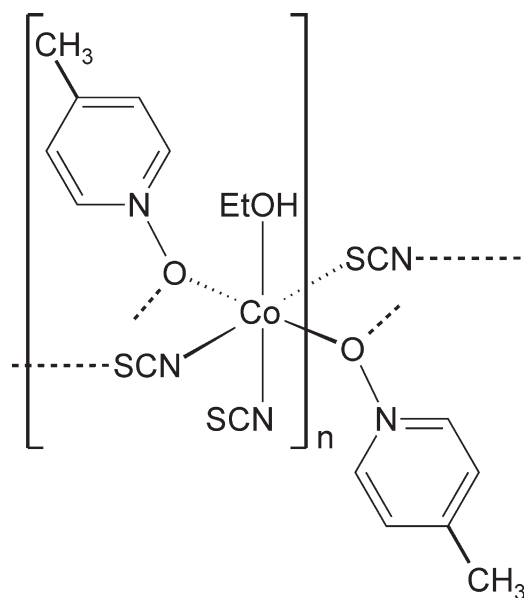
Coordination polymers based on transition-metal thiocyanate coordination polymers are characterized by a pronounced structural variability, which can partly be traced back to the variety of coordination modes of this anionic ligand. This includes mainly the terminal coordination, the  $\mu$ -1,3(*N,S*) and the  $\mu$ -1,3,3(*N,S,S*) bridging modes. With  $\mu$ -1,3(*N,S*) bridging anionic ligands and octahedrally coordinated metal cations the majority of compounds consist of  $M(\text{NCS})_2$  chains, in which the metal centers are connected by pairs of thiocyanate anions. In most cases an all-*trans* coordination is found, which leads to the formation of linear chains (Rams *et al.*, 2017*a*, 2020; Mautner *et al.*, 2018*a,b*). Linear chains are also observed if the co-ligands are in *trans*-positions and the thiocyanate N and S atoms are in *cis*-positions (Rams *et al.*, 2017*b*). For the other or *cis-cis-trans* and the all-*cis* coordination, corrugated chains are observed (Maji *et al.*, 2001; Marsh, 2009; Shi *et al.*, 2006*a*, 2007*a*; Böhme *et al.*, 2020). In contrast, chain compounds in which the metal cations are linked by single  $\mu$ -1,3-bridging thiocyanate anions are rarer (Palion-Gazda *et al.*, 2015; Neumann *et al.*, 2018).

We have been interested in transition-metal thiocyanates for a long time, with special focus on  $\text{Co}(\text{NCS})_2$  chain compounds with pyridine derivatives as coligands (Rams *et al.*, 2017*a,b*, 2020; Böhme *et al.*, 2022). Later we also used pyridine *N*-oxide derivatives as coligands, because they can additionally connect metal cations *via* the  $\mu$ -1,1(*O,O*) bridging mode. In this regard we became interested in 4-methylpyridine *N*-oxide as coligand. With this ligand, two compounds with the composition  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine-}N\text{-oxide})$  (Zhang *et al.*



*al.*, 2006a) and  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})(\text{methanol})$  (Shi *et al.*, 2006a) were reported in the literature. In the first compound, the cobalt cations are octahedrally coordinated by two N- and two S-bonding thiocyanate anions and two bridging 4-methylpyridine *N*-oxide coligands and are connected by pairs of bridging anionic ligands into corrugated chains, which are further connected into layers by the 4-methylpyridine *N*-oxide coligands. In the second compound, the cobalt cations are octahedrally coordinated by one terminal and two bridging thiocyanate anions, two bridging 4-methylpyridine *N*-oxide coligands and one methanol molecule. The metal cations are linked by alternating pairs of  $\mu$ -1,3-bridging thiocyanate anions and  $\mu$ -1,1(*O,O*) bridging 4-methylpyridine *N*-oxide coligands into chains. In the course of our investigations we have synthesized two discrete complexes 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 show a trigonal-bipyramidal or an octahedral coordination (Näther & Jess, 2024a). The first complex can easily be synthesized from methanol, but in some of these batches an additional 4-methylpyridine *N*-oxide compound was detected. Later we have found that a compound with the composition  $\text{Co}_2(\text{NCS})_4(4\text{-methylpyridine } N\text{-oxide})_4(\text{methanol})_2$  was obtained as a by-phase, in which the  $\text{Co}^{\text{II}}$  cations are linked by pairs of  $\mu$ -1,1-bridging 4-methylpyridine *N*-oxide coligands into centrosymmetric dinuclear units (Näther & Jess, 2024b).

Some of the 4-pyridine *N*-oxide compounds mentioned above can also be prepared in ethanol as solvent. However, in some of these batches traces of an additional product were detected by X-ray powder diffraction and therefore a large number of crystallization experiments were performed. In one of these batches crystals suitable for single-crystal X-ray diffraction were accidentally obtained, which proved that a compound with the composition  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})(\text{ethanol})$  had formed.



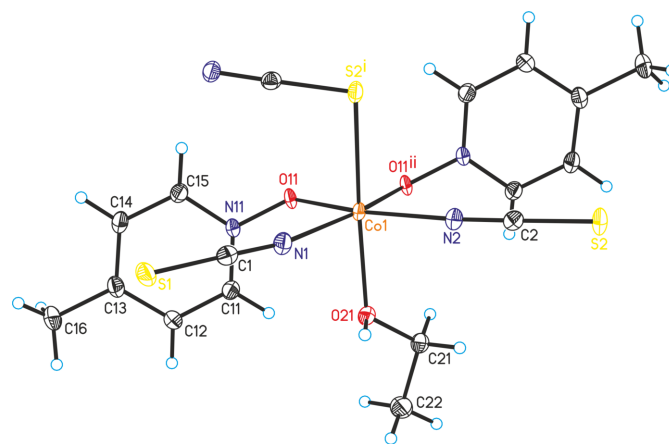
**Table 1**  
Selected geometric parameters (Å, °).

Co1—N1	2.0472 (13)	Co1—O11	2.0971 (10)
Co1—N2	2.0569 (12)	Co1—O11 <sup>ii</sup>	2.1594 (10)
Co1—S2 <sup>i</sup>	2.5171 (4)	Co1—O21	2.1559 (10)
N1—Co1—N2	110.80 (5)	N2—Co1—O21	86.53 (5)
N1—Co1—S2 <sup>i</sup>	90.75 (4)	O11—Co1—S2 <sup>i</sup>	98.02 (3)
N1—Co1—O11 <sup>ii</sup>	160.49 (5)	O11 <sup>ii</sup> —Co1—S2 <sup>i</sup>	95.96 (3)
N1—Co1—O11	89.92 (4)	O11—Co1—O11 <sup>ii</sup>	71.03 (4)
N1—Co1—O21	82.55 (5)	O11—Co1—O21	92.89 (4)
N2—Co1—S2 <sup>i</sup>	85.67 (4)	O21—Co1—S2 <sup>i</sup>	167.20 (3)
N2—Co1—O11 <sup>ii</sup>	88.01 (4)	O21—Co1—O11 <sup>ii</sup>	93.90 (4)
N2—Co1—O11	158.96 (5)		

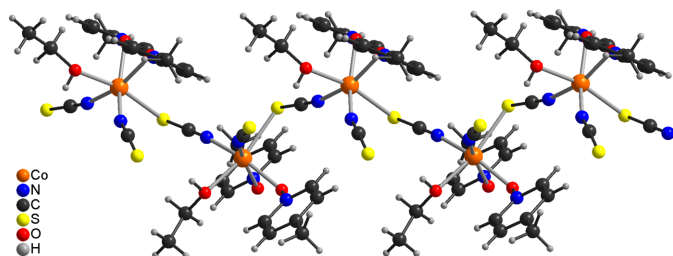
Symmetry codes: (i)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z + 1$ .

## 2. Structural commentary

The asymmetric unit of the title compound,  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})(\text{ethanol})$ , is built up of one cobalt cation, two crystallographically independent thiocyanate anions, one ethanol and one 4-methylpyridine *N*-oxide coligand that are located in general positions. The Co cations are sixfold coordinated by one terminal N-bonded and two  $\mu$ -1,3(*N,S*)-bridging thiocyanate anions, one ethanol molecule and two  $\mu$ -1,1(*O,O*)-bridging 4-methylpyridine *N*-oxide coligands (Fig. 1). The bridging thiocyanate anions and the 4-methylpyridine *N*-oxide coligands are each in *cis*-positions. The Co—N bond length to the terminal anions is slightly shorter than that to the bridging anionic ligands (Table 1). The bond angles deviate from ideal values, which shows that a distorted octahedral coordination is present (Table 1). The  $\text{Co}^{\text{II}}$  cations are linked by single  $\mu$ -1,3(*N,S*)-bridging thiocyanate anions into corrugated chains that proceed along the crystallographic *c*-axis direction (Fig. 2). The chains are linked by two  $\mu$ -1,1(*O,O*)-bridging 4-methylpyridine *N*-oxide coligands into layers *via* four-membered  $\text{Co}_2\text{O}_2$  rings (Fig. 3). These layers consist of large rings built up of six  $\text{Co}^{\text{II}}$  cations, four bridging thiocyanate anions and two bridging 4-methylpyridine *N*-oxide coligands (Fig. 3). Within these rings, each of



**Figure 1**  
Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (i)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z + 1$ .



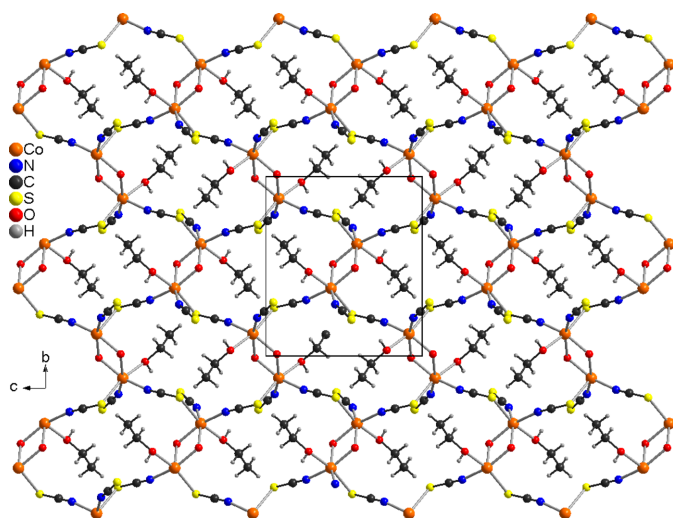
**Figure 2**  
Crystal structure of the title compound with view of a  $\text{Co}(\text{NCS})_2$  chain.

the two  $\text{Co}^{\text{II}}$  cations are linked by pairs of  $\mu$ -1,1(*O,O*)-bridging 4-methylpyridine *N*-oxide coligands into dinuclear units that are further connected by single  $\mu$ -1,3-bridging thiocyanate anions (Fig. 3).

Even though the overall composition of the title compound is very similar to that of  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})(\text{methanol})$ , which has already been reported in the literature, their crystal structures are completely different. In the compound with methanol, the  $\text{Co}^{\text{II}}$  cations are linked by alternating pairs of  $\mu$ -1,3-bridging thiocyanate anions and  $\mu$ -1,1(*O,O*)-bridging 4-methylpyridine *N*-oxide coligands into chains (Shi *et al.*, 2006a). However, layered thiocyanate networks that also consist of condensed rings are known from compounds with pyridine derivatives as coligands. In, for example,  $M(\text{NCS})_2(\text{ethylisonicotinate})_2$  with  $M = \text{Co}, \text{Ni}$  (Suckert *et al.*, 2016), both metal cations are linked by pairs of  $\mu$ -1,3-bridging anions into dinuclear units that, as in the title compound, are further connected by single  $\mu$ -1,3-bridging anionic ligands into layers.

### 3. Supramolecular features

In the crystal structure of the title compound, the layers are parallel to the *bc* plane and are separated by the methyl



**Figure 3**  
Crystal structure of the title compound with view along the crystallographic *a*-axis, showing the layered network. For the 4-methylpyridine *N*-oxide coligands, only the O atoms are shown.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C11}-\text{H11}\cdots\text{S2}^{\text{iii}}$	0.95	2.95	3.4900 (15)	118
$\text{C11}-\text{H11}\cdots\text{O21}$	0.95	2.57	3.2004 (18)	124
$\text{C12}-\text{H12}\cdots\text{S1}^{\text{iv}}$	0.95	2.96	3.8544 (16)	157
$\text{O21}-\text{H21}\cdots\text{S1}^{\text{v}}$	0.82 (2)	2.53 (2)	3.3028 (11)	159 (2)
$\text{C22}-\text{H22C}\cdots\text{S2}^{\text{vi}}$	0.98	2.93	3.7185 (18)	138

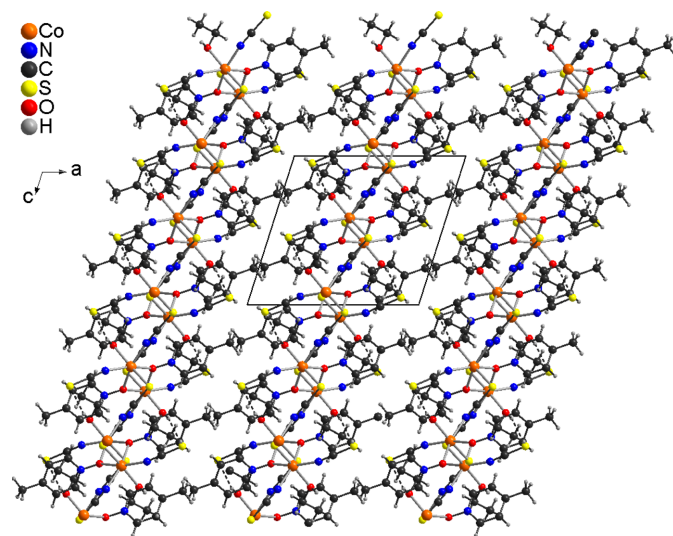
Symmetry codes: (iii)  $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$ ; (iv)  $-x+2, -y+1, -z+1$ ; (v)  $x, -y+\frac{1}{2}, z+\frac{1}{2}$ ; (vi)  $-x+1, -y+1, -z+2$ .

groups of the 4-methylpyridine *N*-oxide coligands (Fig. 3). Therefore, no significant intermolecular interactions are observed between the layers (Table 2). However, intralayer  $\text{C}-\text{H}\cdots\text{S}$  and  $\text{O}-\text{H}\cdots\text{S}$  hydrogen bonding is present with  $\text{C}-\text{H}\cdots\text{S}$  and  $\text{O}-\text{H}\cdots\text{S}$  angles close to linearity (Table 2 and Fig. 4).

### 4. Database survey

As mentioned above, two compounds based on  $\text{Co}(\text{NCS})_2$  and 4-methylpyridine *N*-oxide are already reported in the CSD (version 5.43, last update March 2023; Groom *et al.*, 2016). These include  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})$  (Refcode: MEQKOJ, Zhang *et al.*, 2006a) and  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})(\text{methanol})$  (Refcode: REKBUF, Shi *et al.*, 2006a). Two discrete complexes with the composition  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_3$  and  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_4$  (Näther & Jess, 2024a) as well as one chain compound with the composition  $\text{Co}_2(\text{NCS})_4(4\text{-methylpyridine } N\text{-oxide})_4(\text{methanol})_2$  (Näther & Jess, 2024b) are also reported.

Additionally, several other  $M(\text{NCS})_2$  compounds with 4-methylpyridine *N*-oxide are also listed in the CSD. These include  $M(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})$  with  $M = \text{Ni}$ ,



**Figure 4**  
Crystal structure of the title compound with view along the crystallographic *b*-axis, showing the arrangement of the layers. Intralayer hydrogen bonding is shown as dashed lines.

Cd) (Refcodes: PEDSUN, Shi *et al.*, 2006b; PEDSUN01, Marsh, 2009; TEQKAC, Shi *et al.*, 2006c). With copper(II), a compound with the composition  $\text{Cu}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})$  is reported in which the  $\text{Cu}^{\text{II}}$  cations are octahedrally coordinated and linked into chains by pairs of bridging thiocyanate anions, which are further connected into double chains *via*  $\text{Cu}_2\text{S}_2$  rings (Refcode TEBTAW, Shi *et al.*, 2006d). With  $\text{Ni}^{\text{II}}$  and  $\text{Mn}^{\text{II}}$ , two discrete aqua complexes with the composition  $M(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_2(\text{H}_2\text{O})_2$  ( $M = \text{Ni}$ , Shi *et al.*, 2006a and  $M = \text{Mn}$ , Mautner *et al.*, 2018a,b) are also reported. Three isotopic compounds with the composition  $M(\text{NCS})_2(\text{acetato})_2(\text{H}_2\text{O})_3(4\text{-methylpyridine } N\text{-oxide})$  with  $M = \text{Sm}$ ,  $\text{Eu}$ ,  $\text{Gd}$ ) are also known (Refcodes: GIHBUV, Zhang & Shi, 2007; PIJBIU and PIJBOA, Shi *et al.*, 2007a).

Some  $\text{Co}(\text{NCS})_2$  compounds with other pyridine *N*-oxide derivatives are also known. These include  $\text{Co}(\text{NCS})_2(\text{pyridine } N\text{-oxide})_2(\text{H}_2\text{O})_2$  and  $\text{Co}(\text{NCS})_2(3\text{-hydroxypyridine } N\text{-oxide})_2(\text{H}_2\text{O})_2$ , which consist of discrete octahedral complexes (Refcodes: FONBIU, Shi *et al.*, 2005; IDOYEG, Shi *et al.*, 2006e). They also include  $\text{Co}(\text{NCS})_2(4\text{-methoxypyridine } N\text{-oxide})$ , which is isotopic to its 4-methylpyridine analog (Refcode TERRAK, Zhang *et al.*, 2006b) and  $\text{Co}(\text{NCS})_2(4\text{-nitropyridine } N\text{-oxide})$  (Shi *et al.*, 2007b). Finally, we have also reported some  $\text{Co}(\text{NCS})_2$  compounds with pyridine *N*-oxide derivatives, including  $\text{Co}(\text{NCS})_2(3\text{-cyanopyridine } N\text{-oxide})_4$  (Näther & Jess, 2023),  $\text{Co}(\text{NCS})_2(2\text{-methylpyridine } N\text{-oxide})$  (Näther & Jess, 2024c), and  $\text{Co}(\text{NCS})_2(2\text{-methylpyridine } N\text{-oxide})_3$  (Näther & Jess, 2024d).

## 5. Synthesis and crystallization

$\text{Co}(\text{NCS})_2$  (99%) was purchased from Sigma Aldrich and 4-methylpyridine *N*-oxide (97%) from Thermo Scientific.

### Synthesis:

Crystals of the title compound were accidentally obtained by the reaction of 0.5 mmol (87 mg)  $\text{Co}(\text{SCN})_2$  and 0.5 mmol (54 mg) of 4-methylpyridine *N*-oxide in 1 mL of ethanol. The reaction mixture was stored overnight, which led to the formation of a violet-colored crystalline precipitate. X-ray powder diffraction measurements prove that the majority of the sample consists of the known discrete complex  $\text{Co}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})_3$  (Näther & Jess, 2024a) and that only traces of the title compound are present.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C—H hydrogen atoms were positioned with idealized geometry (methyl H atoms allowed to rotate and not to tip) 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.

## Acknowledgements

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

**Table 3**

Experimental details.

Crystal data	
Chemical formula	$[\text{Co}(\text{NCS})_2(\text{C}_6\text{H}_7\text{NO})(\text{C}_2\text{H}_6\text{O})]$
$M_r$	330.28
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
$a, b, c$ (Å)	11.67627 (7), 11.61861 (6), 10.60662 (7)
$\beta$ (°)	107.5929 (7)
$V$ (Å <sup>3</sup> )	1371.62 (2)
$Z$	4
Radiation type	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	12.65
Crystal size (mm)	0.15 × 0.12 × 0.10 × 0.08 (radius)
Data collection	
Diffraction	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2023)
$T_{\text{min}}, T_{\text{max}}$	0.453, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	23514, 2937, 2909
$R_{\text{int}}$	0.022
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.022, 0.058, 1.05
No. of reflections	2937
No. of parameters	170
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.35, -0.29

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

## References

- Böhme, M., Jochim, A., Rams, M., Lohmiller, T., Suckert, S., Schnegg, A., Plass, W. & Näther, C. (2020). *Inorg. Chem.* **59**, 5325–5338.
- 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.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Maji, T. K., Laskar, I. R., Mostafa, G., Welch, A. J., Mukherjee, P. S. & Chaudhuri, N. E. (2001). *Polyhedron*, **20**, 651–655.
- Marsh, R. E. (2009). *Acta Cryst.* **B65**, 782–783.
- Mautner, F. E., Berger, C., Fischer, R. C., Massoud, S. S. & Vicente, R. (2018a). *Polyhedron*, **141**, 17–24.
- Mautner, F. E., Traber, M., Fischer, R. C., Torvisco, A., Reichmann, K., Speed, S., Vicente, R. & Massoud, S. S. (2018b). *Polyhedron*, **154**, 436–442.
- Näther, C. & Jess, I. (2023). *Acta Cryst.* **E79**, 302–307.
- Näther, C. & Jess, I. (2024a). *Acta Cryst.* **E80**, 174–179.
- Näther, C. & Jess, I. (2024b). *Acta Cryst.* **E80**, 481–485.
- Näther, C. & Jess, I. (2024c). *Acta Cryst.* **E80**, 67–71.
- Näther, C. & Jess, I. (2024d). *Acta Cryst.* **E80**, 463–467.
- Neumann, T., Ceglarska, M., Rams, M., Germann, L. Z., Dinnebie, R. E., Suckert, S., Jess, I. & Näther, C. (2018). *Inorg. Chem.* **57**, 3305–3314.
- Palion-Gazda, J., Machura, B., Lloret, F. & Julve, M. (2015). *Cryst. Growth Des.* **56**, 2380–2388.
- Rams, M., Böhme, M., Kataev, V., Krupskaya, Y., Büchner, B., Plass, W., Neumann, T., Tomkowicz, Z. & Näther, C. (2017a). *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., Tomkowicz, Z., Böhme, M., Plass, W., Suckert, S., Werner, J., Jess, I. & Näther, C. (2017b). *Phys. Chem. Chem. Phys.* **19**, 3232–3243.
- Rigaku OD (2023). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Shi, J. M., Chen, J. N., Wu, C. J. & Ma, J. P. (2007b). *J. Coord. Chem.* **60**, 2009–2013.
- Shi, J. M., Li, W. N., Zhang, F. X., Zhang, X. & Liu, L. D. (2007a). *Chin. J. Struct. Chem.* **26**, 118–121.
- Shi, J. M., Liu, Z., Lu, J. J. & Liu, L. D. (2005). *Acta Cryst.* **E61**, m1133–m1134.
- Shi, J. M., Liu, Z., Wu, C. J., Xu, H. Y. & Liu, L. D. (2006c). *J. Coord. Chem.* **59**, 1883–1889.
- Shi, J. M., Sun, Y. M., Liu, Z. & Liu, L. D. (2006b). *Chem. Phys. Lett.* **418**, 84–89.
- Shi, J. M., Sun, Y. M., Liu, Z., Liu, L. D., Shi, W. & Cheng, P. (2006d). *Dalton Trans.* 376–380.pp.
- Shi, J.-M., Xu, H.-Y. & Liu, L.-D. (2006e). *Acta Cryst.* **E62**, m1577–m1578.
- Shi, J. M. L., Liu, Z., Sun, Y. M., Yi, L. & Liu, L. D. (2006a). *Chem. Phys.* **325**, 237–242.
- Suckert, S., Rams, M., Böhme, M., Germann, L. S., Dinnebier, R. E., Plass, W., Werner, J. & Näther, C. (2016). *Dalton Trans.* **45**, 18190–18201.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Zhang, S.-G., Li, W.-N. & Shi, J.-M. (2006a). *Acta Cryst.* **E62**, m3506–m3608.
- Zhang, S.-G., Li, W.-N. & Shi, J.-M. (2006b). *Acta Cryst.* **E62**, m3398–m3400.
- Zhang, S.-G. & Shi, J.-M. (2007). *Acta Cryst.* **E63**, m1775–m1776.

## supporting information

*Acta Cryst.* (2024). E80, 1029-1033 [https://doi.org/10.1107/S2056989024009058]

## Synthesis and crystal structure of poly[ethanol( $\mu$ -4-methylpyridine *N*-oxide)di- $\mu$ -thiocyanato-cobalt(II)]

Christian Näther and Inke Jess

### Computing details

#### Poly[ethanol( $\mu$ -4-methylpyridine *N*-oxide)di- $\mu$ -thiocyanato-cobalt(II)]

##### Crystal data

[Co(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>7</sub>NO)(C<sub>2</sub>H<sub>6</sub>O)]

$M_r = 330.28$

Monoclinic,  $P2_1/c$

$a = 11.67627(7) \text{ \AA}$

$b = 11.61861(6) \text{ \AA}$

$c = 10.60662(7) \text{ \AA}$

$\beta = 107.5929(7)^\circ$

$V = 1371.62(2) \text{ \AA}^3$

$Z = 4$

$F(000) = 676$

$D_x = 1.599 \text{ Mg m}^{-3}$

Cu  $K\alpha$  radiation,  $\lambda = 1.54184 \text{ \AA}$

Cell parameters from 19460 reflections

$\theta = 4.0\text{--}79.9^\circ$

$\mu = 12.65 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, pink

$0.15 \times 0.12 \times 0.10 \times 0.08$  (radius) 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:  $10.0000 \text{ pixels mm}^{-1}$

$\omega$  scans

Absorption correction: multi-scan  
(CrysAlisPro; Rigaku OD, 2023)

$T_{\min} = 0.453$ ,  $T_{\max} = 1.000$

23514 measured reflections

2937 independent reflections

2909 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 80.4^\circ$ ,  $\theta_{\min} = 4.0^\circ$

$h = -14 \rightarrow 13$

$k = -14 \rightarrow 14$

$l = -11 \rightarrow 13$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.058$

$S = 1.05$

2937 reflections

170 parameters

1 restraint

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 0.9886P]$

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

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

$\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$

Extinction correction: *SHELXL2016/6*

(Sheldrick, 2015b),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00084 (11)

*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	0.56402 (2)	0.37657 (2)	0.58362 (2)	0.01116 (8)
N1	0.70562 (11)	0.28747 (11)	0.55557 (12)	0.0163 (3)
C1	0.77833 (13)	0.25258 (12)	0.51159 (14)	0.0156 (3)
S1	0.88296 (3)	0.20182 (3)	0.45220 (4)	0.02192 (10)
N2	0.51802 (11)	0.31162 (11)	0.74214 (12)	0.0155 (2)
C2	0.47782 (13)	0.29336 (12)	0.82748 (14)	0.0143 (3)
S2	0.41839 (3)	0.26862 (3)	0.94760 (3)	0.01787 (9)
O11	0.56699 (9)	0.48910 (9)	0.43004 (10)	0.0133 (2)
N11	0.66546 (11)	0.50302 (10)	0.38914 (12)	0.0123 (2)
C11	0.76069 (13)	0.56068 (13)	0.46681 (14)	0.0164 (3)
H11	0.759449	0.589098	0.550371	0.020*
C12	0.86013 (13)	0.57840 (13)	0.42474 (15)	0.0179 (3)
H12	0.927076	0.619664	0.479306	0.021*
C13	0.86310 (13)	0.53621 (13)	0.30276 (15)	0.0175 (3)
C14	0.76325 (14)	0.47485 (13)	0.22755 (15)	0.0182 (3)
H14	0.762990	0.443743	0.144637	0.022*
C15	0.66507 (13)	0.45867 (13)	0.27160 (14)	0.0164 (3)
H15	0.597523	0.416577	0.219592	0.020*
C16	0.96938 (15)	0.55720 (18)	0.25409 (17)	0.0289 (4)
H16A	0.984966	0.488350	0.208476	0.043*
H16B	1.040050	0.574519	0.329344	0.043*
H16C	0.952495	0.622453	0.192663	0.043*
O21	0.70560 (9)	0.46801 (9)	0.72670 (10)	0.0153 (2)
H21	0.7507 (19)	0.4167 (18)	0.764 (2)	0.036 (6)*
C21	0.68639 (13)	0.54339 (13)	0.82663 (15)	0.0173 (3)
H21A	0.671358	0.496901	0.898243	0.021*
H21B	0.614811	0.591950	0.787326	0.021*
C22	0.79487 (16)	0.61910 (14)	0.88314 (18)	0.0248 (4)
H22A	0.808629	0.666175	0.812428	0.037*
H22B	0.865522	0.570888	0.922494	0.037*
H22C	0.780882	0.669390	0.951198	0.037*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.01275 (12)	0.01291 (13)	0.00940 (12)	0.00043 (8)	0.00570 (9)	0.00058 (8)
N1	0.0177 (6)	0.0179 (6)	0.0145 (6)	0.0026 (5)	0.0067 (5)	0.0004 (5)
C1	0.0164 (7)	0.0152 (7)	0.0144 (6)	-0.0010 (5)	0.0033 (5)	-0.0004 (5)
S1	0.01501 (17)	0.0262 (2)	0.0272 (2)	-0.00084 (14)	0.01044 (14)	-0.00874 (15)

N2	0.0178 (6)	0.0167 (6)	0.0136 (6)	0.0006 (5)	0.0070 (5)	0.0013 (5)
C2	0.0151 (6)	0.0137 (6)	0.0135 (6)	0.0023 (5)	0.0033 (5)	0.0004 (5)
S2	0.02135 (18)	0.02055 (18)	0.01625 (17)	0.00594 (13)	0.01250 (14)	0.00563 (13)
O11	0.0125 (5)	0.0164 (5)	0.0145 (5)	0.0014 (4)	0.0092 (4)	0.0033 (4)
N11	0.0127 (5)	0.0132 (5)	0.0130 (5)	0.0007 (4)	0.0067 (4)	0.0018 (4)
C11	0.0170 (7)	0.0187 (7)	0.0139 (6)	0.0007 (6)	0.0051 (5)	-0.0004 (5)
C12	0.0149 (7)	0.0213 (7)	0.0181 (7)	-0.0022 (6)	0.0060 (5)	-0.0009 (6)
C13	0.0162 (7)	0.0206 (7)	0.0181 (7)	0.0010 (6)	0.0087 (6)	0.0031 (6)
C14	0.0206 (7)	0.0212 (7)	0.0152 (7)	0.0013 (6)	0.0092 (6)	-0.0008 (6)
C15	0.0183 (7)	0.0173 (7)	0.0145 (6)	-0.0017 (6)	0.0063 (5)	-0.0021 (5)
C16	0.0216 (8)	0.0459 (11)	0.0242 (8)	-0.0054 (7)	0.0143 (7)	-0.0012 (7)
O21	0.0154 (5)	0.0180 (5)	0.0130 (5)	0.0007 (4)	0.0052 (4)	-0.0017 (4)
C21	0.0169 (7)	0.0196 (7)	0.0165 (7)	0.0011 (6)	0.0067 (6)	-0.0039 (6)
C22	0.0225 (8)	0.0266 (9)	0.0263 (8)	-0.0042 (6)	0.0088 (7)	-0.0098 (6)

*Geometric parameters (Å, °)*

Co1—N1	2.0472 (13)	C13—C14	1.393 (2)
Co1—N2	2.0569 (12)	C13—C16	1.501 (2)
Co1—S2 <sup>i</sup>	2.5171 (4)	C14—H14	0.9500
Co1—O11	2.0971 (10)	C14—C15	1.375 (2)
Co1—O11 <sup>ii</sup>	2.1594 (10)	C15—H15	0.9500
Co1—O21	2.1559 (10)	C16—H16A	0.9800
N1—C1	1.158 (2)	C16—H16B	0.9800
C1—S1	1.6438 (15)	C16—H16C	0.9800
N2—C2	1.158 (2)	O21—H21	0.815 (16)
C2—S2	1.6498 (15)	O21—C21	1.4437 (17)
O11—N11	1.3557 (15)	C21—H21A	0.9900
N11—C11	1.3454 (19)	C21—H21B	0.9900
N11—C15	1.3477 (18)	C21—C22	1.509 (2)
C11—H11	0.9500	C22—H22A	0.9800
C11—C12	1.379 (2)	C22—H22B	0.9800
C12—H12	0.9500	C22—H22C	0.9800
C12—C13	1.394 (2)		
N1—Co1—N2	110.80 (5)	C13—C12—H12	119.8
N1—Co1—S2 <sup>i</sup>	90.75 (4)	C12—C13—C16	121.15 (14)
N1—Co1—O11 <sup>ii</sup>	160.49 (5)	C14—C13—C12	117.39 (14)
N1—Co1—O11	89.92 (4)	C14—C13—C16	121.46 (14)
N1—Co1—O21	82.55 (5)	C13—C14—H14	119.5
N2—Co1—S2 <sup>i</sup>	85.67 (4)	C15—C14—C13	120.97 (14)
N2—Co1—O11 <sup>ii</sup>	88.01 (4)	C15—C14—H14	119.5
N2—Co1—O11	158.96 (5)	N11—C15—C14	119.46 (14)
N2—Co1—O21	86.53 (5)	N11—C15—H15	120.3
O11—Co1—S2 <sup>i</sup>	98.02 (3)	C14—C15—H15	120.3
O11 <sup>ii</sup> —Co1—S2 <sup>i</sup>	95.96 (3)	C13—C16—H16A	109.5
O11—Co1—O11 <sup>ii</sup>	71.03 (4)	C13—C16—H16B	109.5
O11—Co1—O21	92.89 (4)	C13—C16—H16C	109.5



O21—Co1—S2 <sup>i</sup>	167.20 (3)	H16A—C16—H16B	109.5
O21—Co1—O11 <sup>ii</sup>	93.90 (4)	H16A—C16—H16C	109.5
C1—N1—Co1	163.29 (12)	H16B—C16—H16C	109.5
N1—C1—S1	178.79 (14)	Co1—O21—H21	103.2 (17)
C2—N2—Co1	166.81 (12)	C21—O21—Co1	124.02 (9)
N2—C2—S2	178.99 (14)	C21—O21—H21	107.9 (17)
C2—S2—Co1 <sup>iii</sup>	100.98 (5)	O21—C21—H21A	109.6
Co1—O11—Co1 <sup>ii</sup>	108.96 (4)	O21—C21—H21B	109.6
N11—O11—Co1	122.53 (8)	O21—C21—C22	110.31 (12)
N11—O11—Co1 <sup>ii</sup>	122.99 (8)	H21A—C21—H21B	108.1
C11—N11—O11	119.16 (12)	C22—C21—H21A	109.6
C11—N11—C15	121.87 (12)	C22—C21—H21B	109.6
C15—N11—O11	118.97 (12)	C21—C22—H22A	109.5
N11—C11—H11	120.1	C21—C22—H22B	109.5
N11—C11—C12	119.79 (13)	C21—C22—H22C	109.5
C12—C11—H11	120.1	H22A—C22—H22B	109.5
C11—C12—H12	119.8	H22A—C22—H22C	109.5
C11—C12—C13	120.49 (14)	H22B—C22—H22C	109.5

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C11—H11 $\cdots$ S2 <sup>iv</sup>	0.95	2.95	3.4900 (15)	118
C11—H11 $\cdots$ O21	0.95	2.57	3.2004 (18)	124
C12—H12 $\cdots$ S1 <sup>v</sup>	0.95	2.96	3.8544 (16)	157
O21—H21 $\cdots$ S1 <sup>iii</sup>	0.82 (2)	2.53 (2)	3.3028 (11)	159 (2)
C22—H22C $\cdots$ S2 <sup>vi</sup>	0.98	2.93	3.7185 (18)	138

Symmetry codes: (iii)  $x, -y+1/2, z+1/2$ ; (iv)  $-x+1, y+1/2, -z+3/2$ ; (v)  $-x+2, -y+1, -z+1$ ; (vi)  $-x+1, -y+1, -z+2$ .