Acta Cryst E
CRYSTALLOGRAPHIC
COMMUNICATIONS

ISSN 2056-9890

Synthesis, crystal structure and thermal properties of diaquabis(4-methylpyridine-κN)bis(thiocyanato-κN)cobalt(II)

Christian Näther* and Jan Boeckmann

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

Received 19 March 2025
Accepted 17 April 2025

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

Keywords: synthesis; crystal structure; cobalt thiocyanate; 4-methylpyridine; thermal properties.

CCDC reference: 2444751

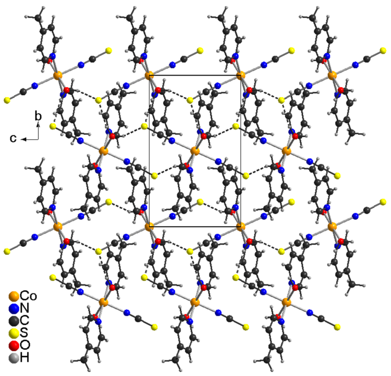
Supporting information: this article has supporting information at journals.iucr.org/e

The reaction of $Co(NCS)_2$ and 4-methylpyridine (C_6H_7N) in water leads to the formation of light-blue single crystals of the title compound, $[Co(NCS)_2(C_6H_7N)_2(H_2O)_2]$. The asymmetric unit consists of one Co^{II} cation (site symmetry $\bar{1}$) as well as one thiocyanate anion, one 4-methylpyridine coligand and one water molecule in general positions to generate *trans*-CoN_4O_2 octahedra. In the crystal, the complexes are linked by O—H$\cdots$S hydrogen bonds into a layered network. Powder X-ray diffraction (PXRD) shows that a pure sample has been obtained. Upon heating, the title compound loses its water molecules and transforms into $Co(NCS)_2(C_6H_7N)_2$, which is already reported in the literature.

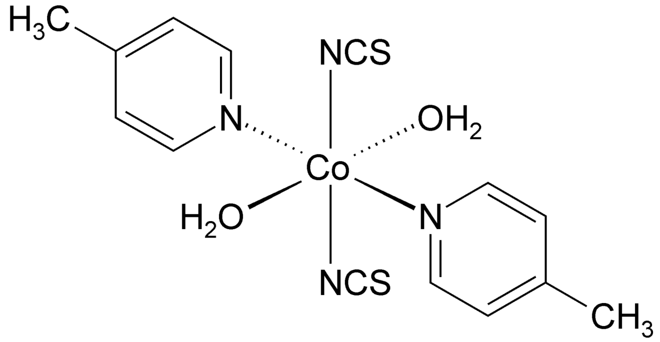
1. Chemical context

The synthesis of new coordination compounds is still an important field in inorganic chemistry. In most cases, they are prepared in solution but there are synthetic alternatives such as molecular milling (Braga *et al.*, 2005, 2006; James *et al.*, 2012; Do & Friščić, 2017; Stolar *et al.*, 2017) or reactions in melts (Müller-Buschbaum, 2005; Höller & Müller-Buschbaum, 2008; Zurawski *et al.*, 2012). We have also developed a new route, which is based on thermal ligand removal, that in the beginning was used for the preparation of new transition-metal halide compounds (Näther *et al.*, 2001, 2002). Later, this method was used for the synthesis of transition-metal thio- and selenocyanate coordination compounds, which were of interest not only because of their versatile structural behavior but also because of their promising magnetic properties. Following this route, discrete complexes with the composition $M(NCS)_2(L)_4$ (M = Mn, Fe, Co, Ni and L = neutral N-donor coligand) are heated in a thermobalance, which mostly leads to a stepwise removal of the coligands and the transformation into new compounds with the composition $M(NCS)_2(L)_2$, in which the metal cations are linked into chains or layers (Werner *et al.*, 2015; Neumann *et al.*, 2018; Jochim *et al.*, 2020*a*). In this context, $Co(NCS)_2$ compounds with chain structures are of special interest, because they can show one-dimensional or three-dimensional ferromagnetic ordering (Mautner *et al.*, 2018; Rams *et al.*, 2017, 2020; Jochim *et al.*, 2020*b*).

However, in some cases the thermogravimetric curves are not well resolved and the isolation of a pure intermediate phase is difficult or even impossible to achieve. In such cases, the usage of precursors, consisting of simple solvato complexes with the composition $M(NCS)_2(L1)_2(L2)_2$ ($L1$ = mono-coordinating neutral N-donor coligand, $L2$ = *e.g.*, H_2O, MeOH, EtOH, MeCN) is of advantage. If they are heated, the



solvent is lost in the beginning in a well-resolved step and the desired intermediate phase is obtained pure (Näther *et al.*, 2013). In this context, we have reported on two isomers of Co(NCS)$_2$(4-chloropyridine)$_2$ in which the metal cations are octahedrally coordinated and linked by pairs of thiocyanate anions into chains (Böhme *et al.*, 2020). In the triclinic isomer, an all-*trans* configuration is observed, leading to the formation of linear chains, whereas in the monoclinic isomer an alternating all-*trans* and *cis–cis–trans* configurations are observed, which results in the formation of corrugated chains. The monoclinic form is obtained from solution, whereas the triclinic form can be obtained by thermal decomposition of the precursor complex Co(NCS)$_2$(4-chloropyridine)$_2$(H$_2$O)$_2$. Solvent-mediated conversion experiments reveal that the monoclinic form with corrugated chains is thermodynamically stable at room-temperature.



In a continuation of this work, we reported the synthesis and crystal structure of the analogous compound Co(NCS)$_2$(4-methylpyridine)$_2$ in which the chlorine atom is replaced by a methyl group (Näther & Boeckmann, 2025). Based on the chloro–methyl exchange rule (Desiraju & Sarma, 1986), we expected the formation of a similar crystal structure that might be isotypic to one of the two forms of Co(NCS)$_2$(4-chloropyridine)$_2$. A single-crystal structure determination of the 4-methylpyridine compound proved that it is isotypic to the monoclinic form of Co(NCS)$_2$(4-chloropyridine)$_2$ that consists of corrugated chains. Based on the results obtained for the 4-chloropyridine ligands, it was of interest if an isomer with linear chains can be prepared by thermal decomposition of a suitable precursor with the composition Co(NCS)$_2$(4-chloropyridine)$_2$(H$_2$O)$_2$, which is not reported in the literature.

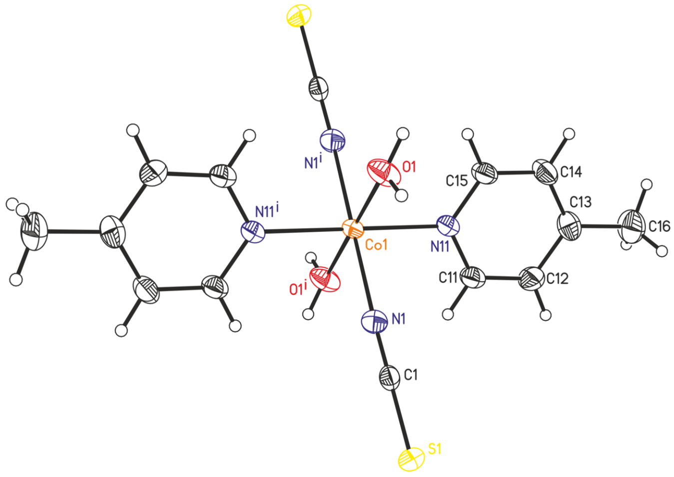


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Symmetry code: (i) $-x + 1, -y, -z$.

Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.090 (3)	Co1—N11	2.162 (2)
Co1—O1	2.105 (2)		
N1^{i}—Co1—O1	86.81 (10)	O1—Co1—N11^{i}	88.16 (9)
N1—Co1—O1	93.19 (10)	O1—Co1—N11	91.84 (9)
N1^{i}—Co1—N11	90.12 (10)	C1—N1—Co1	163.9 (3)
N1—Co1—N11	89.88 (10)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···S1^{ii}	0.96 (4)	2.35 (4)	3.234 (3)	153 (3)
O1—H1*B*···S1^{iii}	0.93 (5)	2.35 (5)	3.252 (2)	164 (5)
C12—H12···S1^{iv}	0.95	2.91	3.833 (3)	164

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

2. Structural commentary

The asymmetric unit of the title compound, Co(NCS)$_2$(C$_6$H$_7$N)$_2$(H$_2$O)$_2$ (C$_6$H$_7$N = 4-methylpyridine) is built up of one cobalt cation located on a crystallographic inversion centre as well as one thiocyanate anion, one 4-methylpyridine ligand and one water molecule that occupy general positions (Fig. 1). The Co cation is therefore sixfold coordinated in a *trans*-CoN$_4$O$_2$ geometry by two terminal N-bonded thiocyanate anions, two 4-methylpyridine ligands and two water molecules (Fig. 1). The bonding angles around the Co centers deviate from the ideal values, which means that the octahedra are slightly distorted (Table 1).

It is noted that the title compound is isotypic to Fe(NCS)$_2$(4-methylpyridine)$_2$(H$_2$O)$_2$ (Cambridge Structural Database refcode VUCCEE; Neumann *et al.*, 2020*a*) and Mn(NCS)$_2$(4-methylpyridine)$_2$(H$_2$O)$_2$ (VUJYAD; Neumann *et al.*, 2020*b*) reported in the literature. That the chloro-methyl-exchange is also valid for these compounds is shown by the fact that the title compound is also isotypic to Ni(NCS)$_2$(4-chloropyridine)$_2$(H$_2$O)$_2$ (GIQQEF; Jochim *et al.*, 2018) and Co(NCS)$_2$(4-chloropyridine)$_2$(H$_2$O)$_2$ (UHUVEB; Böhme *et al.*, 2020).

3. Supramolecular features

In the extended structure of the title compound, the complexes are linked by O—H···S hydrogen bonds into layers that lie parallel to the *bc*-plane (Fig. 2). The O—H···S bond angles are close to linear, which indicates that these are

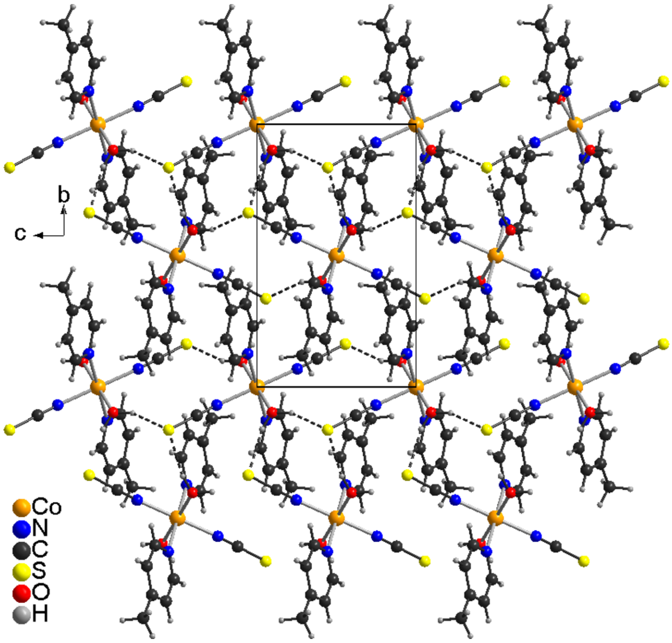


Figure 2
Crystal structure of the title compound in a view along the *a*-axis direction. O—H···S hydrogen bonds are shown as dashed lines.

relatively strong interactions (Table 2). Between the layers, no pronounced directional interactions are observed (Fig. 3).

4. Thermal properties

Comparison of the experimental powder pattern of the residue obtained in the synthesis with that calculated for the title compound shows that a pure crystalline phase has been obtained (Fig. 4).

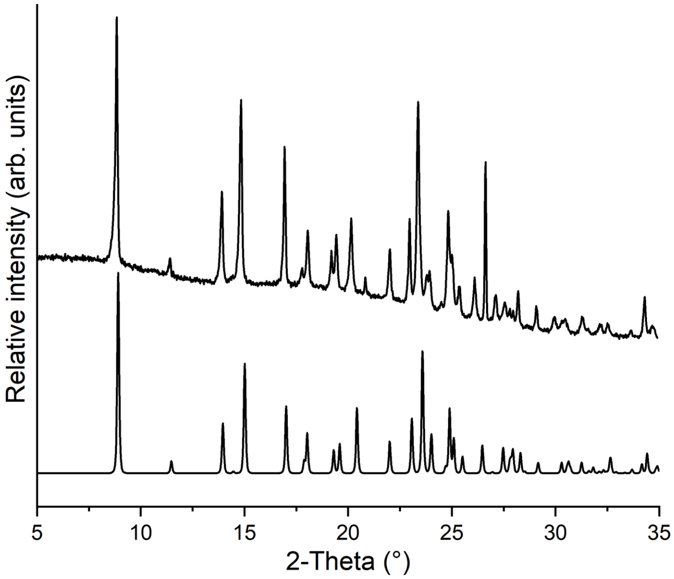


Figure 4
Experimental (top) and calculated (bottom) PXRD patterns for the title compound.

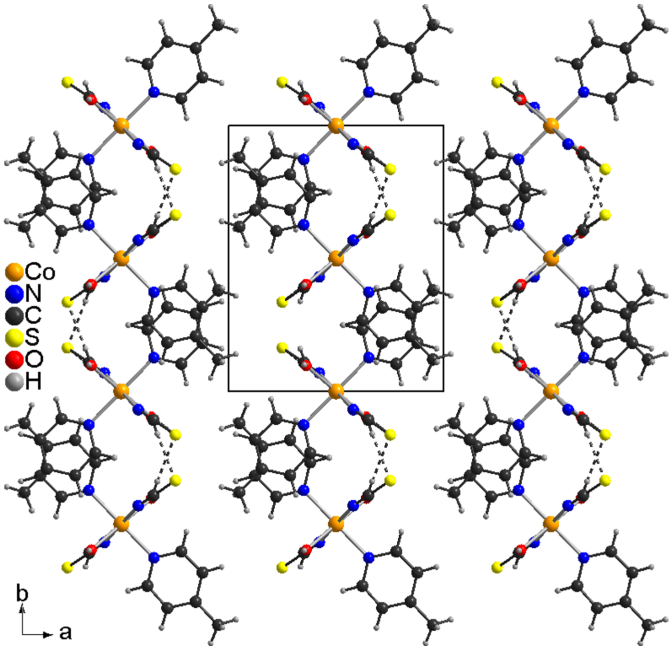


Figure 3
Crystal structure of the title compound in a view along the *c*-axis direction. O—H···S hydrogen bonding is shown as dashed lines.

The thermal properties of the title compound were investigated by differential thermoanalysis coupled to thermogravimetry (DTA–TG). Upon heating, one mass loss is observed in the TG curve accompanied with an endothermic event in the DTA curve at 88°C (Fig. 5). On further heating,

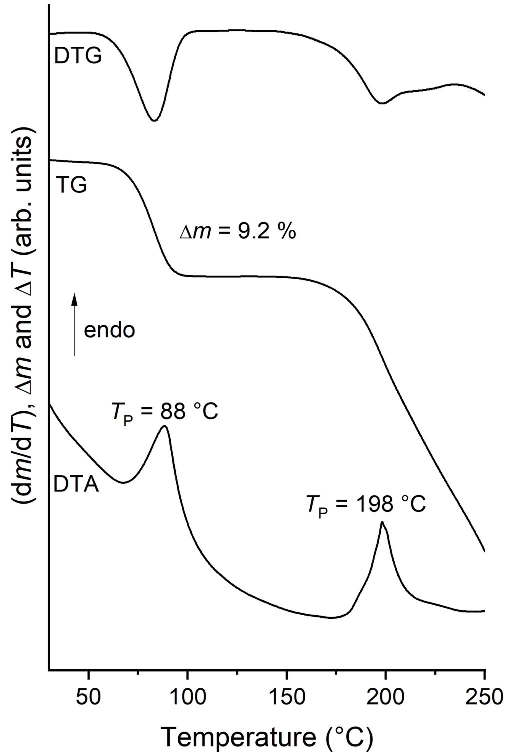


Figure 5
DTG, TG and DTA curves for the title compound. The mass loss is given in % and the peak temperature in °C.

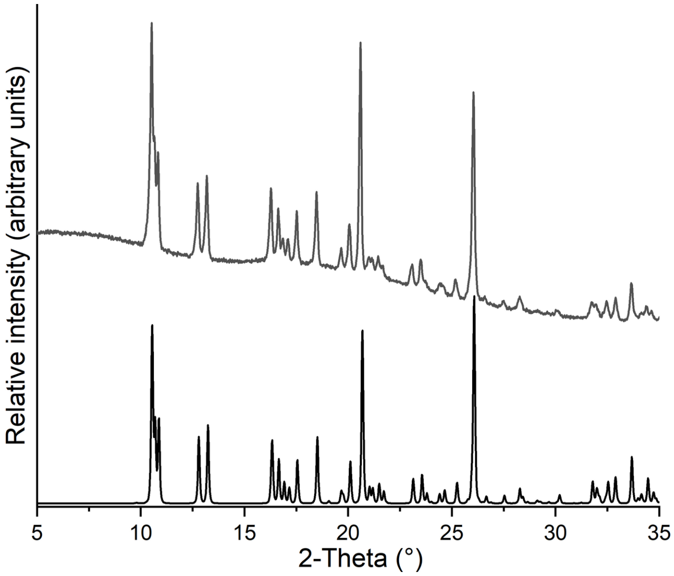


Figure 6
Experimental PXRD pattern of the residue obtained after the first mass loss in a TG measurement of the title compound (top) and the powder pattern for $Co(NCS)_2$(4-methylpyridine)$_2$ calculated from single-crystal data (bottom, Näther & Boeckmann, 2025).

the sample mass decreases continuously with a further poorly resolved mas-losss step, which is apparent in the DTG curve and which is accompanied with a second endothermic event in the DTA curve. The experimental mass loss in the first step of 9.2% is in good agreement with that calculated for the removal of the two water molecules (9.1%). Comparison of the experimental powder pattern of the residue obtained after the first mass loss shows that the monoclinic form with linear chains of $Co(NCS)_2$(4-methylpyridine)$_2$ (Näther & Boeckmann, 2025) has formed, which can also be obtained from solution (Fig. 6). This is in contrast to the observations made for the corresponding 4-chloropyridine compound (see *Chemical context*) and indicates that with 4-methylpyridine only one isomer might be accessible.

5. Database survey

According to a search in the CSD (version 5.43, last update December 2024; Groom *et al.*, 2016) using CONQUEST (Bruno *et al.*, 2002), some compounds containing $Co(NCS)_2$ and 4-methylpyridine have already been reported in the literature. These include a discrete complex with the composition CoNCS(4-methylpyridine)$_3$ with *p*-xylene solvate molecules (QQQGKJ; Solaculu *et al.*, 1974), but because no atomic coordinates are given and no charge balance is achieved, the existence of this compound is questionable. There is also a compound with the composition $Co(NCS)_2$(4-methylpyridine)$_2$-bis(*p*-toluidine)$_2$, which should consists of chains, but even for this structure no atomic coordinates are reported (Refcode: CECDAP; Micu-Semeniuc *et al.*, 1983).

All of the remaining hits describe discrete complexes with the composition $Co(NCS)_2$(4-methylpyridine)$_4$, which forms clathrates with 4-methylpyridine (XIHHEB; Harris *et al.*, 2001 and XIHHEB01; Harris *et al.*, 2003), nitrobenzene (ZZZUXU; Belitskus *et al.*, 1963), *p*-toluidine (CECCOC; Micu-Semeniuc *et al.*, 1983), nitroethane (ZZZUXY; Belitskus *et al.*, 1963) and benzene (ZZZUYI; Belitskus *et al.*, 1963). With one exception (XIHHEB), no atomic coordinates are presented for any of these compounds. The crystal structure of the complex $Co(NCS)_2$(4-methylpyridine)$_4$ is also found, but the unit-cell parameters are almost identical to that of several of the clathrates mentioned above, indicating that a potential solvent was not located (VERNUC; Harris *et al.*, 2003).

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Co(NCS)_2(C_6H_7N)_2(H_2O)_2]$
M_r	397.37
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	200
a, *b*, *c* (Å)	10.1901 (6), 12.2379 (10), 7.6165 (9)
β (°)	103.379 (10)
V (Å^3)	924.04 (15)
Z	2
Radiation type	Mo *Kα*
μ (mm^{-1})	1.17
Crystal size (mm)	0.30 × 0.22 × 0.21
Data collection	
Diffractometer	Stoe IPDS2
Absorption correction	Numerical (*X-SHAPE* and *X-RED32*; Stoe, 2008)
T_{min}, T_{max}	0.793, 0.813
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2179, 2179, 1822
R_{int}	?
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.662
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.143, 1.04
No. of reflections	2179
No. of parameters	117
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.23, −0.56

Computer programs: *X-AREA* (Stoe, 2008), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 1999), *XP* in *SHELXTL-PC* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

6. Synthesis and crystallization

$Co(NCS)_2$ (350.2 mg, 2.06 mmol, Alfa Aesar) and 4-methylpyridine (100 µl, 1.03 mmol, Fluka) were stirred together in 3 ml of water at room temperature in a snap cap vial for 3 d. Single crystals were prepared by the same method in the absence of stirring.

Powder X-ray diffraction measurements were performed using a Stoe STADI P transmission powder diffractometer with Cu $K\alpha_1$ radiation (λ = 1.540598 Å), a Johann-type Ge(111) monochromator and a MYTHEN 1K detector from Dectris. Thermogravimetry and differential thermoanalysis (TG–DTA) measurements were performed in a dynamic nitrogen atmosphere in Al_2O_3 crucibles with a heating rate of 4°C min^{-1} using a STA-PT 1000 thermobalance from Linseis.

The TG–DTA instrument was calibrated using standard reference materials.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C-bound hydrogen atoms were positioned with idealized geometry (methyl H atoms allowed to rotate and not to tip) and were refined with U_{iso}(H) = 1.2U_{eq}(C) (1.5 for methyl H atoms) using a riding model. The O-bound H atoms were located in a difference map and their positions and U_{iso} values were freely refined. The crystal chosen for data collection was twinned and therefore a twin refinement using data in HKLF-5 format was used leading to a BASF factor of 0.173 (3) for the minor twin component.

Acknowledgements

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

References

Belitskus, D., Jeffrey, G. A., McMullan, R. K. & Stephenson, N. C. (1963). *Inorg. Chem.* **2**, 873–875.

Böhme, M., Jochim, A., Rams, M., Lohmiller, T., Suckert, S., Schnegg, A., Plass, W. & Näther, C. (2020). *Inorg. Chem.* **59**, 5325–5338.

Braga, D., Curzi, M., Grepioni, F. & Polito, M. (2005). *Chem. Commun.* pp. 2915–2917.

Braga, D., Giaffreda, S. L., Grepioni, F., Pettersen, A., Maini, L., Curzi, M. & Polito, M. (2006). *Dalton Trans.* pp. 1249–1263.

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

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Desiraju, G. R. & Sarma, J. A. (1986). *Proc. - Indian Acad. Sci. Chem. Sci.* **96**, 599–605.

Do, J. L. & Friščić, T. (2017). *ACS Cent. Sci.* **3**, 13–19.

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

Harris, J. D., Eckles, W. E., Hepp, A. F., Duraj, S. A., Fanwick, P. E., Richardson, J. & Gordon, E. M. (2001). *Mater. Des.* **22**, 625–634.

Harris, J. D., Eckles, W. E., Hepp, A. F., Duraj, S. A., Hehemann, D. G., Fanwick, P. E. & Richardson, J. (2003). *NASA Technical Reports*, 211890.

Höller, C. J. & Müller-Buschbaum, K. (2008). *Inorg. Chem.* **47**, 10141–10149.

James, S. L., Adams, C. J., Bolm, C., Braga, D., Collier, P., Friščić, T., Grepioni, F., Harris, K. D. M., Hyett, G., Jones, W., Krebs, A., Mack, J., Maini, L., Orpen, A. G., Parkin, I. P., Shearouse, W. C., Steed, J. W. & Waddell, D. (2012). *Chem. Soc. Rev.* **41**, 413–447.

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

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

Jochim, A., Rams, M., Neumann, T., Wellm, C., Reinsch, H., Wójtowicz, G. M. & Näther, C. (2018). *Eur. J. Inorg. Chem.* 4779–4789.

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

Micu-Semeniuc, R., Hila, E., Dobos-Roman, G. & Ghergari, L. (1983). *Rev. Roum. Chim.* **28**, 471–475.

Müller-Buschbaum, K. (2005). *Z. Anorg. Allg. Chem.* **631**, 811–828.

Näther, C. & Boeckmann, J. (2025). *Acta Cryst.* E**81**, 58–62.

Näther, C., Greve, J. & Jess, I. (2002). *Solid State Sci.* **4**, 813–820.

Näther, C., Jess, I. & Greve, J. (2001). *Polyhedron*, **20**, 1017–1022.

Näther, C., Wöhlert, S., Boeckmann, J., Wriedt, M. & Jess, I. (2013). *Z. Anorg. Allg. Chem.* **639**, 2696–2714.

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

Neumann, T., Gallo, G., Dinnebier, R. E. & Näther, C. (2020*b*). *Z. Anorg. Allge Chem.* **646**, 88–94.

Neumann, T., Gallo, G., Jess, I., Dinnebier, R. E. & Näther, C. (2020*a*). *CrystEngComm*, **22**, 184–194.

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.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

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

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

Solaculu, I., Sandulescu, D. & Dragulescu, C. (1974). *Rev. Roum. Chim.* **19**, 415–417.

Stoe (2008). *X-AREA*, *X-RED32* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.

Stolar, T., Batzdorf, L., Lukin, S., Žilić, D., Motillo, C., Friščić, T., Emmerling, F., Halasz, I. & Užarević, K. (2017). *Inorg. Chem.* **56**, 6599–6608.

Werner, J., Rams, M., Tomkowicz, Z., Runčevski, T., Dinnebier, R. E., Suckert, S. & Näther, C. (2015). *Inorg. Chem.* **54**, 2893–2901.

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

Zurawski, A., Rybak, J. C., Meyer, L. V., Matthes, P. R., Stepanenko, V., Dannenbauer, N., Würthner, F. & Müller-Buschbaum, K. (2012). *Dalton Trans.* **41**, 4067–4078.

supporting information

Acta Cryst. (2025). E**81**, 420-424 [https://doi.org/10.1107/S2056989025003469]

Synthesis, crystal structure and thermal properties of diaquabis(4-methylpyridine-*κN*)bis(thiocyanato-*κN*)cobalt(II)

Christian Näther and Jan Boeckmann

Computing details

Diaquabis(4-methylpyridine-*κN*)bis(thiocyanato-*κN*)cobalt(II)

Crystal data

$[Co(NCS)_2(C_6H_7N)_2(H_2O)_2]$
$M_r = 397.37$
Monoclinic, $P2_1/c$
$a = 10.1901\ (6)$ Å
$b = 12.2379\ (10)$ Å
$c = 7.6165\ (9)$ Å
$\beta = 103.379\ (10)°$
$V = 924.04\ (15)$ Å^3
$Z = 2$
$F(000) = 410$
$D_x = 1.428$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5888 reflections
$\theta = 2.6–28.1°$
$\mu = 1.17$ mm^{-1}
$T = 200$ K
Block, light blue
0.30 × 0.22 × 0.21 mm

Data collection

Stoe IPDS-2
diffractometer
ω scans
Absorption correction: numerical
(X-Shape and X-Red32; Stoe, 2008)
$T_{min} = 0.793$, $T_{max} = 0.813$
2179 measured reflections
2179 independent reflections
1822 reflections with $I > 2\sigma(I)$
$\theta_{max} = 28.1°$, $\theta_{min} = 2.6°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = 0 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.143$
$S = 1.04$
2179 reflections
117 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1088P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.23$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}
Extinction correction: *SHELXL2016/6*
(Sheldrick 2015b),
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.044 (9)

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	0.500000	0.000000	0.000000	0.0221 (2)
N1	0.5788 (3)	−0.0691 (2)	0.2534 (4)	0.0319 (6)
C1	0.6496 (3)	−0.1080 (2)	0.3783 (4)	0.0227 (6)
S1	0.75122 (7)	−0.16385 (6)	0.55520 (11)	0.0295 (2)
O1	0.3604 (2)	0.09689 (18)	0.0952 (4)	0.0357 (5)
H1A	0.351 (4)	0.100 (3)	0.218 (6)	0.032 (10)*
H1B	0.333 (5)	0.161 (4)	0.032 (7)	0.061 (14)*
N11	0.6515 (2)	0.12690 (18)	0.0581 (4)	0.0262 (5)
C11	0.7790 (3)	0.1036 (2)	0.1405 (5)	0.0327 (7)
H11	0.803034	0.029241	0.164939	0.039*
C12	0.8776 (3)	0.1823 (3)	0.1920 (5)	0.0352 (7)
H12	0.966985	0.161295	0.249329	0.042*
C13	0.8462 (3)	0.2924 (2)	0.1600 (5)	0.0326 (7)
C14	0.7142 (3)	0.3165 (2)	0.0721 (5)	0.0326 (7)
H14	0.687692	0.390105	0.044934	0.039*
C15	0.6213 (3)	0.2326 (2)	0.0241 (5)	0.0294 (6)
H15	0.531593	0.251015	−0.036086	0.035*
C16	0.9504 (4)	0.3801 (3)	0.2155 (7)	0.0495 (10)
H16A	0.916053	0.449122	0.157288	0.074*
H16B	1.032996	0.359451	0.178640	0.074*
H16C	0.970268	0.389082	0.346878	0.074*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0262 (3)	0.0165 (3)	0.0219 (3)	0.00175 (17)	0.0019 (2)	0.00247 (18)
N1	0.0395 (13)	0.0261 (11)	0.0262 (13)	−0.0018 (10)	−0.0002 (11)	0.0060 (10)
C1	0.0284 (12)	0.0190 (11)	0.0211 (13)	−0.0054 (9)	0.0068 (10)	−0.0017 (10)
S1	0.0286 (4)	0.0301 (4)	0.0255 (4)	−0.0001 (3)	−0.0025 (3)	0.0029 (3)
O1	0.0472 (13)	0.0261 (10)	0.0374 (14)	0.0112 (9)	0.0171 (11)	0.0031 (9)
N11	0.0259 (11)	0.0191 (10)	0.0314 (13)	0.0022 (8)	0.0024 (10)	0.0020 (9)
C11	0.0273 (14)	0.0238 (13)	0.0430 (19)	0.0030 (11)	−0.0001 (13)	0.0049 (12)
C12	0.0247 (13)	0.0330 (15)	0.0435 (19)	0.0000 (12)	−0.0011 (12)	0.0037 (14)
C13	0.0332 (15)	0.0275 (14)	0.0400 (18)	−0.0062 (12)	0.0140 (13)	−0.0024 (12)
C14	0.0343 (14)	0.0200 (12)	0.0437 (19)	−0.0007 (11)	0.0094 (13)	0.0022 (12)
C15	0.0252 (12)	0.0221 (12)	0.0399 (17)	0.0035 (10)	0.0055 (12)	0.0049 (12)
C16	0.0386 (18)	0.0418 (19)	0.065 (3)	−0.0149 (15)	0.0063 (17)	−0.0028 (18)

Geometric parameters (Å, º)

Co1—N1	2.090 (3)	C11—H11	0.9500
Co1—N1^{i}	2.090 (3)	C11—C12	1.381 (4)
Co1—O1^{i}	2.105 (2)	C12—H12	0.9500
Co1—O1	2.105 (2)	C12—C13	1.393 (4)
Co1—N11^{i}	2.162 (2)	C13—C14	1.387 (4)
Co1—N11	2.162 (2)	C13—C16	1.501 (4)
N1—C1	1.155 (4)	C14—H14	0.9500
C1—S1	1.646 (3)	C14—C15	1.387 (4)
O1—H1A	0.96 (4)	C15—H15	0.9500
O1—H1B	0.93 (5)	C16—H16A	0.9800
N11—C11	1.337 (4)	C16—H16B	0.9800
N11—C15	1.341 (3)	C16—H16C	0.9800

N1—Co1—N1^{i}	180.0	C15—N11—Co1	122.18 (19)
N1^{i}—Co1—O1	86.81 (10)	N11—C11—H11	118.3
N1^{i}—Co1—O1^{i}	93.19 (10)	N11—C11—C12	123.3 (3)
N1—Co1—O1	93.19 (10)	C12—C11—H11	118.3
N1—Co1—O1^{i}	86.81 (10)	C11—C12—H12	119.9
N1^{i}—Co1—N11^{i}	89.88 (10)	C11—C12—C13	120.1 (3)
N1^{i}—Co1—N11	90.12 (10)	C13—C12—H12	119.9
N1—Co1—N11	89.88 (10)	C12—C13—C16	121.6 (3)
N1—Co1—N11^{i}	90.12 (10)	C14—C13—C12	116.6 (3)
O1—Co1—O1^{i}	180.0	C14—C13—C16	121.9 (3)
O1—Co1—N11^{i}	88.16 (9)	C13—C14—H14	120.1
O1^{i}—Co1—N11	88.16 (9)	C15—C14—C13	119.8 (3)
O1—Co1—N11	91.84 (9)	C15—C14—H14	120.1
O1^{i}—Co1—N11^{i}	91.84 (9)	N11—C15—C14	123.4 (3)
N11^{i}—Co1—N11	180.00 (9)	N11—C15—H15	118.3
C1—N1—Co1	163.9 (3)	C14—C15—H15	118.3
N1—C1—S1	179.5 (3)	C13—C16—H16A	109.5
Co1—O1—H1A	126 (2)	C13—C16—H16B	109.5
Co1—O1—H1B	116 (3)	C13—C16—H16C	109.5
H1A—O1—H1B	113 (4)	H16A—C16—H16B	109.5
C11—N11—Co1	120.91 (18)	H16A—C16—H16C	109.5
C11—N11—C15	116.8 (2)	H16B—C16—H16C	109.5

Co1—N11—C11—C12	−175.4 (3)	C11—C12—C13—C16	179.5 (4)
Co1—N11—C15—C14	175.0 (3)	C12—C13—C14—C15	1.1 (5)
N11—C11—C12—C13	0.5 (6)	C13—C14—C15—N11	0.1 (6)
C11—N11—C15—C14	−0.9 (5)	C15—N11—C11—C12	0.6 (5)
C11—C12—C13—C14	−1.4 (5)	C16—C13—C14—C15	−179.7 (4)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···S1^{ii}	0.96 (4)	2.35 (4)	3.234 (3)	153 (3)
O1—H1*B*···S1^{iii}	0.93 (5)	2.35 (5)	3.252 (2)	164 (5)
C12—H12···S1^{iv}	0.95	2.91	3.833 (3)	164

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