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Synthesis, crystal structure and properties of *catena*-poly[[bis(4-methylpyridine-κN)cobalt(II)]-di-μ-thiocyanato-$\kappa^2 N$:S;$\kappa^2 S$:N], which shows a rare coordination geometry

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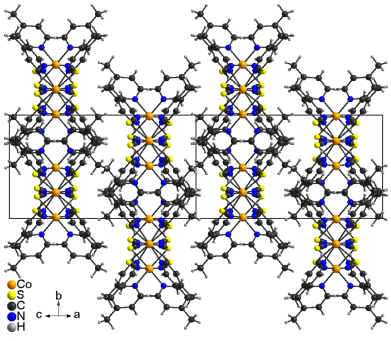
Reaction of $Co(NCS)_2$ with 4-methylpyridine in water leads to the formation of single crystals of the title compound, $[Co(NCS)_2(C_6H_7N)_2]_n$. The asymmetric unit consists of two crystallographically independent thiocyanate anions and two crystallographically independent 4-methylpyridine coligands in general positions, as well as of two different Co^{II} cations, of which one is located on a twofold rotational axis, whereas the second occupies a center of inversion. The methyl H atoms in both 4-methylpyridine ligands are disordered and were refined using a split model. Both Co^{II} cations are octahedrally coordinated by two N- and two S-bonded thiocyanate anions and two 4-methylpyridine coligands and are linked by pairs of 1,3-bridging anionic ligands into chains. Within these chains the cations show an alternating all-*trans* and *cis–cis–trans* configuration, which leads to the formation of corrugated chains. Powder X-ray diffraction proves that a pure crystalline phase has been obtained and the values of the CN stretching vibrations of the anionic ligands observed in the IR and the Raman spectra are in agreement with the presence of bridging anionic ligands.

1. Chemical context

For a long time, our interest has focused on the synthesis and crystal structure of transition-metal thiocyanate coordination compounds based on Mn^{II}, Fe^{II}, Co^{II} and Ni^{II}, because they show a large structural variability, which can partly be traced back to the versatile coordination behavior of this anionic ligand (Näther *et al.*, 2013). In nearly all cases these cations are in an octahedral coordination, even though with cobalt several compounds with a tetrahedral coordination are also known. Within this project we are especially interested in compounds in which the metal cations are linked into chains or layers, because such compounds show versatile magnetic behavior (Neumann *et al.*, 2018; Suckert *et al.*, 2016). This is especially the case for compounds based on cobalt, which can show 1D or 3D ferromagnetic ordering (Mautner *et al.*, 2018; Jochim *et al.*, 2020; Rams *et al.*, 2017*a*, 2020).

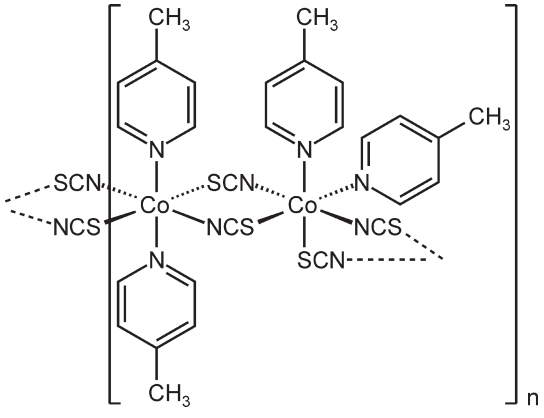
In most cases, chain compounds are observed in which the metal cations are in an octahedral all-*trans* coordination, leading to the formation of linear chains. Linear chains are also observed for a *cis–cis–trans*-coordination if the neutral coligands are in *trans*-positions, which is the case, for example, in $M(NCS)_2$(4-benzoylpyridine)$_2$ with M = Co, Ni [refcodes ODEYII (Rams *et al.*, 2017*b*) and GIQQUV (Jochim *et al.*, 2018)] or in $Co(NCS)_2$(2,3-dimethylpyrazine-1,4-dioxide) (PEVZOG; Shi *et al.*, 2007). Corrugated chains are observed if the two bridging S-bonded thiocyanate anions are in an *trans*-position like in $Mn(NCS)_2$(4-nitropyridine *N*-oxide



(SINKUW; Shi *et al.*, 2006*a*) or in $Ni(NCS)_2$(2,2′-bipyridine (GIQREG; Jochim *et al.*, 2018). If the two bridging N-bonded thiocanate anions are in a *trans*-position like in $Ni(NCS)_2$[1-(2-aminoethyl)pyrrolidine-*N*,*N*′) (ABOBIC; Maji *et al.*, 2001) corrugated chains are also observed, Finally, in $Ni(NCS)_2$(4-methylpyridine *N*-oxide [PEDSUN (Shi *et al.*, 2006*b*) and PEDSUN0 (Marsh, 2009)] an all-*cis* configuration is observed that also leads to the formation of corrugated chains.

In this context it is noted that we have reported on Co and Ni compounds with the composition $Ni(NCS)_2$(4-chloropyridine)$_2$ (UHUVIF and UHUVIF01; Jochim *et al.*, 2018 and $Co(NCS)_2$(4-chloropyridine)$_2$ (GIQQIJ and GIQQIJ01; Böhme *et al.*, 2020) for each of which two isomers exist. In one of these isomers the metal cations are in an all-*trans* configuration, whereas in the second isomer that is thermodynamically stable at room temperature, an alternating all-*trans* and *cis*–*cis*–*trans* configuration is observed. Based on these results, we tried to prepare compounds with $Ni(NCS)_2$ and 4-methylpyridine as ligand for which, because of the chloro–methyl exchange rule (Desiraju & Sarma, 1986), similar structures can be expected, but only one isomer with the composition $Ni(NCS)_2$(4-methylpyridine)$_2$ was obtained, which is isotypic to the stable isomer of $Ni(NCS)_2$(4-chloropyridine)$_2$ with an alternating all-*trans* and *cis*–*cis*–*trans* configuration (Näther & Mangelsen, 2024).

In the course of our systematic work we became interested in $Co(NCS)_2$ compounds with 4-methylpyridine as coligand, to check which of the two isomers might form and if this compound is isotypic to the corresponding Ni compound. It is noted that some of such compounds are already reported with this ligand. Most of them consist of solvates of discrete complexes but one chain compound is reported, for which no atomic coordinates are presented (see *Database survey*).



2. Structural commentary

The asymmetric unit of the title compound, $Co(NCS)_2(C_6H_7N)_2$, is built up of two crystallographically independent thiocyanate anions and two crystallographically independent 4-methylpyridine coligands in general positions, as well as of two crystallographically independent Co^{II} cations, of which one is located on a twofold rotational axis whereas the second occupies a center of inversion (Figs. 1 and 2). The methyl H atoms in both 4-methylpyridine ligands are disordered and were refined in two different orientations. Both Co^{II} cations are octahedrally coordinated by two 4-methylpyridine ligands and two N- and two S-bonding thiocyanate anions (Figs. 1 and 2). One of the Co^{II} cations (Co1) shows a *cis*–*cis*–*trans* configuration with the thiocyanate N atoms in a *trans* position and the pyridine N atom as well as the thiocyanate S atom in *cis* positions (Fig. 2). The second crystallographically independent Co^{II} cation (Co2) shows an all-*trans* configuration (Fig. 2). For the Co^{II} cation that shows a *cis*–*cis*–*trans* configuration, the Co—N distances to the 4-methylpyridine ligands are slightly shorter compared to the cation in the *cis*–*cis*–*trans* configuration (Table 1). Moreover, from the bond lengths and angles it is obvious that the octahedra are slightly distorted.

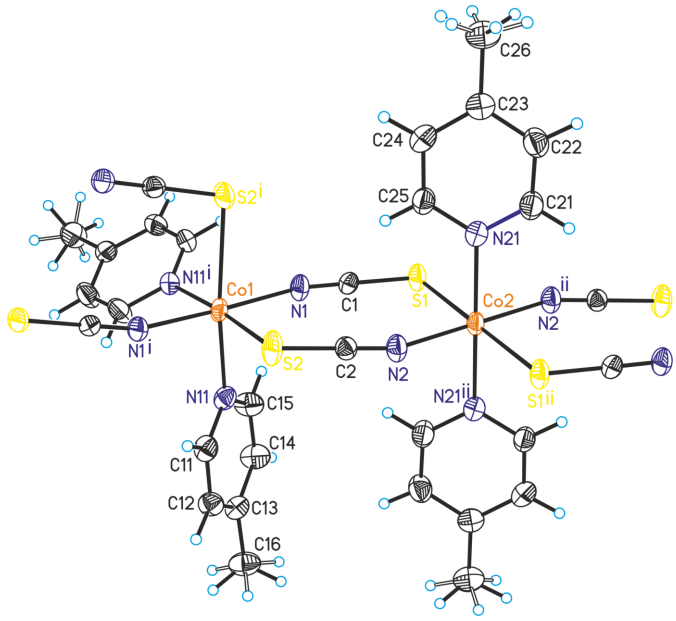


Figure 1
Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (i) $-x+1$, y, $-z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}$, $-y+\frac{1}{2}$, $-z+1$. The disorder of the methyl H atoms is shown with full and open bonds.

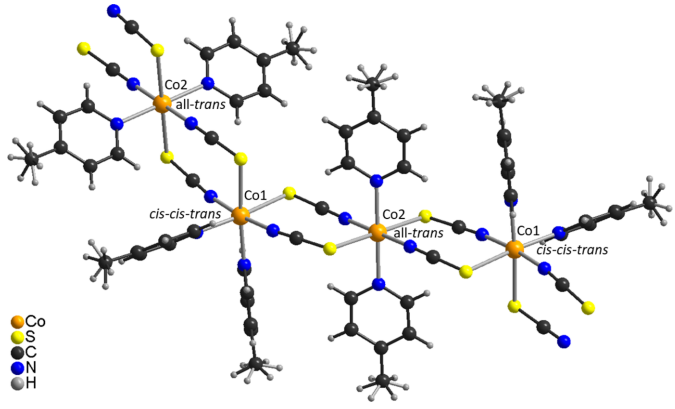


Figure 2
Crystal structure of the title compound with view of a part of a chain with labeling of the Co^{II} cations and showing the actual metal configuration. For clarity the disorder of the methyl H atoms is not shown.

Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.0699 (16)	Co2—S1	2.5752 (4)
Co1—S2	2.6138 (6)	Co2—N2	2.0585 (16)
Co1—N11	2.1437 (16)	Co2—N21	2.1768 (16)
N1^{i}—Co1—N1	174.16 (10)	N2—Co2—S1	93.94 (4)
N1^{i}—Co1—S2	82.53 (5)	N2^{ii}—Co2—S1	86.06 (5)
N1—Co1—S2	93.32 (5)	N2—Co2—N2^{ii}	180.00 (10)
N1^{i}—Co1—N11	93.35 (6)	N2—Co2—N21^{ii}	90.54 (6)
N1—Co1—N11	90.80 (6)	N2—Co2—N21	89.46 (6)
S2^{i}—Co1—S2	89.82 (3)	N21—Co2—S1	90.10 (4)
N11—Co1—S2	90.71 (4)	N21^{ii}—Co2—S1^{ii}	90.09 (4)
N11^{i}—Co1—S2	173.33 (4)	N21^{ii}—Co2—S1	89.90 (4)
N11—Co1—N11^{i}	89.54 (8)	N21—Co2—N21^{ii}	180.0
S1—Co2—S1^{ii}	180.0		

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

The metal cations are linked by pairs of μ-1,3-bridging thiocyanate anions into chains that, because of the alternating all-*trans* and *cis–cis–trans* configurations, are corrugated (Fig. 3). It is noted that the title compound is isotypic to the corresponding compound with Ni(NCS)$_2$ (Näther & Mangelsen, 2024) and to the isomer that is thermodynamically stable at room temperature of Ni(NCS)$_2$(4-chloropyridine)$_2$, which proves that the chloro–methyl exchange rule is valid in this case. From our synthetic work there is no hint of the existence of a second isomer of the title compound as observed for the corresponding 4-chloropyridine compound. Finally, it is noted that the title compound with an alternating all-*trans* and *cis–cis–trans* configuration shows a very rare Co coordination.

3. Supramolecular features

In the crystal structure of the title compound, the chains elongate along [101] with each chain surrounded by six neighboring chains (Fig. 3). There are no significant intermolecular C—H···N or C—H···S contacts and there are also no hints of any π–π stacking interactions (Table 2).

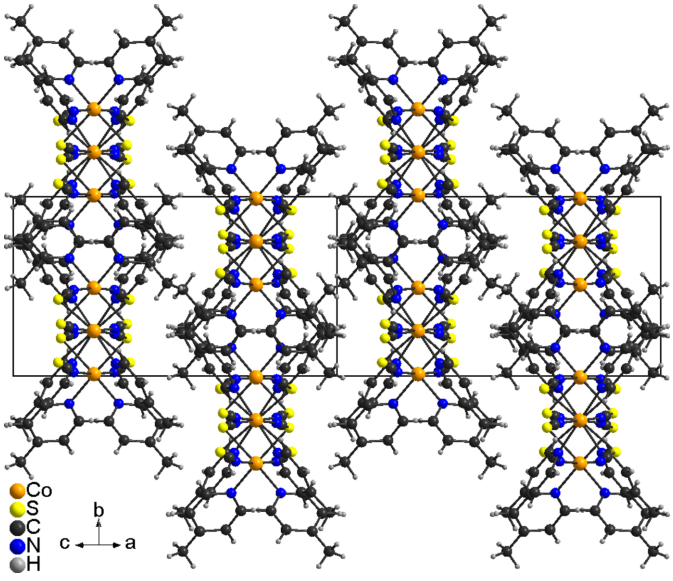


Figure 3
Crystal structure of the title compound in a view along [101]. For clarity the disorder of the methyl H atoms is not shown.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···N1	0.94	2.67	3.131 (3)	111

4. Database survey

A search in the CSD (version 5.43, last update December 2024; Groom *et al.*, 2016) using CONQUEST (Bruno *et al.*, 2002) for compounds based on Co(NCS)$_2$ and 4-methylpyridine revealed that some such compounds are already reported. This includes a compound with the composition Co(NCS)$_2$(4-methylpyridine)4·*p*-xylene in which the Co cations are tetrahedrally coordinated by only one N-bonding thiocyanate anion and three 4-methylpyridine ligands and which crystallizes with additional *p*-xylene solvate molecules (Refcode: QQQGKJ; Solaculu *et al.*, 1974). However, no atomic coordinates are given and no charge balance is achieved, which means that the existence of this compound is questionable. There is also one compound with the composition Co(NCS)$_2$(4-methylpyridine)$_2$bis(*p*-toluidine)$_2$ reported for which also no atomic coordinates are given (Refcode: CECDAP; Micu-Semeniuc *et al.*, 1983). Surprisingly, the unit-cell parameters are very similar and the crystal system identical to that of compounds built up of octahedral discrete complexes with additional solvate molecules (see below).

All remaining compounds consists of discrete complexes with the composition Co(NCS)$_2$(4-methylpyridine)$_4$ that crystallize as clathrates with *p*-toluidine (Refcode CECCOC; Micu-Semeniuc *et al.*, 1983), 4-methylpyridine [Refcodes: XIHHEB (Harris *et al.*, 2001) and XIHHEB01 (Harris *et al.*, 2003)] and nitrobenzene (Refcode ZZZUXU), nitroethane (Refcode: ZZZUXY) and benzene solvate (Refcode: ZZZUYI; Belitskus *et al.*, 1963). However, only for one of these compounds (XIHHEB) are atomic coordinates available. Finally, the crystal structure of the pure complex Co(NCS)$_2$(4-methylpyridine)$_4$ is also reported but the unit-cell parameters are identical to that of several clathrates, which indicates that the solvent was not located (Refcode: VERNUC; Harris *et al.*, 2003).

5. Additional investigations

Powder X-ray diffraction measurements prove that the title compound has been obtained as a pure phase (Fig. 4). In the IR and Raman spectrum the CN stretching vibration is observed at 2108 and 2095 cm^{-1} (IR) and at 2100 cm^{-1} (Raman), which confirms the presence of μ-1,3-bridging thiocyanate anions (Fig. 5). To determine whether the title compound can be transformed into a discrete aqua complex with the composition Co(NCS)$_2$(4-methylpyridine)$_2$(H$_2$O)$_2$, which exists for the corresponding compound with 4-chloropyridine (Böhme *et al.*, 2020), a sample of the title compound

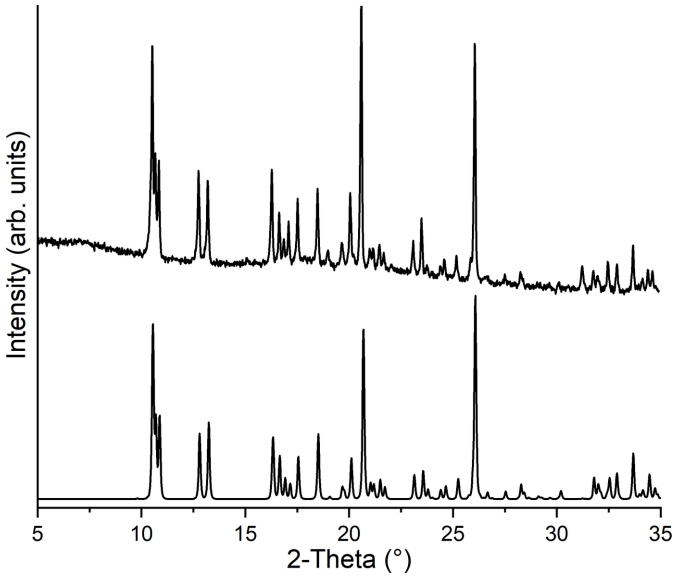


Figure 4
Experimental (top) and calculated (bottom) X-ray powder pattern for the title compound.

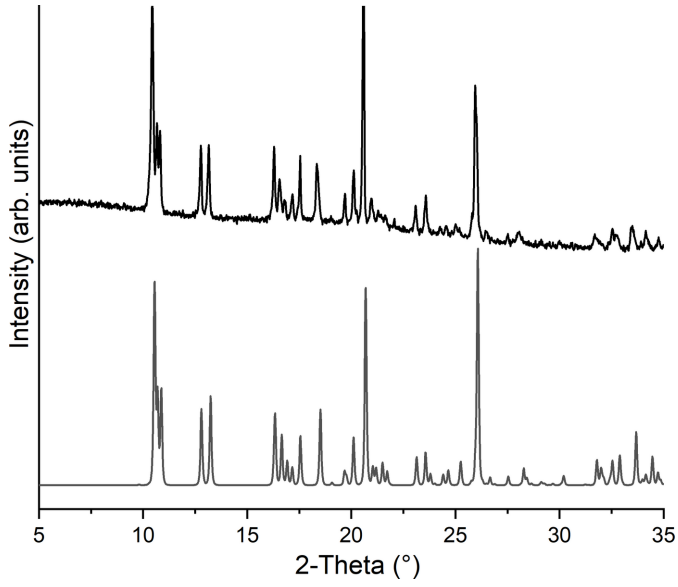


Figure 6
Experimental X-ray powder pattern of a sample of the title compound stored for 2 d in a humid atmosphere (top) and the calculated powder pattern (bottom).

was stored for 2 d in a humid atmosphere, but no changes were observed (Fig. 6).

6. Synthesis and crystallization

Synthesis

4-Methylpyridine and $Co(NCS)_2$ were obtained from Sigma-Aldrich. The title compound was prepared by the reaction of $Co(NCS)_2$ (350.2 mg, 2.06 mmol) and 4-methylpyridine (100 µL, 1.03 mmol) in 3 mL of water. The reaction mixture was stirred for 2 d at 393 K in a closed glass tube. $C_{14}H_{14}CoN_4S_2$ (361.34): calculated C 46.53, H 3.91, N 15.50, S 17.75; found C 46.2, H 3.7, N 15.3, S 17.4. Single crystals were prepared by the same method without stirring. The purity was proven by powder X-ray diffraction (see Fig. 4). An IR and a Raman spectrum of the title compound can be seen in Fig. 5.

Experimental details

Elemental analysis was performed with a vario MICRO cube from Elementar Analysensysteme GmbH. IR spectra were recorded at room temperature on a Bruker Vertex70 FT-IR spectrometer using a broadband spectral range extension VERTEX FM for full mid and far IR. Raman spectra were recorded on a Bruker RAM II FT-Raman spectrometer using a liquid nitrogen cooled, highly sensitive Ge detector, 1064 nm radiation and 3 cm^{-1} resolution. X-ray powder diffraction experiments 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.

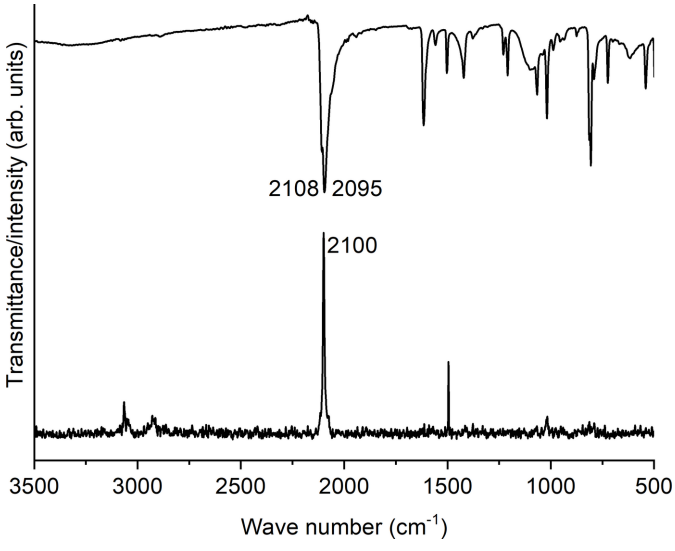


Figure 5
IR (top) and Raman (bottom) spectra of the title compound. The CN stretching vibration of the thiocyanate anions is given.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydrogen atoms were positioned with idealized geometry (methyl H atoms allowed to rotate but 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 methyl H atoms in both crystallographically independent 4-methylpyridine ligands are disordered and were refined in two orientations rotated by 60°.

Acknowledgements

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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.

Brandenburg, K. & Putz, H. (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.

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.

Jochim, A., Rams, M., Böhme, M., Ceglarska, M., Plass, W. & Näther, C. (2020). *Dalton Trans.* **49**, 15310–15322.

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

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.* B**65**, 782–783.

Mautner, F. A., Traber, M., Fischer, R., 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.

Näther, C. & Mangelsen, S. (2024). *Acta Cryst.* E**80**, 771–776.

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.

Rams, M., Böhme, M., Kataev, V., Krupskaya, Y., Büchner, B., Plass, W., Neumann, T., Tomkowicz, Z. & Näther, C. (2017*a*). *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. (2017*b*). *Phys. Chem. Chem. Phys.* **19**, 3232–3243.

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

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

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Co(NCS)_2(C_6H_7N)_2]$
M_r	361.34
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	220
a, *b*, *c* (Å)	20.1106 (12), 9.2112 (4), 19.2309 (12)
β (°)	116.353 (6)
V (Å^3)	3192.2 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.33
Crystal size (mm)	0.19 × 0.15 × 0.12
Data collection	
Diffractometer	Stoe *IPDS2*
Absorption correction	Numerical (*X-RED* and *X-SHAPE*; Stoe, 2008)
T_{min}, T_{max}	0.685, 0.763
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18094, 3840, 3249
R_{int}	0.030
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.095, 1.04
No. of reflections	3840
No. of parameters	195
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.54, −0.44

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

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

Shi, J. M., Chen, J. N. & Liu, L. D. (2006*a*). *Pol. J. Chem.* **80**, 1909–1912.

Shi, J. M., Li, W. N., Zhang, F. X., Zhang, X. & Liu, L. D. (2007). *Chin. J. Struct. Chem.* **26**, 118–121.

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

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.

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.

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Synthesis, crystal structure and properties of *catena*-poly[[bis(4-methylpyridine-κN)cobalt(II)]-di-μ-thiocyanato-$\kappa^2 N$:S;$\kappa^2 S$:N], which shows a rare coordination geometry

Christian Näther and Jan Boeckmann

Computing details

***catena*-Poly[[bis(4-methylpyridine-κN)cobalt(II)]-di-μ-thiocyanato-$\kappa^2 N$:S;$\kappa^2 S$:N]**

Crystal data

$[Co(NCS)_2(C_6H_7N)_2]$
M_r = 361.34
Monoclinic, $C2/c$
a = 20.1106 (12) Å
b = 9.2112 (4) Å
c = 19.2309 (12) Å
β = 116.353 (6)°
V = 3192.2 (3) Å^3
Z = 8
$F(000)$ = 1480
D_x = 1.504 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 18094 reflections
θ = 2.4–28.0°
μ = 1.33 mm^{-1}
T = 220 K
Block, violet
0.19 × 0.15 × 0.12 mm

Data collection

Stoe IPDS-2 diffractometer
Graphite monochromator
ω scans
Absorption correction: numerical (X-Red and X-Shape; Stoe, 2008)
T_{min} = 0.685, T_{max} = 0.763
18094 measured reflections
3840 independent reflections
3249 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 28.0°, θ_{min} = 2.4°
h = −26→26
k = −12→12
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.095
S = 1.04
3840 reflections
195 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 0.3181P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}
Extinction correction: SHELXL-2016/6 (Sheldrick 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0057 (5)

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}	Occ. (<1)
Co1	0.500000	0.49107 (4)	0.250000	0.02383 (11)	
Co2	0.750000	0.250000	0.500000	0.02301 (11)	
S1	0.66193 (2)	0.42603 (6)	0.52245 (2)	0.02860 (13)	
C1	0.59987 (9)	0.4576 (2)	0.43277 (10)	0.0227 (3)	
N1	0.55673 (9)	0.47963 (18)	0.36976 (9)	0.0282 (3)	
S2	0.58146 (3)	0.29010 (6)	0.22966 (3)	0.03552 (15)	
C2	0.64772 (10)	0.2750 (2)	0.31844 (10)	0.0241 (3)	
N2	0.69410 (9)	0.26457 (19)	0.38096 (9)	0.0289 (3)	
N11	0.57409 (8)	0.65628 (18)	0.24774 (9)	0.0272 (3)	
C11	0.59645 (10)	0.6656 (2)	0.19205 (11)	0.0295 (4)	
H11	0.577925	0.597731	0.151360	0.035*	
C12	0.64542 (11)	0.7701 (2)	0.19119 (11)	0.0307 (4)	
H12	0.658799	0.772892	0.150181	0.037*	
C13	0.67484 (10)	0.8707 (2)	0.25094 (11)	0.0293 (4)	
C14	0.65122 (12)	0.8613 (2)	0.30850 (13)	0.0375 (5)	
H14	0.669143	0.927491	0.349996	0.045*	
C15	0.60160 (12)	0.7551 (2)	0.30501 (12)	0.0358 (5)	
H15	0.586236	0.751641	0.344562	0.043*	
C16	0.72997 (13)	0.9827 (3)	0.25418 (15)	0.0423 (5)	
H16A	0.719681	1.011652	0.201869	0.063*	0.3193
H16B	0.779623	0.942496	0.280015	0.063*	0.3193
H16C	0.726370	1.066719	0.282752	0.063*	0.3193
H16D	0.764102	1.002260	0.307889	0.063*	0.6807
H16E	0.704159	1.071415	0.229743	0.063*	0.6807
H16F	0.757413	0.947192	0.227005	0.063*	0.6807
N21	0.67949 (8)	0.06822 (18)	0.49669 (9)	0.0280 (3)	
C21	0.70667 (11)	−0.0423 (2)	0.54644 (12)	0.0348 (4)	
H21	0.758041	−0.045551	0.578635	0.042*	
C22	0.66266 (12)	−0.1523 (2)	0.55279 (13)	0.0374 (4)	
H22	0.684392	−0.227674	0.588788	0.045*	
C23	0.58650 (11)	−0.1515 (2)	0.50608 (12)	0.0306 (4)	
C24	0.55912 (11)	−0.0391 (2)	0.45241 (12)	0.0333 (4)	
H24	0.508301	−0.035451	0.417935	0.040*	
C25	0.60634 (10)	0.0673 (2)	0.44959 (11)	0.0304 (4)	
H25	0.586322	0.142359	0.413022	0.036*	
C26	0.53661 (13)	−0.2648 (2)	0.51418 (14)	0.0404 (5)	
H26A	0.485301	−0.234544	0.485588	0.061*	0.6344
H26B	0.548454	−0.276466	0.568562	0.061*	0.6344
H26C	0.543875	−0.356370	0.493626	0.061*	0.6344

H26D	0.566452	−0.343709	0.546263	0.061*	0.3656
H26E	0.503299	−0.301788	0.463289	0.061*	0.3656
H26F	0.507879	−0.221883	0.538224	0.061*	0.3656

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01963 (17)	0.0287 (2)	0.01631 (17)	0.000	0.00182 (13)	0.000
Co2	0.01948 (17)	0.0281 (2)	0.01689 (17)	0.00358 (12)	0.00393 (13)	0.00223 (13)
S1	0.0267 (2)	0.0373 (3)	0.0161 (2)	0.00936 (18)	0.00425 (17)	0.00090 (17)
C1	0.0198 (7)	0.0243 (8)	0.0228 (8)	0.0022 (6)	0.0083 (6)	−0.0016 (7)
N1	0.0247 (7)	0.0350 (9)	0.0190 (7)	0.0046 (6)	0.0044 (6)	−0.0003 (6)
S2	0.0337 (3)	0.0424 (3)	0.0187 (2)	0.0092 (2)	0.00094 (19)	−0.00481 (19)
C2	0.0243 (8)	0.0255 (9)	0.0229 (8)	0.0033 (6)	0.0109 (7)	0.0013 (7)
N2	0.0274 (7)	0.0356 (9)	0.0202 (7)	0.0072 (6)	0.0075 (6)	0.0015 (6)
N11	0.0232 (7)	0.0311 (8)	0.0246 (7)	−0.0022 (6)	0.0082 (6)	−0.0051 (6)
C11	0.0295 (8)	0.0335 (10)	0.0230 (8)	−0.0015 (7)	0.0093 (7)	−0.0077 (8)
C12	0.0329 (9)	0.0344 (10)	0.0285 (9)	−0.0002 (8)	0.0170 (8)	−0.0036 (8)
C13	0.0252 (8)	0.0294 (10)	0.0328 (9)	−0.0006 (7)	0.0125 (7)	−0.0041 (8)
C14	0.0426 (11)	0.0395 (12)	0.0343 (10)	−0.0130 (9)	0.0205 (9)	−0.0160 (9)
C15	0.0428 (11)	0.0392 (11)	0.0317 (10)	−0.0107 (9)	0.0224 (9)	−0.0133 (9)
C16	0.0437 (12)	0.0404 (12)	0.0498 (13)	−0.0125 (9)	0.0271 (11)	−0.0095 (10)
N21	0.0245 (7)	0.0297 (9)	0.0272 (8)	0.0017 (6)	0.0092 (6)	0.0005 (6)
C21	0.0287 (9)	0.0331 (10)	0.0347 (10)	0.0013 (8)	0.0069 (8)	0.0033 (9)
C22	0.0380 (10)	0.0312 (11)	0.0363 (10)	0.0011 (8)	0.0106 (9)	0.0057 (9)
C23	0.0343 (9)	0.0289 (9)	0.0329 (9)	−0.0008 (8)	0.0187 (8)	−0.0064 (8)
C24	0.0256 (8)	0.0385 (11)	0.0350 (10)	0.0006 (8)	0.0126 (8)	−0.0046 (9)
C25	0.0260 (8)	0.0340 (10)	0.0288 (9)	0.0049 (7)	0.0101 (7)	0.0022 (8)
C26	0.0438 (11)	0.0358 (11)	0.0477 (12)	−0.0072 (9)	0.0260 (10)	−0.0082 (10)

Geometric parameters (Å, º)

Co1—N1^{i}	2.0699 (16)	C14—C15	1.377 (3)
Co1—N1	2.0699 (16)	C15—H15	0.9400
Co1—S2^{i}	2.6138 (6)	C16—H16A	0.9700
Co1—S2	2.6138 (6)	C16—H16B	0.9700
Co1—N11	2.1437 (16)	C16—H16C	0.9700
Co1—N11^{i}	2.1437 (16)	C16—H16D	0.9700
Co2—S1	2.5752 (4)	C16—H16E	0.9700
Co2—S1^{ii}	2.5753 (4)	C16—H16F	0.9700
Co2—N2	2.0585 (16)	N21—C21	1.336 (3)
Co2—N2^{ii}	2.0585 (16)	N21—C25	1.342 (2)
Co2—N21	2.1768 (16)	C21—H21	0.9400
Co2—N21^{ii}	2.1768 (16)	C21—C22	1.386 (3)
S1—C1	1.6448 (18)	C22—H22	0.9400
C1—N1	1.153 (2)	C22—C23	1.390 (3)
S2—C2	1.6401 (18)	C23—C24	1.392 (3)
C2—N2	1.153 (2)	C23—C26	1.503 (3)

N11—C11	1.336 (2)	C24—H24	0.9400
N11—C15	1.344 (2)	C24—C25	1.382 (3)
C11—H11	0.9400	C25—H25	0.9400
C11—C12	1.382 (3)	C26—H26A	0.9700
C12—H12	0.9400	C26—H26B	0.9700
C12—C13	1.388 (3)	C26—H26C	0.9700
C13—C14	1.387 (3)	C26—H26D	0.9700
C13—C16	1.495 (3)	C26—H26E	0.9700
C14—H14	0.9400	C26—H26F	0.9700

N1^{i}—Co1—N1	174.16 (10)	C13—C16—H16D	109.5
N1^{i}—Co1—S2	82.53 (5)	C13—C16—H16E	109.5
N1—Co1—S2	93.32 (5)	C13—C16—H16F	109.5
N1^{i}—Co1—S2^{i}	93.32 (5)	H16A—C16—H16B	109.5
N1—Co1—S2^{i}	82.53 (5)	H16A—C16—H16C	109.5
N1^{i}—Co1—N11	93.35 (6)	H16A—C16—H16D	141.1
N1^{i}—Co1—N11^{i}	90.80 (6)	H16A—C16—H16E	56.3
N1—Co1—N11	90.80 (6)	H16A—C16—H16F	56.3
N1—Co1—N11^{i}	93.34 (6)	H16B—C16—H16C	109.5
S2^{i}—Co1—S2	89.82 (3)	H16B—C16—H16D	56.3
N11—Co1—S2	90.71 (4)	H16B—C16—H16E	141.1
N11^{i}—Co1—S2	173.33 (4)	H16B—C16—H16F	56.3
N11—Co1—S2^{i}	173.33 (4)	H16C—C16—H16D	56.3
N11^{i}—Co1—S2^{i}	90.71 (4)	H16C—C16—H16E	56.3
N11—Co1—N11^{i}	89.54 (8)	H16C—C16—H16F	141.1
S1—Co2—S1^{ii}	180.0	H16D—C16—H16E	109.5
N2—Co2—S1	93.94 (4)	H16D—C16—H16F	109.5
N2^{ii}—Co2—S1^{ii}	93.94 (4)	H16E—C16—H16F	109.5
N2^{ii}—Co2—S1	86.06 (5)	C21—N21—Co2	120.72 (13)
N2—Co2—S1^{ii}	86.06 (4)	C21—N21—C25	117.11 (18)
N2—Co2—N2^{ii}	180.00 (10)	C25—N21—Co2	121.95 (14)
N2—Co2—N21^{ii}	90.54 (6)	N21—C21—H21	118.5
N2—Co2—N21	89.46 (6)	N21—C21—C22	123.07 (19)
N2^{ii}—Co2—N21	90.54 (6)	C22—C21—H21	118.5
N2^{ii}—Co2—N21^{ii}	89.46 (7)	C21—C22—H22	119.9
N21—Co2—S1	90.10 (4)	C21—C22—C23	120.2 (2)
N21^{ii}—Co2—S1^{ii}	90.09 (4)	C23—C22—H22	119.9
N21^{ii}—Co2—S1	89.90 (4)	C22—C23—C24	116.29 (18)
N21—Co2—S1^{ii}	89.91 (4)	C22—C23—C26	121.6 (2)
N21—Co2—N21^{ii}	180.0	C24—C23—C26	122.07 (19)
C1—S1—Co2	101.18 (6)	C23—C24—H24	119.9
N1—C1—S1	179.55 (16)	C25—C24—C23	120.27 (18)
C1—N1—Co1	164.70 (14)	C25—C24—H24	119.9
C2—S2—Co1	100.25 (6)	N21—C25—C24	122.98 (19)
N2—C2—S2	179.70 (18)	N21—C25—H25	118.5
C2—N2—Co2	162.72 (14)	C24—C25—H25	118.5
C11—N11—Co1	123.13 (13)	C23—C26—H26A	109.5
C11—N11—C15	116.78 (17)	C23—C26—H26B	109.5

C15—N11—Co1	120.08 (13)	C23—C26—H26C	109.5
N11—C11—H11	118.3	C23—C26—H26D	109.5
N11—C11—C12	123.36 (17)	C23—C26—H26E	109.5
C12—C11—H11	118.3	C23—C26—H26F	109.5
C11—C12—H12	120.0	H26A—C26—H26B	109.5
C11—C12—C13	119.95 (17)	H26A—C26—H26C	109.5
C13—C12—H12	120.0	H26A—C26—H26D	141.1
C12—C13—C16	122.08 (17)	H26A—C26—H26E	56.3
C14—C13—C12	116.57 (18)	H26A—C26—H26F	56.3
C14—C13—C16	121.35 (18)	H26B—C26—H26C	109.5
C13—C14—H14	119.9	H26B—C26—H26D	56.3
C15—C14—C13	120.20 (18)	H26B—C26—H26E	141.1
C15—C14—H14	119.9	H26B—C26—H26F	56.3
N11—C15—C14	123.12 (17)	H26C—C26—H26D	56.3
N11—C15—H15	118.4	H26C—C26—H26E	56.3
C14—C15—H15	118.4	H26C—C26—H26F	141.1
C13—C16—H16A	109.5	H26D—C26—H26E	109.5
C13—C16—H16B	109.5	H26D—C26—H26F	109.5
C13—C16—H16C	109.5	H26E—C26—H26F	109.5
Co1—N11—C11—C12	−178.58 (15)	C15—N11—C11—C12	0.0 (3)
Co1—N11—C15—C14	177.88 (18)	C16—C13—C14—C15	−178.6 (2)
Co2—N21—C21—C22	172.50 (17)	N21—C21—C22—C23	0.2 (3)
Co2—N21—C25—C24	−172.73 (15)	C21—N21—C25—C24	2.0 (3)
N11—C11—C12—C13	1.0 (3)	C21—C22—C23—C24	2.2 (3)
C11—N11—C15—C14	−0.8 (3)	C21—C22—C23—C26	−176.8 (2)
C11—C12—C13—C14	−1.3 (3)	C22—C23—C24—C25	−2.5 (3)
C11—C12—C13—C16	177.9 (2)	C23—C24—C25—N21	0.4 (3)
C12—C13—C14—C15	0.6 (3)	C25—N21—C21—C22	−2.3 (3)
C13—C14—C15—N11	0.5 (4)	C26—C23—C24—C25	176.55 (18)

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2; (ii) −*x*+3/2, −*y*+1/2, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···N1	0.94	2.67	3.131 (3)	111