



Crystal structure of bis(3,5-dimethylpyridine- κ N)-bis(methanol- κ O)bis(thiocyanato- κ N)cobalt(II)

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Technology, Austria**Keywords:** crystal structure; cobalt(II) thiocyanate complex; 3,5-dimethylpyridine ligand; hydrogen bonding.**CCDC reference:** 1517370**Supporting information:** this article has
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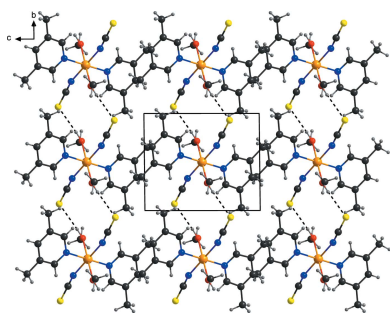
The asymmetric unit of the title complex, $[\text{Co}(\text{NCS})_2(\text{C}_7\text{H}_9\text{N})_2(\text{CH}_3\text{OH})_2]$, comprises of one Co^{II} cation located on a centre of inversion, one thiocyanate ligand, one methanol ligand and one 3,5-dimethylpyridine ligand. The Co^{II} cation is octahedrally coordinated by two terminal N-bonding thiocyanate anions, two methanol molecules and two 3,5-dimethylpyridine ligands into a discrete complex. The complex molecules are linked by intermolecular O—H...S hydrogen bonding into chains that elongate in the direction parallel to the *b* axis.

1. Chemical context

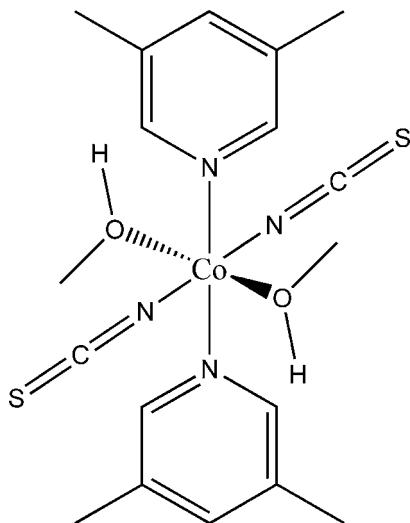
For a long time, the synthesis of new molecular magnetic materials with desired physical properties has been a topic of interest in coordination chemistry (Liu *et al.*, 2015). To reach this goal, paramagnetic cations must be linked by small anionic ligands such as, for example, thiocyanate anions that can mediate magnetic exchange between the cations (Palion-Gazda *et al.*, 2015; Massoud *et al.*, 2013). In this context, our group has already reported several thiocyanato coordination polymers which – depending on the metal cation and the neutral co-ligand – show different magnetic phenomena including a slow relaxation of the magnetization (Werner *et al.*, 2014, 2015*a,b,c*). In this regard, discrete complexes are also of interest because a transformation into the desired polymeric compounds can be achieved through thermal decomposition, as shown in one of our previous studies (Näther *et al.*, 2013). During our systematic work, compounds based on 3,5-dimethylpyridine as co-ligand should be prepared, for which only one thiocyanato compound is known (Price & Stone, 1984; Nassimbeni *et al.*, 1986). In the course of our investigations with Co^{II} as the transition metal, crystals of the title compound, $[\text{Co}(\text{NCS})_2(\text{C}_7\text{H}_9\text{N})_2(\text{CH}_3\text{OH})_2]$, were obtained and characterized by single crystal X-ray diffraction. Unfortunately, no single-phase crystalline powder could be synthesized, which prevented further investigations of physical properties.

2. Structural commentary

The asymmetric unit of the title compound comprises of one Co^{II} cation, one thiocyanato anion, one methanol molecule and one neutral 3,5-dimethylpyridine co-ligand. The Co^{II} cation is located on a center of inversion; the thiocyanate anion, the methanol molecule as well as the 3,5-dimethylpyridine ligand are each located on general positions. The Co^{II} cation is octahedrally coordinated by two terminal N-bonded



thiocyanato ligands, two methanol molecules and two 3,5-dimethylpyridine ligands in an all-*trans* configuration (Fig. 1). The Co–N bond length to the thiocyanate anion is significantly shorter [2.0898 (19) Å] than to the pyridine N atom of the 3,5-dimethylpyridine ligand [2.1602 (17) Å], which is in agreement with values reported in the literature (Goodgame *et al.*, 2003; Wöhlert *et al.*, 2014).



3. Supramolecular features

The discrete complexes in the crystal are linked by pairs of intermolecular O–H···S hydrogen bonds between the hydroxyl H atom of the methanol ligand and the thiocyanato S atom of an adjacent complex into chains propagating parallel to the *b* axis (Fig. 2, Table 1). These pairs are located around centres of inversion.

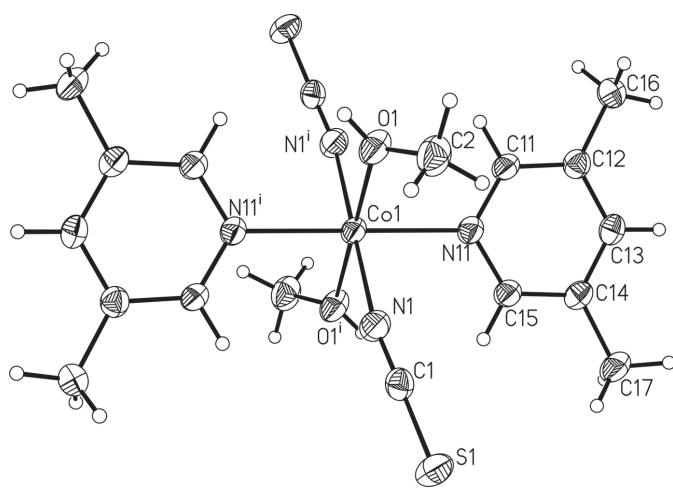


Figure 1
View of a discrete complex of the title compound, showing the atom labelling and anisotropic displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x, -y + 1, -z + 1$.]

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1–H1···S1 ⁱ	0.84	2.45	3.2885 (17)	175

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

4. Database survey

To the best of our knowledge, there is only one thiocyanato coordination compound with 3,5-dimethylpyridine as a co-ligand deposited in the Cambridge Structure Database (Version 5.37, last update 2015; Groom *et al.*, 2016). The structure consists of an Ni^{II} cation octahedrally coordinated by four 3,5-dimethylpyridine ligands and two N-bonded thiocyanate anions (Price *et al.*, 1984; Nassimbeni *et al.*, 1986). A general search for coordination compounds with 3,5-dimethylpyridine resulted in 159 structures, including the aforementioned ones. Exemplary are two Co compounds: in the first, the cation is octahedrally coordinated by two 3,5-dimethylpyridine ligands as well as one μ -1,3-bridging and one μ -1,1-bridging azide anion, linking them into chains (Lu *et al.*, 2012), whereas in the second compound, the Co^{II} atom is octahedrally coordinated by four 3,5-dimethylpyridine ligands and two chloride anions, forming a discrete complex (Martone *et al.*, 2007).

5. Synthesis and crystallization

Co(NCS)₂ and 3,5-dimethylpyridine were purchased from Alfa Aesar. Crystals of the title compound suitable for single crystal X-ray diffraction were obtained by the reaction of 43.8 mg Co(NCS)₂ (0.25 mmol) with 28.5 μ l 3,5-dimethylpyridine (0.6 mmol) in methanol (1.5 ml) after a few days.

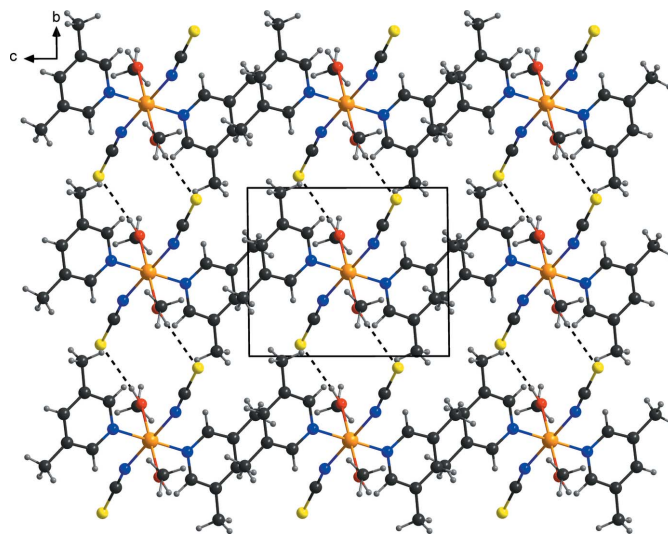


Figure 2
The crystal structure of the title compound in a view along the *a* axis, showing the intermolecular hydrogen bonding as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Co(NCS) ₂ (C ₇ H ₉ N) ₂ (CH ₄ O) ₂]
<i>M_r</i>	453.48
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	170
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.7027 (5), 7.8688 (5), 9.1970 (5)
α , β , γ (°)	87.403 (5), 81.419 (5), 76.295 (5)
<i>V</i> (Å ³)	535.48 (6)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.02
Crystal size (mm)	0.15 × 0.09 × 0.04
Data collection	
Diffractometer	Stoe IPDS2
Absorption correction	Numerical (<i>X-SHAPE</i> and <i>X-RED32</i> ; Stoe & Cie, 2008)
<i>T</i> _{min} , <i>T</i> _{max}	0.885, 0.923
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	6258, 2431, 2052
<i>R</i> _{int}	0.024
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.648
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.034, 0.094, 1.08
No. of reflections	2431
No. of parameters	127
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.37, -0.37

Computer programs: *X-AREA* (Stoe & Cie, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *XP* in *SHELXTL* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 1999) and *pubCIF* (Westrip, 2010).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C–H hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ using a riding model. The O–H hydrogen atom was located in a difference map. For refinement, the bond length was constrained to 0.84 Å, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, using a riding model.

Acknowledgements

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Crystal structure of bis(3,5-dimethylpyridine- κ N)bis(methanol- κ O)bis(thiocyanato- κ N)cobalt(II)

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2008); cell refinement: *X-AREA* (Stoe & Cie, 2008); data reduction: *X-AREA* (Stoe & Cie, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(3,5-dimethylpyridine- κ N)bis(methanol- κ O)bis(thiocyanato- κ N)cobalt(II)

Crystal data

[Co(NCS)₂(C₇H₉N)₂(CH₄O)₂]

$M_r = 453.48$

Triclinic, $P\bar{1}$

$a = 7.7027$ (5) Å

$b = 7.8688$ (5) Å

$c = 9.1970$ (5) Å

$\alpha = 87.403$ (5)°

$\beta = 81.419$ (5)°

$\gamma = 76.295$ (5)°

$V = 535.48$ (6) Å³

$Z = 1$

$F(000) = 237$

$D_x = 1.406$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6258 reflections

$\theta = 2.2$ – 27.4 °

$\mu = 1.02$ mm⁻¹

$T = 170$ K

Block, blue

$0.15 \times 0.09 \times 0.04$ mm

Data collection

Stoe IPDS-2

diffractometer

ω scans

Absorption correction: numerical

(X-SHAPE and X-RED32; Stoe & Cie, 2008)

$T_{\min} = 0.885$, $T_{\max} = 0.923$

6258 measured reflections

2431 independent reflections

2052 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 27.4$ °, $\theta_{\min} = 2.2$ °

$h = -9 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.094$

$S = 1.08$

2431 reflections

127 parameters

0 restraints

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 0.2412P]$

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

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

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.37$ e Å⁻³

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.0000	0.5000	0.5000	0.02492 (13)
N1	0.1343 (3)	0.6688 (3)	0.3719 (2)	0.0319 (4)
C1	0.2064 (3)	0.7782 (3)	0.3253 (2)	0.0282 (4)
S1	0.30808 (9)	0.93060 (7)	0.25699 (6)	0.03616 (16)
O1	0.2263 (2)	0.2834 (2)	0.45808 (19)	0.0347 (4)
H1	0.2416	0.1917	0.4098	0.042*
C2	0.4115 (3)	0.2961 (4)	0.4380 (3)	0.0406 (6)
H2A	0.4455	0.3340	0.3370	0.061*
H2B	0.4891	0.1816	0.4566	0.061*
H2C	0.4261	0.3815	0.5069	0.061*
N11	0.1118 (3)	0.5678 (2)	0.68521 (19)	0.0268 (4)
C11	0.1607 (3)	0.4492 (3)	0.7899 (2)	0.0281 (4)
H11	0.1514	0.3327	0.7775	0.034*
C12	0.2242 (3)	0.4871 (3)	0.9156 (2)	0.0282 (4)
C13	0.2358 (3)	0.6584 (3)	0.9313 (2)	0.0291 (4)
H13	0.2780	0.6900	1.0158	0.035*
C14	0.1865 (3)	0.7841 (3)	0.8251 (2)	0.0287 (4)
C15	0.1263 (3)	0.7319 (3)	0.7033 (2)	0.0272 (4)
H15	0.0937	0.8165	0.6291	0.033*
C16	0.2780 (3)	0.3476 (3)	1.0281 (2)	0.0343 (5)
H16A	0.3882	0.2640	0.9867	0.051*
H16B	0.1807	0.2864	1.0554	0.051*
H16C	0.3001	0.4014	1.1155	0.051*
C17	0.1983 (4)	0.9710 (3)	0.8375 (3)	0.0374 (5)
H17A	0.2179	1.0218	0.7388	0.056*
H17B	0.2991	0.9747	0.8899	0.056*
H17C	0.0855	1.0382	0.8917	0.056*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0324 (2)	0.0230 (2)	0.0224 (2)	-0.01104 (16)	-0.00600 (15)	-0.00096 (14)
N1	0.0419 (11)	0.0315 (9)	0.0264 (9)	-0.0160 (8)	-0.0056 (8)	0.0007 (7)
C1	0.0330 (11)	0.0299 (10)	0.0226 (9)	-0.0070 (9)	-0.0062 (8)	-0.0034 (8)
S1	0.0456 (4)	0.0304 (3)	0.0358 (3)	-0.0184 (3)	-0.0004 (3)	-0.0018 (2)
O1	0.0328 (9)	0.0303 (8)	0.0428 (9)	-0.0089 (7)	-0.0054 (7)	-0.0103 (7)
C2	0.0308 (12)	0.0427 (13)	0.0512 (14)	-0.0114 (10)	-0.0092 (10)	-0.0056 (11)
N11	0.0334 (10)	0.0255 (9)	0.0240 (8)	-0.0101 (7)	-0.0064 (7)	-0.0018 (7)
C11	0.0367 (12)	0.0226 (10)	0.0278 (10)	-0.0104 (9)	-0.0071 (8)	-0.0014 (8)

C12	0.0304 (11)	0.0300 (11)	0.0252 (10)	-0.0089 (9)	-0.0037 (8)	-0.0014 (8)
C13	0.0320 (11)	0.0314 (11)	0.0261 (10)	-0.0098 (9)	-0.0051 (8)	-0.0059 (8)
C14	0.0322 (11)	0.0260 (10)	0.0292 (10)	-0.0096 (9)	-0.0027 (8)	-0.0045 (8)
C15	0.0323 (11)	0.0249 (10)	0.0261 (10)	-0.0091 (8)	-0.0051 (8)	-0.0008 (8)
C16	0.0418 (13)	0.0339 (12)	0.0299 (11)	-0.0110 (10)	-0.0114 (9)	0.0027 (9)
C17	0.0480 (14)	0.0283 (11)	0.0410 (13)	-0.0161 (10)	-0.0097 (11)	-0.0050 (9)

Geometric parameters (Å, °)

Co1—N1	2.0898 (19)	C11—C12	1.390 (3)
Co1—N1 ⁱ	2.0898 (19)	C11—H11	0.9500
Co1—O1 ⁱ	2.1311 (16)	C12—C13	1.388 (3)
Co1—O1	2.1311 (16)	C12—C16	1.502 (3)
Co1—N11 ⁱ	2.1602 (17)	C13—C14	1.386 (3)
Co1—N11	2.1602 (17)	C13—H13	0.9500
N1—C1	1.164 (3)	C14—C15	1.388 (3)
C1—S1	1.636 (2)	C14—C17	1.505 (3)
O1—C2	1.438 (3)	C15—H15	0.9500
O1—H1	0.8399	C16—H16A	0.9800
C2—H2A	0.9800	C16—H16B	0.9800
C2—H2B	0.9800	C16—H16C	0.9800
C2—H2C	0.9800	C17—H17A	0.9800
N11—C11	1.342 (3)	C17—H17B	0.9800
N11—C15	1.342 (3)	C17—H17C	0.9800
N1—Co1—N1 ⁱ	180.0	C15—N11—Co1	121.16 (14)
N1—Co1—O1 ⁱ	87.76 (7)	N11—C11—C12	123.78 (19)
N1 ⁱ —Co1—O1 ⁱ	92.24 (7)	N11—C11—H11	118.1
N1—Co1—O1	92.24 (7)	C12—C11—H11	118.1
N1 ⁱ —Co1—O1	87.76 (7)	C13—C12—C11	116.89 (19)
O1 ⁱ —Co1—O1	180.0	C13—C12—C16	122.06 (19)
N1—Co1—N11 ⁱ	92.30 (7)	C11—C12—C16	121.05 (19)
N1 ⁱ —Co1—N11 ⁱ	87.70 (7)	C14—C13—C12	120.79 (19)
O1 ⁱ —Co1—N11 ⁱ	89.25 (6)	C14—C13—H13	119.6
O1—Co1—N11 ⁱ	90.75 (6)	C12—C13—H13	119.6
N1—Co1—N11	87.70 (7)	C13—C14—C15	117.59 (19)
N1 ⁱ —Co1—N11	92.30 (7)	C13—C14—C17	122.42 (19)
O1 ⁱ —Co1—N11	90.75 (6)	C15—C14—C17	120.0 (2)
O1—Co1—N11	89.25 (6)	N11—C15—C14	123.23 (19)
N11 ⁱ —Co1—N11	180.0	N11—C15—H15	118.4
C1—N1—Co1	167.28 (17)	C14—C15—H15	118.4
N1—C1—S1	179.04 (19)	C12—C16—H16A	109.5
C2—O1—Co1	124.49 (14)	C12—C16—H16B	109.5
C2—O1—H1	97.4	H16A—C16—H16B	109.5
Co1—O1—H1	131.5	C12—C16—H16C	109.5
O1—C2—H2A	109.5	H16A—C16—H16C	109.5
O1—C2—H2B	109.5	H16B—C16—H16C	109.5
H2A—C2—H2B	109.5	C14—C17—H17A	109.5

O1—C2—H2C	109.5	C14—C17—H17B	109.5
H2A—C2—H2C	109.5	H17A—C17—H17B	109.5
H2B—C2—H2C	109.5	C14—C17—H17C	109.5
C11—N11—C15	117.71 (17)	H17A—C17—H17C	109.5
C11—N11—Co1	121.05 (13)	H17B—C17—H17C	109.5

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1...S1 ⁱⁱ	0.84	2.45	3.2885 (17)	175

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