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Crystal structure of bis(pyridine-4-carbothioamide-κN^1)bis(thiocyanato-κN)cobalt(II) methanol monosolvate

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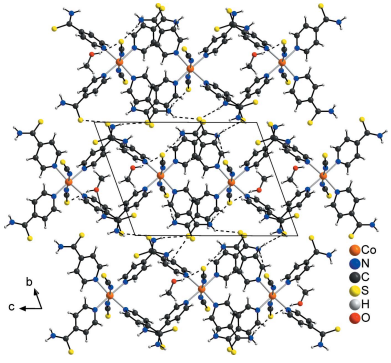
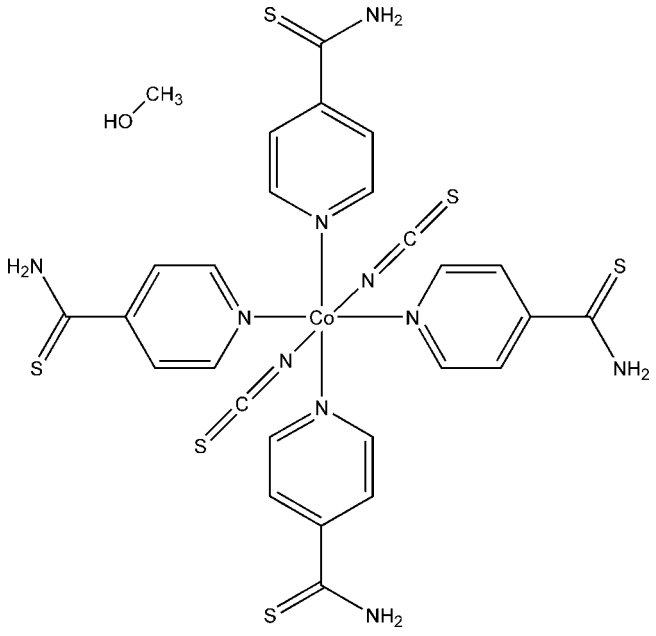
The asymmetric unit of the title compound, $[Co(NCS)_2(C_6H_6NS)_4]\cdot CH_3OH$, consists of one cobalt(II) cation, two thiocyanate anions, four pyridine-4-carbothioamide ligands and one methanol molecule that are located in general positions. The Co^{II} cations are coordinated by two terminal N-bonding thiocyanate anions and four N-bonding pyridine-4-carbothioamide ligands, resulting in discrete and slightly distorted octahedral complexes. These complexes are linked into a three-dimensional network *via* intermolecular N—H···S hydrogen bonding between the amino H atoms and the thiocyanate and pyridine-4-carbothioamide S atoms. From this arrangement, channels are formed in which the methanol solvate molecules are embedded and linked to the host structure by intermolecular O—H···S and N—H···O hydrogen bonding.

1. Chemical context

Thio- and selenocyanate anions are useful ligands for the synthesis of new coordination compounds and polymers because of their versatile coordination behaviour (Massoud *et al.*, 2013; Kabesova *et al.*, 1995). Compounds in which the metal cations are linked by these ligands are of special interest because magnetic exchange can be mediated (Palion-Gazda *et al.*, 2015; Boeckmann & Näther, 2012; Wöhlert *et al.*, 2013). In this context, we are especially interested in cobalt compounds in which the metal cations are octahedrally coordinated by two neutral co-ligands and four anionic ligands. In the corresponding structures, the central cations are linked into chains by mutual pairs of anionic ligands. Some of these compounds show a slow relaxation of the magnetization, which in part can be traced back to single-chain magnetism (Rams *et al.*, 2017*a*,*b*; Wöhlert *et al.*, 2012). To study the influence of the neutral co-ligand on the magnetic properties, different pyridine derivatives substituted in the 4-position, *e.g.* 4-benzoylpyridine, 4-vinylpyridine, 4-(4-chlorobenzyl)pyridine and 4-(3-phenylpropyl)pyridine have been investigated (Rams *et al.*, 2017*b*; Werner *et al.*, 2014, 2015). In this regard, we also became interested in pyridine-4-carbothioamide as a ligand, because in this case the $Co(NCS)_2$ chains can be linked into layers by pairs of intermolecular hydrogen bonds between the amino H atoms and the thioamide S atom. Unfortunately, the desired compound with composition $Co(NCS)_2$(pyridine-4-carbothioamide)$_2$ could not be prepared from solution. Alternatively, we attempted to synthesize discrete solvato complexes as precursors that might transform into the desired compound on thermal annealing, as has been shown



previously (Boeckmann & Näther, 2012). In the course of these investigations, crystals of the title compound were grown and characterized by single crystal X-ray diffraction. Unfortunately, no single-phase crystalline product could be obtained which prevented further investigations.



2. Structural commentary

The asymmetric unit of the title compound, $[Co(NCS)_2(C_6H_6NS)_4]\cdot CH_3OH$, consists of one Co^{II} cation, two thiocyanate anions, four 4-pyridindethioamide co-ligands and one one methanol molecule, all located in general positions. The Co^{II} cation is sixfold coordinated by two terminal N-bonded thiocyanate anions and four N-bonded pyridine-4-carbothioamide ligands, resulting in discrete and slightly distorted octahedra (Fig. 1). The Co—N bond lengths to the thiocyanate anions of 2.0847 (14) and 2.0865 (14) Å are significantly shorter then those to the pyridine N atoms of the pyridine-4-carbothioamide ligand [2.1608 (13)–2.1933 (14) Å], in agreement with values reported in the literature (Goodgame *et al.*, 2003; Prananto *et al.*, 2017).

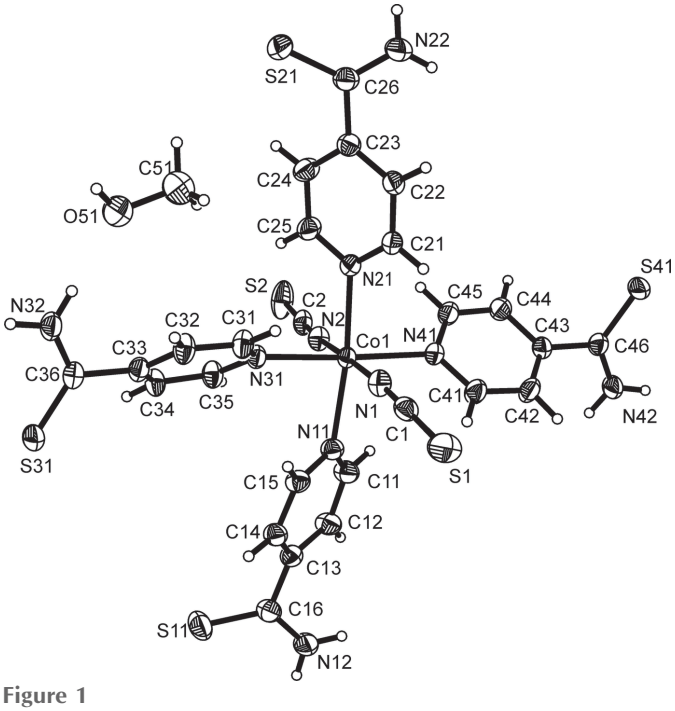


Figure 1
View of the asymmetric unit of the title compound, with atom labelling and displacement ellipsoids drawn at the 50% probability level.

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

D—H···A	D—H	H···A	D···A	D—H···A
N12—H11*N*···S2^{i}	0.88	2.45	3.3010 (16)	163
N12—H12*N*···S41^{ii}	0.88	2.64	3.3589 (16)	140
C21—H21···S2^{iii}	0.95	2.89	3.7626 (16)	153
N22—H21*N*···S31^{iv}	0.88	2.69	3.4969 (17)	152
N22—H22*N*···S11^{iv}	0.88	2.71	3.5691 (17)	166
C31—H31···N1	0.95	2.65	3.137 (2)	112
C34—H34···S21^{v}	0.95	2.95	3.8809 (17)	165
C35—H35···S1^{vi}	0.95	2.85	3.6906 (17)	148
C35—H35···N2	0.95	2.68	3.203 (2)	115
N32—H31*N*···O51	0.88	1.99	2.863 (2)	173
N32—H32*N*···S41^{vii}	0.88	2.67	3.5176 (14)	163
N42—H41*N*···S1^{viii}	0.88	2.49	3.3580 (16)	171
N42—H42*N*···S31^{ix}	0.88	2.64	3.4935 (14)	165
O51—H51···S2^{v}	0.84	2.43	3.1994 (17)	153

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x-1, y+1, z$; (iii) $x+1, y, z$; (iv) $x+1, y-1, z$; (v) $-x, -y+1, -z$; (vi) $x-1, y, z$; (vii) $x-1, y+1, z-1$; (viii) $-x+1, -y+1, -z+1$; (ix) $x+1, y-1, z+1$.

3. Supramolecular features

The discrete complexes are linked into a three-dimensional network by centrosymmetric pairs of intermolecular N—H···S hydrogen bonds between the amino H atoms and the 4-pyridindethioamide S atoms as well as by additional N—H···S hydrogen bonds involving the thiocyanate S atoms (Fig. 2, Table 1). By this arrangement, channels extending parallel the *a* axis are formed in which the methanol solvate molecules are located (Fig. 2). The solvent molecules are connected to the network *via* intermolecular O—H···S hydrogen bonding between the hydroxyl H atoms and the thiocyanate S atoms (Table 1). It is noted that the methanol molecules also act as acceptors for N—H···O hydrogen bonding from the amino group of neighbouring complexes. There are also additional short contacts between some of the aromatic hydrogen atoms and the two types of S atoms (thiocyanate, 4-pyridindethioamide), which are indicative of weak C—H···S interactions (Table 1).

4. Database survey

There are no structures of cobalt(II) thiocyanate compounds with pyridine-4-carbothioamide as co-ligand reported in the Cambridge Structure Database (Groom *et al.*, 2016). There is only one compound with cadmium, in which the Cd^{II} cations

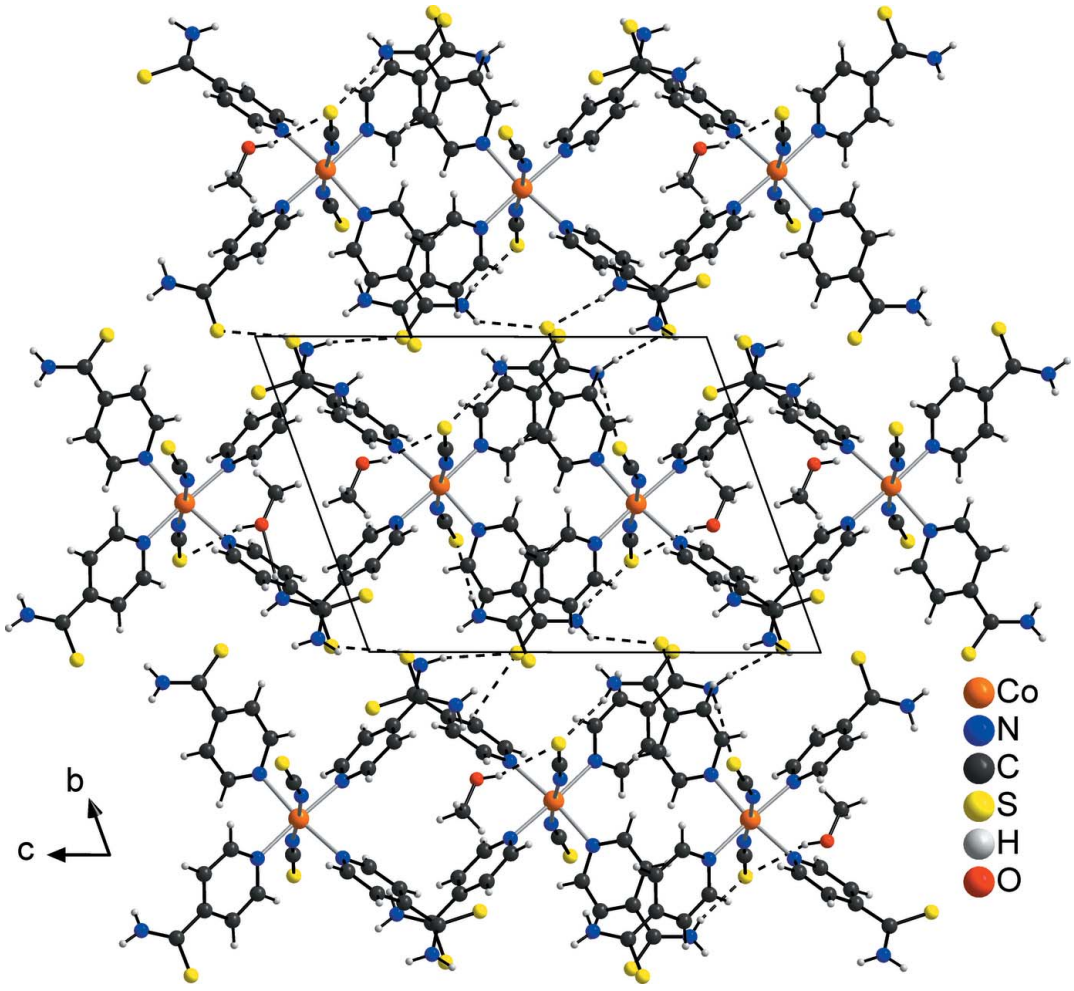


Figure 2
Crystal structure of the title compound in a view along the *a* axis. Intermolecular hydrogen bonding is shown by dashed lines.

are octahedrally coordinated by two terminal N-bonded pyridinethioamide ligands and four thiocyanate anions. The Cd^{II} cations are linked by pairs of the anionic ligands into linear chains, which corresponds exactly to the structure in which we were originally interested (Neumann *et al.*, 2016).

5. Synthesis and crystallization

$Co(NCS)_2$ and pyridine-4-carbothioamide were purchased from Alfa Aesar. Crystals of the title compound suitable for single crystal X-ray diffraction were obtained by the reaction of 8.8 mg $Co(NCS)_2$ (0.05 mmol) with 27.6 mg pyridine-4-carbothioamide (0.2 mmol) in methanol (0.5 ml). The reaction mixture was heated to boiling and then left on the turned-off heating plate to cool down slowly. During this process, crystals of the title compound formed.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The aromatic hydrogen atoms, the methyl hydrogen atoms and the hydrogen atom of the hydroxy function were positioned with idealized geometry (the hydroxy hydrogen atom was 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 amino hydrogen atoms were located in a difference map. Their N—H bond lengths were set to ideal values and refined with $U_{iso}(H) = 1.5U_{eq}(N)$.

Acknowledgements

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Funding information

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Table 2
Experimental details.

Crystal data	
Chemical formula	$[Co(NCS)_2(C_6H_6NS)_4]\cdot CH_4O$
M_r	759.88
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	200
a, b, c (Å)	9.3136 (3), 12.4532 (5), 16.1799 (6)
α, β, γ (°)	70.584 (3), 89.453 (3), 74.996 (3)
V (Å^3)	1703.51 (11)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.91
Crystal size (mm)	0.15 × 0.10 × 0.06
Data collection	
Diffractometer	Stoe IPDS1
Absorption correction	Numerical (*X-RED32* and *X-SHAPE*; Stoe, 2008)
T_{min}, T_{max}	0.781, 0.926
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26748, 8222, 6873
R_{int}	0.029
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.661
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.080, 1.07
No. of reflections	8222
No. of parameters	409
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.37

Computer programs: *X-AREA* (Stoe, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *publCIF* (Westrip, 2010) and *DIAMOND* (Brandenburg, 1999).

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Crystal structure of bis(pyridine-4-carbothioamide-κN^1)bis(thiocyanato-κN)cobalt(II) methanol monosolvate

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Computing details

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

Bis(pyridine-4-carbothioamide-κN^1)bis(thiocyanato-κN)cobalt(II) methanol monosolvate

Crystal data

$[Co(NCS)_2(C_6H_6NS)_4]\cdot CH_4O$
$M_r = 759.88$
Triclinic, $P\overline{1}$
$a = 9.3136$ (3) Å
$b = 12.4532$ (5) Å
$c = 16.1799$ (6) Å
$\alpha = 70.584$ (3)°
$\beta = 89.453$ (3)°
$\gamma = 74.996$ (3)°
$V = 1703.51$ (11) Å^3
$Z = 2$
$F(000) = 782$
$D_x = 1.481$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 26748 reflections
$\theta = 1.8$–28.0°
$\mu = 0.91$ mm^{-1}
$T = 200$ K
Block, violet
0.15 × 0.10 × 0.06 mm

Data collection

Stoe IPDS-1 diffractometer
ω scans
Absorption correction: numerical (X-RED32 and X-SHAPE; Stoe, 2008)
$T_{min} = 0.781$, $T_{max} = 0.926$
26748 measured reflections
8222 independent reflections
6873 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 28.0°$, $\theta_{min} = 1.8°$
$h = -12\rightarrow12$
$k = -16\rightarrow16$
$l = -21\rightarrow21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.080$
$S = 1.07$
8222 reflections
409 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.3232P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0030 (7)

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}
Co1	0.27982 (2)	0.47102 (2)	0.28964 (2)	0.02307 (7)
N1	0.46073 (15)	0.54348 (13)	0.26565 (9)	0.0314 (3)
C1	0.55593 (18)	0.58580 (14)	0.27195 (11)	0.0300 (3)
S1	0.68741 (5)	0.64636 (5)	0.28192 (4)	0.04785 (13)
N2	0.09728 (15)	0.40149 (12)	0.32138 (9)	0.0299 (3)
C2	0.00111 (19)	0.35654 (15)	0.33143 (11)	0.0318 (3)
S2	−0.13229 (6)	0.28999 (5)	0.34636 (4)	0.05500 (16)
N11	0.17465 (15)	0.61256 (12)	0.34077 (9)	0.0281 (3)
C11	0.1060 (2)	0.59454 (15)	0.41509 (11)	0.0334 (4)
H11	0.1198	0.5155	0.4536	0.040*
C12	0.0159 (2)	0.68505 (15)	0.43884 (11)	0.0344 (4)
H12	−0.0278	0.6683	0.4934	0.041*
C13	−0.00972 (19)	0.80101 (14)	0.38169 (11)	0.0294 (3)
C14	0.06193 (19)	0.82030 (14)	0.30472 (11)	0.0307 (3)
H14	0.0474	0.8982	0.2640	0.037*
C15	0.15440 (19)	0.72529 (14)	0.28799 (11)	0.0292 (3)
H15	0.2066	0.7402	0.2364	0.035*
C16	−0.1113 (2)	0.90116 (15)	0.40209 (11)	0.0334 (4)
S11	−0.24145 (7)	1.00294 (5)	0.32725 (3)	0.05019 (14)
N12	−0.09385 (19)	0.90110 (14)	0.48257 (10)	0.0391 (3)
H11N	−0.0195	0.8485	0.5191	0.059*
H12N	−0.1533	0.9521	0.5031	0.059*
N21	0.37050 (14)	0.34643 (12)	0.22359 (8)	0.0261 (3)
C21	0.51800 (17)	0.30357 (14)	0.22423 (10)	0.0282 (3)
H21	0.5816	0.3224	0.2597	0.034*
C22	0.58254 (18)	0.23326 (14)	0.17595 (11)	0.0289 (3)
H22	0.6880	0.2046	0.1787	0.035*
C23	0.49188 (18)	0.20501 (14)	0.12339 (10)	0.0282 (3)
C24	0.33894 (19)	0.24933 (16)	0.12248 (12)	0.0346 (4)
H24	0.2730	0.2326	0.0870	0.041*
C25	0.28281 (18)	0.31776 (16)	0.17335 (11)	0.0322 (3)
H25	0.1777	0.3459	0.1729	0.039*
C26	0.55584 (19)	0.13437 (15)	0.06639 (11)	0.0321 (3)
S21	0.48865 (5)	0.17821 (4)	−0.03746 (3)	0.03921 (11)
N22	0.6715 (2)	0.04167 (14)	0.10307 (11)	0.0461 (4)
H21N	0.7089	0.0010	0.0689	0.069*
H22N	0.7012	0.0187	0.1592	0.069*
N31	0.16434 (14)	0.59080 (12)	0.16328 (8)	0.0258 (3)
C31	0.24284 (18)	0.63003 (16)	0.09577 (10)	0.0313 (3)

H31	0.3480	0.5977	0.1024	0.038*
C32	0.17817 (18)	0.71544 (16)	0.01669 (11)	0.0327 (4)
H32	0.2379	0.7391	−0.0303	0.039*
C33	0.02558 (18)	0.76625 (14)	0.00659 (10)	0.0274 (3)
C34	−0.05686 (18)	0.72709 (15)	0.07659 (11)	0.0310 (3)
H34	−0.1616	0.7607	0.0726	0.037*
C35	0.01598 (18)	0.63816 (15)	0.15246 (11)	0.0302 (3)
H35	−0.0419	0.6092	0.1991	0.036*
C36	−0.04773 (18)	0.85862 (15)	−0.07826 (10)	0.0288 (3)
S31	−0.17011 (6)	0.98271 (4)	−0.07939 (3)	0.03822 (11)
N32	−0.00718 (17)	0.83122 (13)	−0.14892 (9)	0.0343 (3)
H31N	0.0501	0.7620	−0.1472	0.051*
H32N	−0.0518	0.8772	−0.2010	0.051*
N41	0.39825 (15)	0.34459 (12)	0.41333 (9)	0.0274 (3)
C41	0.4822 (2)	0.37337 (15)	0.46472 (11)	0.0361 (4)
H41	0.4923	0.4517	0.4457	0.043*
C42	0.5548 (2)	0.29474 (15)	0.54422 (11)	0.0367 (4)
H42	0.6105	0.3199	0.5795	0.044*
C43	0.54595 (18)	0.17943 (14)	0.57193 (10)	0.0278 (3)
C44	0.4615 (2)	0.14806 (14)	0.51807 (11)	0.0330 (4)
H44	0.4534	0.0693	0.5343	0.040*
C45	0.3894 (2)	0.23294 (14)	0.44069 (11)	0.0323 (3)
H45	0.3304	0.2108	0.4050	0.039*
C46	0.62759 (18)	0.09095 (14)	0.65609 (10)	0.0285 (3)
S41	0.76058 (5)	−0.02709 (4)	0.65401 (3)	0.03816 (11)
N42	0.59116 (17)	0.11527 (13)	0.72785 (9)	0.0342 (3)
H41N	0.5124	0.1720	0.7285	0.051*
H42N	0.6389	0.0731	0.7799	0.051*
O51	0.1577 (2)	0.59710 (15)	−0.13645 (10)	0.0604 (4)
H51	0.1793	0.6081	−0.1886	0.091*
C51	0.2618 (3)	0.4961 (2)	−0.07977 (18)	0.0658 (7)
H51A	0.3545	0.5159	−0.0713	0.099*
H51B	0.2823	0.4334	−0.1057	0.099*
H51C	0.2209	0.4686	−0.0229	0.099*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02305 (11)	0.02408 (11)	0.01983 (11)	−0.00347 (8)	−0.00100 (7)	−0.00676 (8)
N1	0.0281 (7)	0.0329 (7)	0.0307 (7)	−0.0080 (6)	−0.0002 (5)	−0.0080 (6)
C1	0.0281 (8)	0.0293 (8)	0.0294 (8)	−0.0015 (6)	0.0040 (6)	−0.0109 (6)
S1	0.0289 (2)	0.0497 (3)	0.0759 (4)	−0.0142 (2)	0.0085 (2)	−0.0329 (3)
N2	0.0279 (7)	0.0324 (7)	0.0271 (7)	−0.0077 (6)	0.0011 (5)	−0.0073 (5)
C2	0.0301 (8)	0.0346 (8)	0.0236 (7)	−0.0040 (7)	−0.0031 (6)	−0.0044 (6)
S2	0.0428 (3)	0.0648 (3)	0.0469 (3)	−0.0303 (3)	−0.0122 (2)	0.0069 (2)
N11	0.0322 (7)	0.0265 (6)	0.0260 (6)	−0.0070 (5)	0.0032 (5)	−0.0102 (5)
C11	0.0453 (10)	0.0263 (8)	0.0259 (8)	−0.0083 (7)	0.0061 (7)	−0.0067 (6)
C12	0.0477 (10)	0.0293 (8)	0.0254 (8)	−0.0087 (7)	0.0099 (7)	−0.0097 (6)

C13	0.0341 (8)	0.0284 (8)	0.0257 (7)	−0.0074 (6)	0.0022 (6)	−0.0100 (6)
C14	0.0393 (9)	0.0252 (7)	0.0260 (8)	−0.0083 (7)	0.0026 (7)	−0.0071 (6)
C15	0.0354 (8)	0.0291 (8)	0.0248 (7)	−0.0108 (6)	0.0058 (6)	−0.0100 (6)
C16	0.0409 (9)	0.0284 (8)	0.0288 (8)	−0.0069 (7)	0.0061 (7)	−0.0093 (6)
S11	0.0599 (3)	0.0417 (3)	0.0312 (2)	0.0116 (2)	−0.0026 (2)	−0.00872 (19)
N12	0.0483 (9)	0.0359 (8)	0.0302 (7)	−0.0006 (7)	0.0017 (7)	−0.0158 (6)
N21	0.0254 (6)	0.0280 (6)	0.0242 (6)	−0.0041 (5)	0.0003 (5)	−0.0103 (5)
C21	0.0250 (7)	0.0312 (8)	0.0271 (8)	−0.0032 (6)	−0.0024 (6)	−0.0116 (6)
C22	0.0257 (7)	0.0297 (8)	0.0281 (8)	−0.0022 (6)	0.0002 (6)	−0.0099 (6)
C23	0.0318 (8)	0.0264 (7)	0.0255 (7)	−0.0068 (6)	0.0036 (6)	−0.0085 (6)
C24	0.0308 (8)	0.0432 (9)	0.0378 (9)	−0.0120 (7)	0.0035 (7)	−0.0226 (8)
C25	0.0249 (7)	0.0411 (9)	0.0354 (9)	−0.0079 (7)	0.0020 (6)	−0.0200 (7)
C26	0.0341 (8)	0.0313 (8)	0.0321 (8)	−0.0071 (7)	0.0046 (7)	−0.0136 (7)
S21	0.0365 (2)	0.0477 (3)	0.0331 (2)	−0.00146 (19)	−0.00106 (18)	−0.02079 (19)
N22	0.0574 (10)	0.0387 (8)	0.0337 (8)	0.0081 (7)	−0.0027 (7)	−0.0175 (7)
N31	0.0243 (6)	0.0291 (6)	0.0203 (6)	−0.0036 (5)	−0.0007 (5)	−0.0067 (5)
C31	0.0235 (7)	0.0419 (9)	0.0239 (8)	−0.0050 (7)	0.0009 (6)	−0.0081 (7)
C32	0.0262 (8)	0.0435 (9)	0.0224 (7)	−0.0080 (7)	0.0017 (6)	−0.0046 (7)
C33	0.0285 (7)	0.0288 (7)	0.0223 (7)	−0.0065 (6)	−0.0020 (6)	−0.0063 (6)
C34	0.0233 (7)	0.0350 (8)	0.0277 (8)	−0.0030 (6)	−0.0010 (6)	−0.0054 (6)
C35	0.0251 (7)	0.0357 (8)	0.0242 (8)	−0.0065 (6)	0.0018 (6)	−0.0042 (6)
C36	0.0272 (7)	0.0319 (8)	0.0238 (7)	−0.0081 (6)	−0.0019 (6)	−0.0047 (6)
S31	0.0474 (3)	0.0316 (2)	0.0262 (2)	0.00146 (18)	−0.00544 (18)	−0.00684 (16)
N32	0.0354 (7)	0.0369 (8)	0.0229 (7)	−0.0026 (6)	−0.0028 (6)	−0.0055 (6)
N41	0.0302 (7)	0.0261 (6)	0.0225 (6)	−0.0041 (5)	−0.0043 (5)	−0.0067 (5)
C41	0.0490 (10)	0.0265 (8)	0.0295 (8)	−0.0110 (7)	−0.0111 (7)	−0.0044 (6)
C42	0.0491 (10)	0.0305 (8)	0.0287 (8)	−0.0116 (7)	−0.0134 (7)	−0.0066 (7)
C43	0.0288 (7)	0.0268 (7)	0.0239 (7)	−0.0023 (6)	−0.0022 (6)	−0.0072 (6)
C44	0.0400 (9)	0.0251 (8)	0.0316 (8)	−0.0085 (7)	−0.0052 (7)	−0.0067 (6)
C45	0.0374 (9)	0.0283 (8)	0.0294 (8)	−0.0085 (7)	−0.0071 (7)	−0.0076 (6)
C46	0.0312 (8)	0.0272 (7)	0.0245 (7)	−0.0063 (6)	−0.0026 (6)	−0.0065 (6)
S41	0.0462 (3)	0.0309 (2)	0.0285 (2)	0.00573 (18)	−0.00729 (18)	−0.01084 (16)
N42	0.0372 (8)	0.0336 (7)	0.0243 (7)	0.0010 (6)	−0.0035 (6)	−0.0081 (6)
O51	0.0771 (11)	0.0529 (9)	0.0403 (8)	0.0034 (8)	−0.0046 (8)	−0.0176 (7)
C51	0.0840 (18)	0.0442 (12)	0.0592 (15)	−0.0041 (12)	−0.0121 (13)	−0.0144 (11)

Geometric parameters (Å, º)

Co1—N1	2.0847 (14)	N22—H21N	0.8800
Co1—N2	2.0865 (14)	N22—H22N	0.8800
Co1—N21	2.1608 (13)	N31—C31	1.335 (2)
Co1—N31	2.1783 (12)	N31—C35	1.342 (2)
Co1—N41	2.1792 (13)	C31—C32	1.382 (2)
Co1—N11	2.1933 (14)	C31—H31	0.9500
N1—C1	1.164 (2)	C32—C33	1.384 (2)
C1—S1	1.6300 (18)	C32—H32	0.9500
N2—C2	1.157 (2)	C33—C34	1.386 (2)
C2—S2	1.6381 (18)	C33—C36	1.495 (2)

N11—C11	1.336 (2)	C34—C35	1.384 (2)
N11—C15	1.343 (2)	C34—H34	0.9500
C11—C12	1.384 (2)	C35—H35	0.9500
C11—H11	0.9500	C36—N32	1.323 (2)
C12—C13	1.391 (2)	C36—S31	1.6605 (17)
C12—H12	0.9500	N32—H31N	0.8800
C13—C14	1.386 (2)	N32—H32N	0.8799
C13—C16	1.489 (2)	N41—C45	1.336 (2)
C14—C15	1.377 (2)	N41—C41	1.336 (2)
C14—H14	0.9500	C41—C42	1.381 (2)
C15—H15	0.9500	C41—H41	0.9500
C16—N12	1.314 (2)	C42—C43	1.379 (2)
C16—S11	1.6594 (18)	C42—H42	0.9500
N12—H11N	0.8799	C43—C44	1.389 (2)
N12—H12N	0.8800	C43—C46	1.495 (2)
N21—C21	1.338 (2)	C44—C45	1.380 (2)
N21—C25	1.346 (2)	C44—H44	0.9500
C21—C22	1.383 (2)	C45—H45	0.9500
C21—H21	0.9500	C46—N42	1.314 (2)
C22—C23	1.388 (2)	C46—S41	1.6690 (17)
C22—H22	0.9500	N42—H41N	0.8800
C23—C24	1.386 (2)	N42—H42N	0.8800
C23—C26	1.496 (2)	O51—C51	1.408 (3)
C24—C25	1.380 (2)	O51—H51	0.8400
C24—H24	0.9500	C51—H51A	0.9800
C25—H25	0.9500	C51—H51B	0.9800
C26—N22	1.326 (2)	C51—H51C	0.9800
C26—S21	1.6572 (18)		

N1—Co1—N2	176.11 (6)	N22—C26—C23	115.73 (15)
N1—Co1—N21	92.32 (5)	N22—C26—S21	124.05 (14)
N2—Co1—N21	91.06 (5)	C23—C26—S21	120.11 (12)
N1—Co1—N31	91.36 (5)	C26—N22—H21N	115.1
N2—Co1—N31	90.73 (5)	C26—N22—H22N	121.5
N21—Co1—N31	87.09 (5)	H21N—N22—H22N	123.0
N1—Co1—N41	89.20 (5)	C31—N31—C35	117.36 (13)
N2—Co1—N41	88.87 (5)	C31—N31—Co1	119.81 (10)
N21—Co1—N41	90.24 (5)	C35—N31—Co1	122.41 (11)
N31—Co1—N41	177.29 (5)	N31—C31—C32	123.04 (15)
N1—Co1—N11	87.53 (6)	N31—C31—H31	118.5
N2—Co1—N11	89.35 (5)	C32—C31—H31	118.5
N21—Co1—N11	172.94 (5)	C31—C32—C33	119.40 (16)
N31—Co1—N11	85.85 (5)	C31—C32—H32	120.3
N41—Co1—N11	96.82 (5)	C33—C32—H32	120.3
C1—N1—Co1	163.69 (14)	C32—C33—C34	118.04 (14)
N1—C1—S1	178.93 (16)	C32—C33—C36	120.67 (15)
C2—N2—Co1	171.72 (14)	C34—C33—C36	121.28 (14)
N2—C2—S2	178.71 (16)	C35—C34—C33	118.87 (15)

C11—N11—C15	116.99 (14)	C35—C34—H34	120.6
C11—N11—Co1	123.49 (11)	C33—C34—H34	120.6
C15—N11—Co1	118.44 (11)	N31—C35—C34	123.21 (15)
N11—C11—C12	123.40 (15)	N31—C35—H35	118.4
N11—C11—H11	118.3	C34—C35—H35	118.4
C12—C11—H11	118.3	N32—C36—C33	114.27 (15)
C11—C12—C13	119.03 (16)	N32—C36—S31	124.92 (12)
C11—C12—H12	120.5	C33—C36—S31	120.80 (12)
C13—C12—H12	120.5	C36—N32—H31N	124.0
C14—C13—C12	117.78 (15)	C36—N32—H32N	120.1
C14—C13—C16	121.00 (15)	H31N—N32—H32N	114.8
C12—C13—C16	121.22 (15)	C45—N41—C41	117.06 (14)
C15—C14—C13	119.26 (15)	C45—N41—Co1	120.25 (10)
C15—C14—H14	120.4	C41—N41—Co1	122.68 (11)
C13—C14—H14	120.4	N41—C41—C42	123.16 (16)
N11—C15—C14	123.42 (16)	N41—C41—H41	118.4
N11—C15—H15	118.3	C42—C41—H41	118.4
C14—C15—H15	118.3	C43—C42—C41	119.50 (15)
N12—C16—C13	115.95 (15)	C43—C42—H42	120.2
N12—C16—S11	123.07 (14)	C41—C42—H42	120.2
C13—C16—S11	120.95 (13)	C42—C43—C44	117.72 (14)
C16—N12—H11N	120.2	C42—C43—C46	120.89 (14)
C16—N12—H12N	123.4	C44—C43—C46	121.37 (14)
H11N—N12—H12N	116.3	C45—C44—C43	119.03 (15)
C21—N21—C25	117.15 (14)	C45—C44—H44	120.5
C21—N21—Co1	120.78 (10)	C43—C44—H44	120.5
C25—N21—Co1	121.75 (11)	N41—C45—C44	123.49 (15)
N21—C21—C22	123.32 (14)	N41—C45—H45	118.3
N21—C21—H21	118.3	C44—C45—H45	118.3
C22—C21—H21	118.3	N42—C46—C43	116.01 (14)
C21—C22—C23	119.39 (15)	N42—C46—S41	124.26 (12)
C21—C22—H22	120.3	C43—C46—S41	119.69 (12)
C23—C22—H22	120.3	C46—N42—H41N	122.5
C24—C23—C22	117.47 (15)	C46—N42—H42N	123.2
C24—C23—C26	120.86 (15)	H41N—N42—H42N	114.2
C22—C23—C26	121.61 (15)	C51—O51—H51	109.5
C25—C24—C23	119.77 (15)	O51—C51—H51A	109.5
C25—C24—H24	120.1	O51—C51—H51B	109.5
C23—C24—H24	120.1	H51A—C51—H51B	109.5
N21—C25—C24	122.88 (15)	O51—C51—H51C	109.5
N21—C25—H25	118.6	H51A—C51—H51C	109.5
C24—C25—H25	118.6	H51B—C51—H51C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H11*N*···S2^{i}	0.88	2.45	3.3010 (16)	163
N12—H12*N*···S41^{ii}	0.88	2.64	3.3589 (16)	140

C21—H21···S2^{iii}	0.95	2.89	3.7626 (16)	153
N22—H21*N*···S31^{iv}	0.88	2.69	3.4969 (17)	152
N22—H22*N*···S11^{iv}	0.88	2.71	3.5691 (17)	166
C31—H31···N1	0.95	2.65	3.137 (2)	112
C34—H34···S21^{v}	0.95	2.95	3.8809 (17)	165
C35—H35···S1^{vi}	0.95	2.85	3.6906 (17)	148
C35—H35···N2	0.95	2.68	3.203 (2)	115
N32—H31*N*···O51	0.88	1.99	2.863 (2)	173
N32—H32*N*···S41^{vii}	0.88	2.67	3.5176 (14)	163
N42—H41*N*···S1^{viii}	0.88	2.49	3.3580 (16)	171
N42—H42*N*···S31^{ix}	0.88	2.64	3.4935 (14)	165
O51—H51···S2^{v}	0.84	2.43	3.1994 (17)	153

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*−1, *y*+1, *z*; (iii) *x*+1, *y*, *z*; (iv) *x*+1, *y*−1, *z*; (v) −*x*, −*y*+1, −*z*; (vi) *x*−1, *y*, *z*; (vii) *x*−1, *y*+1, *z*−1; (viii) −*x*+1, −*y*+1, −*z*+1; (ix) *x*+1, *y*−1, *z*+1.