Synthesis, crystal structure and thermal properties of poly[bis[μ_2-3-(aminomethyl)pyridine]bis(thiocyanato)cobalt(II)]

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The reaction of Co(NCS)$_2$ with 3-(aminomethyl)pyridine as coligand leads to the formation of crystals of the title compound, [Co(NCS)$_2$(C$_6$H$_8$N$_2$)$_2$]$_n$, that were characterized by single-crystal X-ray analysis. In the crystal structure, the Co^{II} cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions as well as two pyridine and two amino N atoms of four symmetry-equivalent 3-(aminomethyl)pyridine coligands with all pairs of equivalent atoms in a *trans* position. The Co^{II} cations are linked by the 3-(aminomethyl)pyridine coligands into layers parallel to the *ac* plane. These layers are further linked by intermolecular N—H···S hydrogen bonding into a three-dimensional network. The purity of the title compound was determined by X-ray powder diffraction and its thermal behavior was investigated by differential scanning calorimetry and thermogravimetry.

1. Chemical context

Coordination compounds based on thiocyanate anions show a variety of structures, that can be traced back to the versatile coordination behavior of this ligand (Buckingham, 1994, Wöhlert *et al.*, 2014; Werner *et al.*, 2015a). Even if the majority of compounds contain only terminal N-bonded ligands, there is a large number of compounds in which the metal cations are linked by these anionic ligands into networks of different dimensionality (Đaković *et al.*, 2010; Kozísková *et al.*, 1990; Kabešová *et al.*, 1990; Prananto *et al.*, 2017; Suckert *et al.*, 2016; Wellm *et al.*, 2018). In those cases where the metal cations are octahedrally coordinated, different isomers can additionally be found, in which the metal cations are either all-*trans* or *cis–cis–trans* coordinated (Böhme *et al.*, 2020; Rams *et al.*, 2017). Which kind of compound is observed depends among other things on the nature of the metal cation, because the synthesis of compounds with bridging anionic ligands is easier with chalcophilic cations such as, for example, Cd^{II}, whereas less chalcophilic metal cations such as Mn^{II}, Fe^{II} and especially Co^{II} and Ni^{II} in several cases lead to the formation of compounds with terminal N-bonded thiocyanate anions. This is of importance because this anionic ligand is able to mediate substantial magnetic exchange (Bassey *et al.*, 2020; Mekui-memba *et al.*, 2018; Palion-Gazda *et al.*, 2015; Mousavi *et al.*, 2020), which can lead to compounds that show a variety of magnetic properties. Co^{II} is of special importance because of its high magnetic anisotropy (Mautner *et al.*, 2018; Jochim *et al.*, 2020; Neumann *et al.*, 2019). This led to a renewed interest into compounds in which the metal cations are linked by these anionic ligands into chains or layers and an increasing number
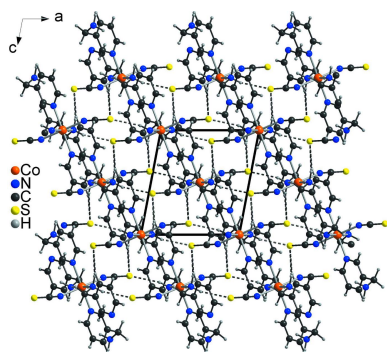
have been reported in the literature over the last decade (Jin *et al.*, 2007; Shi *et al.*, 2006; Mautner *et al.*, 2018).
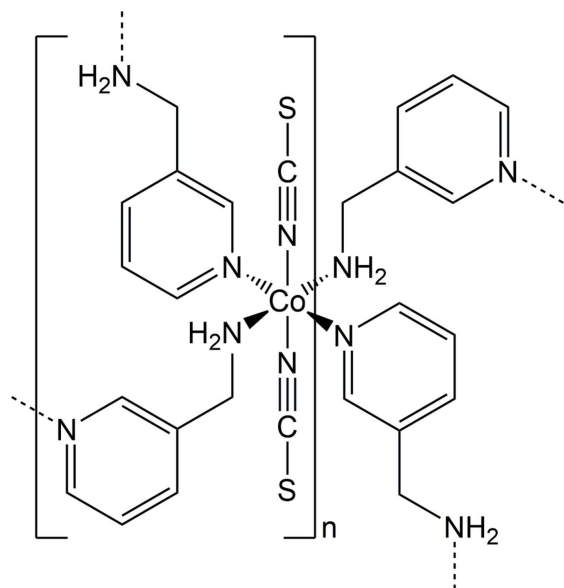
In our own investigations we are especially interested in transition-metal thiocyanate coordination polymers based on cobalt in which the metal cations are linked by μ-1,3-bridging anionic ligands into chains, because these compounds can show single-chain magnet (SCM) behavior. These are compounds in which the spins are ferromagnetically aligned along a chain with strong magnetic exchange within the chain and only weak interchain interactions to prevent 3D ordering (Sun *et al.*, 2010; Miyasaka *et al.*, 2005). In the course of this project we have prepared a large number of compounds with the general composition $M(NCS)_2(L)_2$ where L represents a pyridine derivative substituted at the 4-position (Werner *et al.*, 2015*b*; Rams *et al.*, 2017, 2020). In principle, SCM behavior can also be observed in 2D compounds if the ferromagnetic chains are linked into layers by bridging ligands that do not mediate strong magnetic exchange. Therefore, we became interested in 3-(aminomethyl)pyridine as it can coordinate to metal cations *via* the pyridine and the amino N atom and for which no cobalt(II) thiocyanate compounds had been reported. Therefore, we reacted $Co(NCS)_2$ with 3-(aminomethyl)pyridine in different molar ratios, which always led to the formation of crystalline powders with the composition $Co(NCS)_2$(3-(aminomethylpyridine)$_2$ (see *Synthesis and crystallization*). This composition indicated that either the organic coligand does not bridge neighboring metal centers or that only terminal-coordinated thiocyanate anions are present. IR spectroscopic measurements reveal that the CN stretching vibration of the anionic ligand is observed at 2077cm^{-1}, which points to the presence of terminal N-bonded anionic ligands (Fig. S1). To prove these assumptions, single crystals were grown and characterized by single-crystal X-ray diffraction, which proves that this crystalline phase is isotypic to the corresponding Cd compound already reported in the literature, in which the Cd^{II} or Co^{II} cations are linked into layers by the 3-(aminomethyl)pyridine ligands (see *Structural commentary*). Comparison

of the experimental X-ray powder pattern with that calculated from the single-crystal data proves that a pure crystalline phase has been obtained (Fig. S2). For the more chalcophilic Cd^{II} cations another compound with the composition $Cd(NCS)_2$(3-(aminomethylpyridine) is known, in which the Cd^{II} cations are linked by bridging anionic ligands. With $Co(NCS)_2$ we found no access to this compound in solution and, therefore, we tried to prepare a 3-(aminomethyl)-pyridine-deficient phase by thermal ligand removal from the title compound. Therefore, the title compound was investigated by thermogravimetry coupled to differential scanning calorimetry (TG-DSC). Upon heating at a rate of 8°C min^{-1} the compound starts to decompose at about 215°C and upon further heating a steady mass loss with no discrete decomposition events is observed (Fig. S3). To increase the resolution a second TG-DSC measurement with 1°C min^{-1} was performed, which does not improve the resolution significantly (Fig. S4). Based on these measurements, there is no indication for the formation of another currently unknown 3-(aminomethyl)pyridine-deficient compound.

2. Structural commentary

The asymmetric unit of the title compound, $Co(NCS)_2(C_6H_8N_2)_2$, consists of one Co^{II} cation that is located on a center of inversion as well as one thiocyanate anion and one 3-(aminomethyl)pyridine coligand in general positions (Fig. 1). The Co^{II} cations are sixfold coordinated by two symmetry-equivalent terminal N-bonded anionic ligands as well as four symmetry-equivalent 3-(aminomethyl)pyridine coligands, of which two are coordinated through the pyridine N atom and two through the amino N atom to the cations, with each pair of identical atoms in the *trans* position to each other
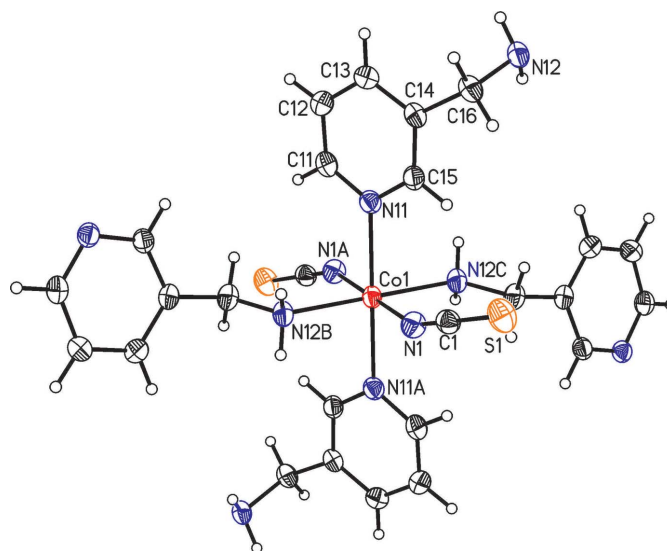

Figure 1
Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry codes: A = −x, −y + 1, −z, B = $\frac{1}{2}$ − x, −$\frac{1}{2}$ − y, $\frac{1}{2}$ − z, C = −$\frac{1}{2}$ + x, $\frac{3}{2}$ − y, −$\frac{1}{2}$ + z. Color code: Co (red), N (blue) and S (orange).

Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.1038 (16)	Co1—N11	2.2107 (15)
Co1—N2^i	2.1821 (15)		
N1^{ii}—Co1—N1	180.00 (8)	N1—Co1—N11	89.41 (6)
N1—Co1—N2^{iii}	91.95 (6)	N2^{iii}—Co1—N11	89.67 (6)
N1—Co1—N2^i	88.05 (6)	N2^i—Co1—N11	90.33 (6)
N1^{ii}—Co1—N11	90.59 (6)	N11—Co1—N11^{ii}	180.0

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C11—H11$\cdots$N1^{ii}	0.95	2.69	3.207 (3)	115
C12—H12$\cdots$S1^i	0.95	2.93	3.696 (2)	138
C15—H15$\cdots$N1	0.95	2.66	3.163 (2)	114
N2—H1$N2\cdots$S1^{iv}	0.91	2.87	3.7430 (17)	162
N2—H2$N2\cdots$S1^v	0.91	2.65	3.5044 (17)	157

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

(Fig. 1). The Co—N bond lengths to the amino N atom are significantly shorter than those to the pyridine N atoms, indicating that this is the stronger interaction (Table 1). The bond angles around the Co^{II} centers deviate by less than 1.95 (6)° from the ideal values, which indicates that the octahedra are only slightly distorted (Table 1). This is also obvious from the octahedral angle variance of 1.6 and the mean octahedral quadratic elongation of 1.001 calculated using the method of Robinson (Robinson *et al.*, 1971). The Co cations are linked by bridging 3-(aminomethyl)pyridine ligands into layers that are parallel to the *bc* plane (Fig. 2). These layers are constructed of large rings that consist of four Co^{II} cations and four 3-(aminomethyl)pyridine coligands (Fig. 2).

3. Supramolecular features

The Co(NCS)$_2$ layers are arranged in stacks that elongate along the crystallographic *a*-axis direction (Fig. 2). The layers
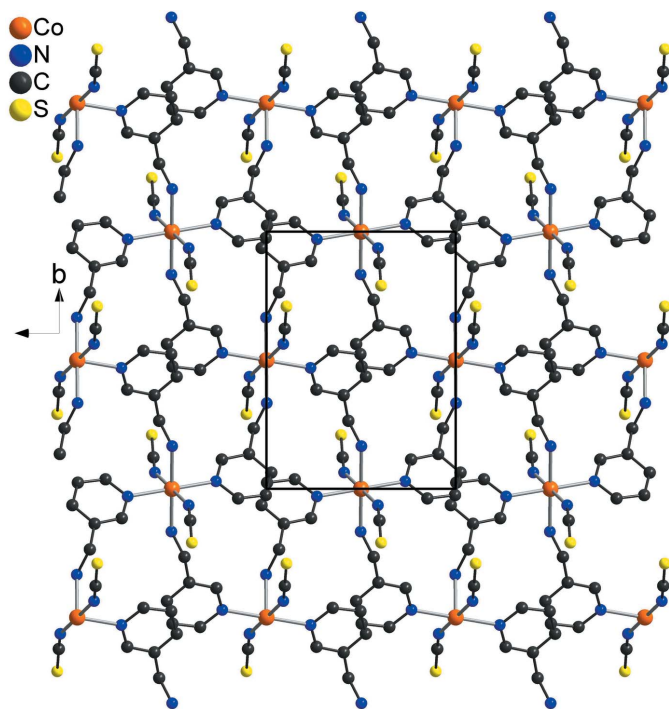
are linked into a three-dimensional network by intermolecular N—H$\cdots$S hydrogen bonding between the thiocyanate S atoms and the amino H atoms, in which the S atoms act as acceptors for two of these hydrogen bonds (Fig. 3 and Table 2). The N—H$\cdots$S angles are close to linear, which indicates that this is a strong interaction. There are additional C—H$\cdots$S and C—H$\cdots$N intra- and intermolecular interactions, but their geometrical parameters indicate that these are not strong interactions (Table 2).

4. Database survey

In the Cambridge Structural Database (CSD version 5.42, last update November 2020; Groom *et al.*, 2016) no cobalt thiocyanate compounds with 3-(aminomethyl)pyridine as coligand are reported. However, some compounds based on Zn(NCS)$_2$ and Cd(NCS)$_2$ are published, in which the cations are always octahedrally coordinated (Neumann *et al.*, 2017). This includes Cd(NCS)$_2$[3-(aminomethyl)pyridine]$_2$-tris[3-(aminomethyl)]-pyridine solvate (QEKYOX), in which the Cd^{II} cations are also linked into layers, that contain large pores, in

Figure 2
Crystal structure of the title compound viewed along the crystallographic *a* axis. The H atoms are omitted for clarity.
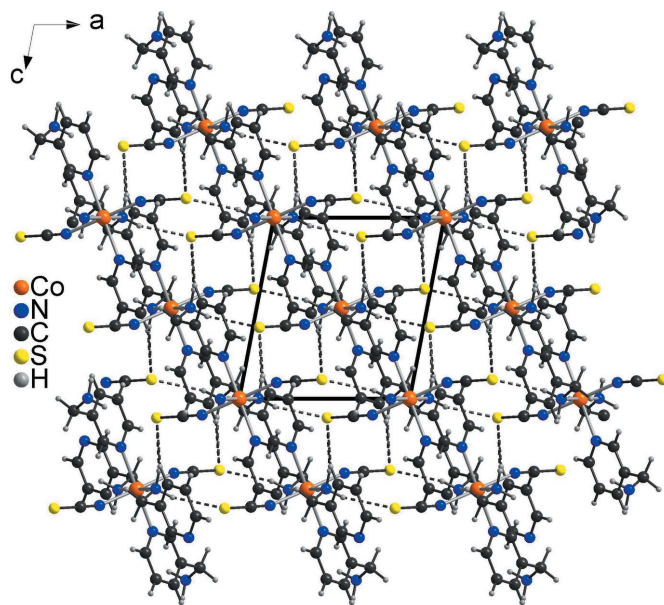

Figure 3
Crystal structure of the title compound viewed along the crystallographic *b* axis. Intermolecular N—H$\cdots$S hydrogen bonds are shown as dashed lines.

which additional 3-(aminomethyl)pyridine solvate molecules are embedded. The same report also describes M(NCS)$_2$[3-(aminomethyl)pyridine]$_2$ [M = Cd (QEKZEO), Zn (QEKYUD)], which is isotypic to the title compound. Finally, two compounds with the composition M(NCS)$_2$[3-(aminomethyl)pyridine] [M = Cd (QEKZIS), Zn (QEKZAK)] are reported. The Zn compound consists of dimers, in which each two Zn^{II} cations are linked by each two 3-(aminomethyl)pyridine ligands. In contrast, in the crystal structure of the Cd compound, the Cd^{II} cations are linked into chains by the 3-(aminomethyl)pyridine ligands that are further connected into layers by μ-1,3-bridging thiocyanate anions. This compound is the only one which shows an *cis–cis–trans* coordination of the metal cations.

5. Synthesis and crystallization

Experimental details

Elemental analysis was performed using a EURO EA elemental analyzer fabricated by EURO VECTOR Instruments. The IR spectrum was measured using an ATI Mattson Genesis Series FTIR Spectrometer, control software: WINFIRST, from ATI Mattson. The PXRD measurement was performed with Cu $K\alpha_1$ radiation (λ = 1.540598 Å) using a Stoe Transmission Powder Diffraction System (STADI P) that is equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator. Thermogravimetry and differential scanning calorimetry (TG-DSC) measurements were performed in a dynamic nitrogen atmosphere in Al$_2$O$_3$ crucibles using a STA-PT 1600 thermobalance from Linseis. The instrument was calibrated using standard reference materials.

Synthesis

3-(Aminomethyl)pyridine and Co(NCS)$_2$ were purchased from Alfa Aesar. All chemicals were used without further purification. Single crystals were obtained by reacting 1 mmol Co(NCS)$_2$ (175.1 mg) with 0.2 mmol 3-(aminomethyl)pyridine (216.3 mg) in 3 mL of ethanol. After approximately one week blue-colored crystals were obtained, which were suitable for single crystal X-ray analysis. For the synthesis of crystalline powders the same amounts of reactants were stirred in 1 mL of ethanol for 3 d. The blue-colored precipitate was filtered and dried in air. Yield: 70%. Elemental analysis calculated for C$_{14}$H$_{16}$N$_6$CoS$_2$ (391.4 g mol^{-1}) C 42.96%, H 4.12%, N 21.47%, S 16.39%, found: C 42.82%, H 4.01%, N 21.32%, S 16.29%. IR: ν = 3282 (*m*), 3245 (*m*), 3161 (*w*), 3058 (*w*), 3049 (*w*), 2979 (*w*), 2955 (*sh*), 2946 (*w*), 2874 (*vw*), 2862 (*sh*), 2077 (*vs*), 2033 (*w*), 1603 (*sh*), 1595 (*m*), 1582 (*m*), 1480 (*m*), 1447 (*w*), 1429 (*m*), 1361 (*w*), 1344 (*w*), 1333 (*w*), 1248 (*w*), 1229 (*w*), 1191 (*m*), 1150 (*m*), 1136 (*s*), 1103 (*m*), 1053 (*m*), 1039 (*w*), 990 (*s*), 965 (*m*), 943 (*w*), 933 (*m*), 895 (*w*), 852 (*m*), 841 (*sh*), 807 (*s*), 785 (*m*), 715 (*s*), 646 (*m*), 628 (*m*), 568 (*s*), 509 (*w*) cm^{-1}.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All non-hydrogen atoms were

Table 3
Experimental details.

Crystal data	
Chemical formula	[Co(NCS)$_2$(C$_6$H$_8$N$_2$)$_2$]
M_r	391.38
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	200
a, b, c (Å)	8.2442 (4), 11.9186 (4), 8.9204 (4)
β ($°$)	100.807 (4)
V (Å^3)	860.97 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.25
Crystal size (mm)	0.20 × 0.15 × 0.12
Data collection	
Diffractometer	STOE IPDS2
Absorption correction	Numerical (*X-AREA*; Stoe & Cie, 2002)
T_{min}, T_{max}	0.709, 0.886
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13295, 1871, 1702
R_{int}	0.029
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.071, 1.15
No. of reflections	1871
No. of parameters	106
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.23

Computer programs: *X-AREA* (Stoe & Cie, 2002), *SHELXS97* (Sheldrick, 2008), *SHELXL2016/6* (Sheldrick, 2015), *DIAMOND* (Brandenburg & Putz, 1999) and *publCIF* (Westrip, 2010).

refined anisotropically. C—H and N—H H atoms were located in difference maps but positioned with idealized geometry and refined isotropically with U_{iso}(H) = 1.2U_{eq}(C) (1.5 for amino H atoms) using a riding model.

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Synthesis, crystal structure and thermal properties of poly[bis[μ_2-3-(amino-methyl)pyridine]bis(thiocyanato)cobalt(II)]

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-AREA* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Poly[bis[μ_2-3-(aminomethyl)pyridine]bis(thiocyanato)cobalt(II)]

Crystal data

[Co(NCS)$_2$(C$_6$H$_8$N$_2$)$_2$]	$F(000) = 402$
$M_r = 391.38$	$D_x = 1.510$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.2442$ (4) Å	Cell parameters from 13295 reflections
$b = 11.9186$ (4) Å	$\theta = 2.9$–27.0°
$c = 8.9204$ (4) Å	$\mu = 1.25$ mm^{-1}
$\beta = 100.807$ (4)°	$T = 200$ K
$V = 860.97$ (6) Å^3	Block, light blue
$Z = 2$	$0.20 \times 0.15 \times 0.12$ mm

Data collection

STOE IPDS-2 diffractometer	1871 independent reflections
	1702 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.029$
Absorption correction: numerical (X-AREA; Stoe & Cie, 2002)	$\theta_{max} = 27.0°$, $\theta_{min} = 2.9°$
	$h = -10 \rightarrow 10$
$T_{min} = 0.709$, $T_{max} = 0.886$	$k = -15 \rightarrow 15$
13295 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.029$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.071$	
$S = 1.15$	H-atom parameters constrained
1871 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.3351P]$
106 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.30$ e Å^{-3}
	$\Delta\rho_{min} = -0.22$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Co1	0.000000	0.500000	0.000000	0.02255 (11)
N1	0.2001 (2)	0.56371 (13)	−0.08934 (18)	0.0295 (3)
C1	0.3105 (2)	0.62263 (15)	−0.0971 (2)	0.0267 (4)
S1	0.46298 (6)	0.70951 (4)	−0.10573 (7)	0.03779 (14)
N11	0.14044 (19)	0.52941 (12)	0.23318 (17)	0.0259 (3)
C11	0.1228 (2)	0.46286 (15)	0.3504 (2)	0.0293 (4)
H11	0.044225	0.403768	0.332043	0.035*
C12	0.2131 (3)	0.47585 (16)	0.4966 (2)	0.0314 (4)
H12	0.198637	0.425522	0.575614	0.038*
C13	0.3246 (2)	0.56334 (16)	0.5256 (2)	0.0304 (4)
H13	0.388294	0.573805	0.625018	0.036*
C14	0.3425 (2)	0.63566 (14)	0.4080 (2)	0.0260 (4)
C15	0.2496 (2)	0.61412 (14)	0.2644 (2)	0.0266 (4)
H15	0.263911	0.662217	0.183003	0.032*
C16	0.4576 (2)	0.73543 (15)	0.4332 (2)	0.0296 (4)
H16A	0.561774	0.712435	0.500465	0.035*
H16B	0.484490	0.758046	0.333897	0.035*
N2	0.38938 (19)	0.83381 (12)	0.50202 (18)	0.0271 (3)
H1N2	0.389470	0.816364	0.601345	0.032*
H2N2	0.281758	0.840369	0.455359	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02203 (18)	0.01854 (17)	0.02615 (17)	−0.00132 (12)	0.00208 (12)	0.00035 (12)
N1	0.0261 (8)	0.0300 (8)	0.0322 (8)	−0.0025 (6)	0.0051 (6)	0.0014 (6)
C1	0.0269 (9)	0.0261 (8)	0.0271 (9)	0.0034 (7)	0.0047 (7)	−0.0018 (7)
S1	0.0301 (3)	0.0337 (3)	0.0503 (3)	−0.0084 (2)	0.0094 (2)	−0.0046 (2)
N11	0.0263 (8)	0.0229 (7)	0.0275 (7)	−0.0014 (6)	0.0021 (6)	−0.0015 (6)
C11	0.0305 (10)	0.0230 (8)	0.0345 (10)	−0.0039 (7)	0.0063 (8)	−0.0023 (7)
C12	0.0375 (11)	0.0277 (9)	0.0289 (9)	−0.0021 (7)	0.0065 (8)	0.0028 (7)
C13	0.0348 (10)	0.0289 (9)	0.0263 (9)	−0.0005 (8)	0.0031 (7)	−0.0027 (7)
C14	0.0260 (9)	0.0212 (8)	0.0307 (9)	0.0004 (7)	0.0052 (7)	−0.0038 (7)
C15	0.0289 (9)	0.0210 (8)	0.0289 (9)	−0.0008 (7)	0.0033 (7)	0.0004 (6)
C16	0.0282 (9)	0.0248 (9)	0.0350 (9)	−0.0028 (7)	0.0042 (8)	−0.0045 (7)
N2	0.0270 (8)	0.0208 (7)	0.0326 (8)	−0.0016 (6)	0.0036 (6)	−0.0010 (6)

Geometric parameters (Å, º)

Co1—N1[i]	2.1038 (16)	C12—C13	1.382 (3)
Co1—N1	2.1038 (16)	C12—H12	0.9500
Co1—N2[ii]	2.1821 (15)	C13—C14	1.387 (3)
Co1—N2[iii]	2.1821 (15)	C13—H13	0.9500
Co1—N11	2.2107 (15)	C14—C15	1.388 (3)
Co1—N11[i]	2.2107 (15)	C14—C16	1.511 (2)
N1—C1	1.162 (2)	C15—H15	0.9500
C1—S1	1.6415 (19)	C16—N2	1.482 (2)
N11—C11	1.342 (2)	C16—H16A	0.9900
N11—C15	1.346 (2)	C16—H16B	0.9900
C11—C12	1.384 (3)	N2—H1N2	0.9100
C11—H11	0.9500	N2—H2N2	0.9100
N1[i]—Co1—N1	180.00 (8)	C13—C12—H12	120.6
N1[i]—Co1—N2[ii]	88.05 (6)	C11—C12—H12	120.6
N1—Co1—N2[ii]	91.95 (6)	C12—C13—C14	119.24 (18)
N1[i]—Co1—N2[iii]	91.95 (6)	C12—C13—H13	120.4
N1—Co1—N2[iii]	88.05 (6)	C14—C13—H13	120.4
N2[ii]—Co1—N2[iii]	180.0	C13—C14—C15	117.69 (17)
N1[i]—Co1—N11	90.59 (6)	C13—C14—C16	121.98 (17)
N1—Co1—N11	89.41 (6)	C15—C14—C16	120.33 (16)
N2[ii]—Co1—N11	89.67 (6)	N11—C15—C14	124.18 (17)
N2[iii]—Co1—N11	90.33 (6)	N11—C15—H15	117.9
N1[i]—Co1—N11[i]	89.41 (6)	C14—C15—H15	117.9
N1—Co1—N11[i]	90.59 (6)	N2—C16—C14	114.06 (15)
N2[ii]—Co1—N11[i]	90.33 (6)	N2—C16—H16A	108.7
N2[iii]—Co1—N11[i]	89.67 (6)	C14—C16—H16A	108.7
N11—Co1—N11[i]	180.0	N2—C16—H16B	108.7
C1—N1—Co1	156.84 (15)	C14—C16—H16B	108.7
N1—C1—S1	177.97 (17)	H16A—C16—H16B	107.6
C11—N11—C15	116.60 (16)	C16—N2—Co1[iv]	121.54 (11)
C11—N11—Co1	121.68 (12)	C16—N2—H1N2	106.9
C15—N11—Co1	121.71 (12)	Co1[iv]—N2—H1N2	106.9
N11—C11—C12	123.39 (17)	C16—N2—H2N2	106.9
N11—C11—H11	118.3	Co1[iv]—N2—H2N2	106.9
C12—C11—H11	118.3	H1N2—N2—H2N2	106.7
C13—C12—C11	118.85 (17)		
C15—N11—C11—C12	−1.8 (3)	Co1—N11—C15—C14	−179.17 (13)
Co1—N11—C11—C12	177.39 (15)	C13—C14—C15—N11	1.8 (3)
N11—C11—C12—C13	1.7 (3)	C16—C14—C15—N11	−177.78 (17)
C11—C12—C13—C14	0.2 (3)	C13—C14—C16—N2	−79.6 (2)
C12—C13—C14—C15	−1.8 (3)	C15—C14—C16—N2	100.0 (2)

C12—C13—C14—C16	177.72 (17)	C14—C16—N2—Co1iv	−164.90 (12)
C11—N11—C15—C14	0.0 (3)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···N1i	0.95	2.69	3.207 (3)	115
C12—H12···S1iii	0.95	2.93	3.696 (2)	138
C15—H15···N1	0.95	2.66	3.163 (2)	114
N2—H1*N*2···S1v	0.91	2.87	3.7430 (17)	162
N2—H2*N*2···S1vi	0.91	2.65	3.5044 (17)	157

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