Crystal structure of bis(tetramethylthiourea-κS)bis-(thiocyanato-κN)cobalt(II)

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In the course of systematic investigations on the synthesis of $Co(NCS)_2$ coordination compounds with different thiourea ligands, the title compound, $[Co(NCS)_2(C_5H_{12}N_2S)_2]$, was obtained. In this compound the Co^{II} cations are coordinated by two crystallographically independent N-bonded thiocyanate anions and two tetramethylthiourea ligands into discrete complexes that are located in general positions and show a strongly distorted tetrahedral geometry. Intermolecular C—H⋯S hydrogen bonds of different strength can be observed between the discrete complexes, which are connected by pairs of hydrogen bonds into zigzag-like chains that elongate in the b-axis direction. These chains are additionally linked by strong C—H⋯S hydrogen bonds along the a-axis direction, resulting in the formation of layers that are parallel to the ab plane. There is also one weak intramolecular C—H⋯S hydrogen bond between two neighbouring thiourea ligands within the complexes. Comparison of the experimental PXRD pattern with that calculated from the single-crystal data prove that a pure phase has been obtained. Thermoanalytical investigations reveal that this compound melts at 364 K and decomposes upon further heating.

1. Chemical context

The thiocyanate anion is a very versatile ligand, which can coordinate in many different ways to metal cations, leading to compounds with a variety of coordination networks (Buckingham, 1994; Haasnoot et al., 1984; Barnett et al., 2002; Bhowmik et al., 2010; Abedi et al., 2016). This ligand is also able to mediate reasonable magnetic exchange (Palion-Gazda et al., 2015), which is one reason why we have been interested in transition-metal thiocyanate coordination compounds for many years. In this context, we are especially interested in compounds of the general composition $[M(NCS)_2(L)_2]_n$, in which paramagnetic first-row transition-metal cations M such as Mn^{II}, Fe^{II}, Co^{II} or Ni^{II} are octahedrally coordinated by two N- and two S-bonding thiocyanate anions and two coligands L that usually consist of pyridine derivatives. Depending on the nature of the coligand, the metal cations are connected into chains by pairs of μ-1,3 coordinating anionic ligands (Mautner et al., 2018; Prananto et al., 2017; Shurdha et al., 2013; Jin et al., 2007; Böhme et al., 2020), or they are linked into layers with different layer topologies (Werner et al., 2015a; Neumann et al., 2018a; Suckert et al., 2016). The chain compounds show either ferromagnetism (Neumann et al., 2019), antiferromagnetism (Jochim et al., 2020) or they represent antiferromagnetic phases of single-chain magnets (Mautner et al., 2018; Rams et al., 2017, 2020; Werner et al., 2015b), whereas the layer compounds are in most cases ferromagnets (Suckert
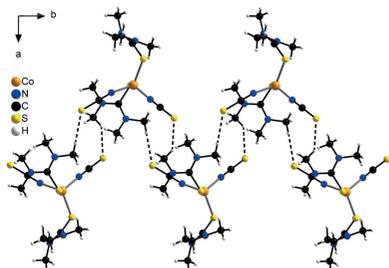
research communications

et al., 2016). For this composition a third structure type is known, in which the metal cations are tetrahedrally coordinated, forming discrete complexes with only N-terminally bonded thiocyanate anions (Neumann *et al.*, 2018b). For some coligands, at least two of the three isomers can be obtained. With 4-acetylpyridine as coligand, for example, the chain as well as the layer isomer can be prepared, with the latter representing the thermodynamically stable form at room temperature (Werner *et al.*, 2015a). If 4-methoxypyridine is used as coligand, the chain isomer as well as the tetrahedral discrete complex can be obtained, and in this case the chain compound is thermodynamically stable at room temperature (Mautner *et al.*, 2018; Rams *et al.*, 2020). Finally, different polymorphic modifications can also be obtained for discrete complexes (Neumann *et al.*, 2018b).
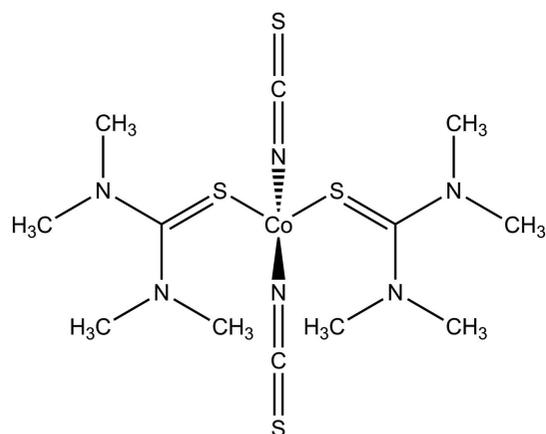
However, in all previous work we exclusively used N-donor coligands for the synthesis of $Co(NCS)_2$ thiocyanate coordination polymers, and to investigate the influence of the coligand on the structure and the magnetic behaviour, we became interested in donor ligands that can coordinate *via* a sulfur atom, including thiourea derivatives. With thiourea, the crystal structure of one $Co(NCS)_2$ coordination compound has already been already reported, and in this case the Co cations are linked by pairs of thiourea sulfur atoms, whereas the thiocyanate anions are only terminally N-bonded (Rajarajan *et al.*, 2012). Independent of this, we used ethylenethiourea as coligand and obtained a compound with the composition $[Co(NCS)_2(ethylenethiourea)_2]_n$. Single-crystal structure determination proves that, in this case, the Co^{II} cations are connected by pairs of thiocyanate ligands into chains, which corresponds exactly to the desired structure (Jochim *et al.*, 2020). In contrast to the analogous compounds with N-donor coligands, this compound shows antiferromagnetic ordering but no relaxations of single chains. To investigate this in more detail, we used tetramethylthiourea as coligand and obtained crystals of the title compound $Co(NCS)_2(tetramethylthiourea)_2$. Surprisingly, this compound consists of discrete complexes, in which the Co^{II} cations are tetrahedrally coordinated, which is also reflected in its IR spectra, where the C—N stretching vibration of the thiocyanate anion is observed at 2048 cm^{-1} (see Fig. S1 in the supporting information). The powder diffraction pattern reveals that a pure product has

Table 1
Selected geometric parameters (Å, °).

Co1—N1	1.9484 (17)	Co1—S11	2.3157 (5)
Co1—N2	1.9499 (17)	Co1—S21	2.3196 (6)
N1—Co1—N2	106.56 (7)	N1—Co1—S21	117.66 (5)
N1—Co1—S11	102.86 (5)	N2—Co1—S21	97.67 (6)
N2—Co1—S11	121.40 (5)	S11—Co1—S21	111.564 (19)

been obtained (Fig. S2). The thermogravimetric (TG) curve shows that all tetramethylthiourea ligands are emitted in one step (theoretical mass loss: 60.2%), which is accompanied by an exothermic peak in the differential thermoanalysis (DTA) curve (Fig. S3). However, two endothermic peaks are observed at low temperatures where the sample mass does not change. To investigate this phenomenon in more detail, measurements using differential scanning calorimetry (DSC) were performed, which prove that the first endothermic signal is reversible with some hysteresis, pointing to some structural transition (Fig. S4), which could explain why no changes in the PXRD pattern are observed after cooling. The second endothermic peak is irreversible, but thermomicroscopic measurements prove that this event corresponds to melting, which means that upon cooling no crystallization is observed (Figs. S5 and S6).

2. Structural commentary

The asymmetric unit of the title compound contains two crystallographically independent tetramethylthiourea molecules, two thiocyanate anions and one Co^{II} cation in general positions (Fig. 1). The Co^{II} cations are coordinated by two N-bonded thiocyanate anions and two tetramethylthiourea molecules into discrete complexes, with bonds lengths and angles similar to those reported in the literature (Table 1). The
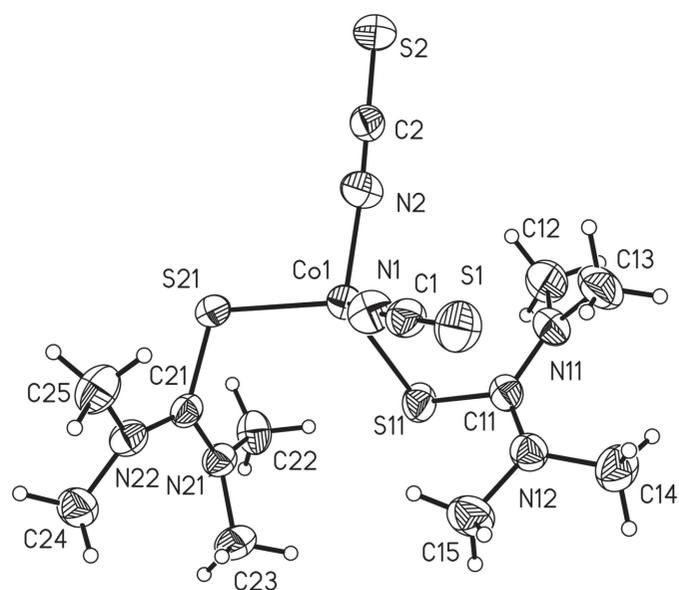
Figure 1
View of the asymmetric unit of the title compound with the atom labelling and displacement ellipsoids drawn at the 50% probability level.

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C12—H12B···S1^{i}	0.98	2.93	3.906 (2)	174
C14—H14A···S2^{ii}	0.98	2.93	3.741 (2)	141
C22—H22C···S11	0.98	2.61	3.442 (2)	143
C24—H24A···S1^{iii}	0.98	2.92	3.878 (2)	166

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

coordination polyhedra around the Co^{II} cations can be described as strongly distorted tetrahedra (Table 1), which is also obvious from the tetrahedral angle variance $\sigma_{\theta\langle\text{tet}\rangle}^2 = 81.0$ and the mean tetrahedral quadratic elongation $\langle\lambda_{\text{tet}}\rangle = 1.036$ (Robinson *et al.*, 1971). The C—N bond lengths between the thioketone C and the amino groups are significantly shorter than those between the amino groups and the methyl C atoms, which points to some degree of double-bond character of the former. This is expected as thioketones are subject to thioketone–enthiole tautomerism similar to the tautomerism found for regular ketones, which is also supported by the fact that the CNMe$_2$ groups are planar with angles close to 120° (Devillanova, 2007). The NMe$_2$ groups of the same coligand are twisted against each other with angles of 45.74 (9) and 46.32 (8)° for the two crystallographically independent tetramethylthiourea coligands.

3. Supramolecular features

As can be seen in Table 2, two sets of hydrogen bonds can be found for which the $D-\text{H}\cdots A$ angles are either relatively near to 180° (174.0 and 166.2°) or far from 180° (142.8 and 140.8°), which is indicative for strong or relatively weak hydrogen bonds, respectively. Although nearly all of these hydrogen bonds are intermolecular bonds between the thiocyanate sulfur and a C—H hydrogen atom from an adjacent complex, in one case relatively weak intramolecular hydrogen
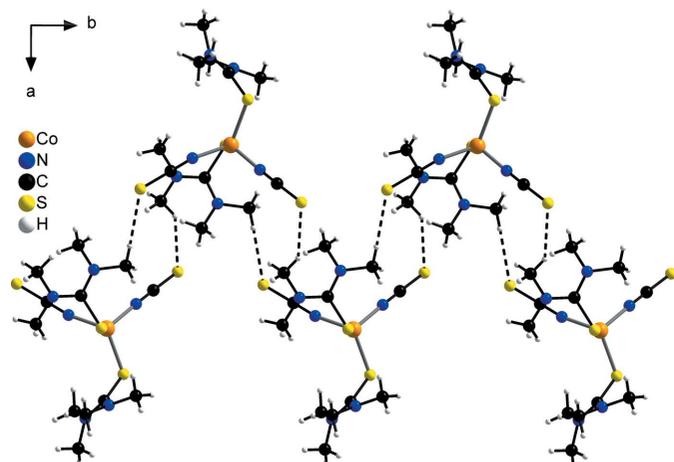
Figure 2
Crystal structure of the title compound with a view of the chains that run along the *b*-axis direction with intermolecular C—H···S hydrogen bonds shown as dashed lines.
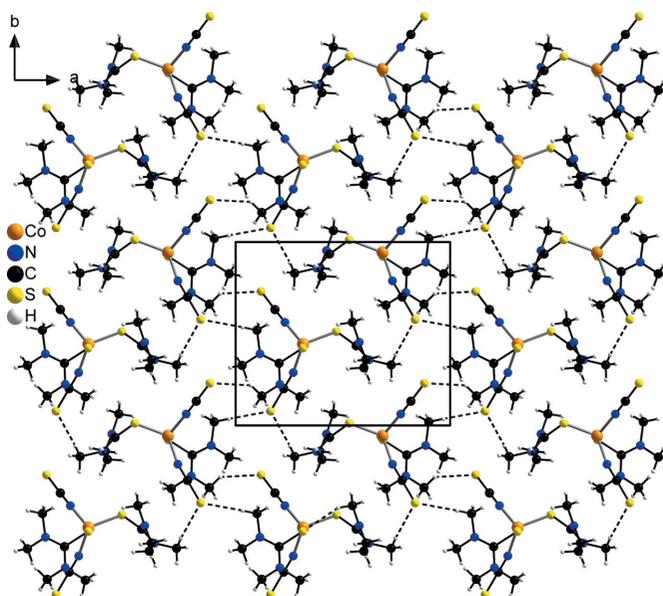
Figure 3
Crystal structure of the title compound with a view along the *c* axis of the layers. Intermolecular C—H···S hydrogen bonds are shown as dashed lines.

C—H···S bonding between two different tetramethylthiourea molecules of the same discrete complex is found. Each complex is connected to two different neighbouring complexes by pairs of C—H···S$_{\text{NCS}}$ hydrogen bonds between the tetramethylthiourea coligands and the thiocyanate anions. This leads to the formation of zigzag-like chains along the *b*-axis direction (Fig. 2), which are further connected by additional single C—H···S$_{\text{NCS}}$ hydrogen bonds into layers that are parallel to the *ab* plane (Fig. 3). These layers are stacked along the *c*-axis direction with no pronounced intermolecular interactions between them (Fig. 4).

4. Database survey

In the Cambridge Structural Database (Version 5.41, last update November 2019; Groom *et al.*, 2016) only 72 compounds containing transition-metal cations and tetramethylthiourea are reported, but none of them contains thiocyanate anions. This search also reveals that no tetrahedral Co(NCS)$_2$ compounds with other thiourea derivatives are known, but one chain compound with the composition
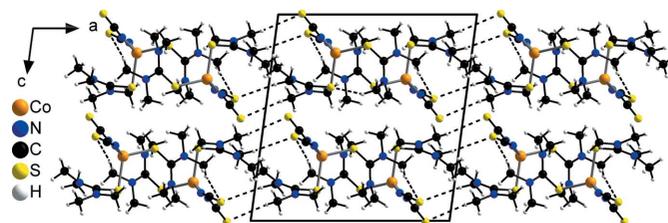
Figure 4
Crystal structure of the title compound with a view in the direction of the layers along the *b* axis. Intermolecular C—H···S hydrogen bonds are shown as dashed lines.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Co(NCS)_2(C_5H_{12}N_2S)_2]$
M_r	439.54
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	200
a, b, c (Å)	13.3288 (13), 11.2140 (8), 13.8579 (13)
β (°)	97.667 (8)
V (Å^3)	2052.8 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.25
Crystal size (mm)	$0.19 \times 0.15 \times 0.10$
Data collection	
Diffractometer	Stoe IPDS2
Absorption correction	Numerical (X-RED and X-$SHAPE$; Stoe & Cie, 2002)
T_{min}, T_{max}	0.644, 0.805
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14562, 4409, 3826
R_{int}	0.044
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.084, 1.02
No. of reflections	4409
No. of parameters	217
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, −0.39

Computer programs: X-$AREA$ (Stoe & Cie, 2002), $SHELXS97$ and XP (Sheldrick, 2008), $SHELXL2018/3$ (Sheldrick, 2015), $DIAMOND$ (Brandenburg & Putz, 1999) and $publCIF$ (Westrip, 2010).

$[Co(NCS)_2(thiourea)_2]_n$ has been reported (Rajarajan *et al.*, 2012). However, several structures built up of discrete tetrahedral complexes with cobalt thiocyanate and a variety of N-containing ligands are reported in the CCDC. These include, for example, bis(3-methylpyridine)diisothiocyanatocobalt(II) (Böckmann *et al.* 2011) and bis(quinoline)diisothiocyanatocobalt(II) (Mirčeva & Golič, 1990). It is noted that, in several cases, pyridine or imidazole derivatives are used that have large substituents adjacent to the coordinating N atoms, which might enforce the formation of a tetrahedral complex for steric reasons.

5. Synthesis and crystallization

General

Co(NCS)$_2$ and tetramethylthiourea were purchased from Sigma Aldrich and were used without further purification.

Synthesis

A suspension of Co(NCS)$_2$ (0.50 mmol, 87.5 mg) and tetramethylthiourea (1.00 mmol, 132.23 mg) in 0.75 mL water was stored at 281 K. After a few days, deep-blue-coloured crystals were obtained, which were filtered off, and ground into powder or used for single-crystal structure determination. It is noted that no crystalline product could be obtained from an analogous reaction at room temperature. Elemental analysis calculated for $C_{12}H_{24}N_6CoS_4$ (439.56 g mol^{-1}) C 32.79, H 5.50, N 19.12%, S 29.18, found: C 32.37, H 5.38, N 18.75, S 28.64.

Experimental details

Elemental analysis was performed using an EURO EA elemental analyser 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) equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator.

DTA–TG measurements were performed in a dynamic nitrogen atmosphere (100 sccm) in Al$_2$O$_3$ crucibles using a STA-PT 1600 thermobalance from Linseis. The instrument was calibrated using standard reference materials.

The DSC measurements were performed with a DSC 1 Star System with *STARe Excellence Software* from Mettler-Toledo AG. The instrument was calibrated using standard reference materials.

Thermomicroscopic measurements were performed using a hot-stage FP82 from Mettler and a BX60 microscope from Olympus, using the software analysis package from Mettler.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All non-hydrogen atoms were refined anisotropically. The C—H atoms were positioned with idealized geometry (allowed to rotate but not to tip) and refined isotropically with $U_{iso}(H) = 1.5U_{eq}(C)$.

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supporting information

Crystal structure of bis(tetramethylthiourea-*κS*)bis(thiocyanato-*κN*)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: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *XP* (Sheldrick, 2008) and *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(tetramethylthiourea-*κS*)bis(thiocyanato-*κN*)cobalt(II)

Crystal data

[Co(NCS)$_2$(C$_5$H$_{12}$N$_2$S)$_2$]	$F(000) = 916$
$M_r = 439.54$	$D_x = 1.422$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 13.3288$ (13) Å	Cell parameters from 14562 reflections
$b = 11.2140$ (8) Å	$\theta = 2.4$–27.0°
$c = 13.8579$ (13) Å	$\mu = 1.25$ mm^{-1}
$\beta = 97.667$ (8)°	$T = 200$ K
$V = 2052.8$ (3) Å^3	Block, blue
$Z = 4$	$0.19 \times 0.15 \times 0.10$ mm

Data collection

Stoe IPDS-2 diffractometer	4409 independent reflections
ω scans	3826 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (X-Red and X-Shape; Stoe & Cie, 2002)	$R_{int} = 0.044$
	$\theta_{max} = 27.0°$, $\theta_{min} = 2.4°$
$T_{min} = 0.644$, $T_{max} = 0.805$	$h = -15 \rightarrow 16$
14562 measured reflections	$k = -13 \rightarrow 14$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.084$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
4409 reflections	$\Delta\rho_{min} = -0.39$ e Å^{-3}
217 parameters	Extinction correction: SHELXL2018/3 (Sheldrick 2018),
0 restraints	Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Hydrogen site location: inferred from neighbouring sites	Extinction coefficient: 0.0092 (16)

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	0.31466 (2)	0.44406 (2)	0.18631 (2)	0.03623 (10)
N1	0.26892 (14)	0.28853 (15)	0.13540 (11)	0.0473 (4)
C1	0.22426 (14)	0.20050 (17)	0.11758 (12)	0.0400 (4)
S1	0.16309 (4)	0.07801 (5)	0.09170 (4)	0.05239 (14)
N2	0.23001 (14)	0.56237 (15)	0.11124 (12)	0.0476 (4)
C2	0.18324 (14)	0.63196 (16)	0.06226 (12)	0.0389 (4)
S2	0.11944 (5)	0.73069 (6)	−0.00388 (4)	0.05992 (16)
S11	0.31339 (4)	0.42243 (5)	0.35233 (3)	0.04323 (13)
C11	0.20254 (13)	0.33900 (15)	0.34598 (11)	0.0346 (3)
N11	0.11381 (12)	0.39071 (14)	0.31533 (11)	0.0410 (3)
C12	0.09967 (18)	0.51955 (19)	0.32179 (17)	0.0551 (5)
H12A	0.150522	0.552429	0.372410	0.083*
H12B	0.031805	0.536217	0.338259	0.083*
H12C	0.107221	0.556414	0.259049	0.083*
C13	0.02995 (16)	0.3274 (2)	0.25917 (16)	0.0580 (5)
H13A	0.053452	0.249499	0.239227	0.087*
H13B	0.004558	0.374051	0.201245	0.087*
H13C	−0.024519	0.316034	0.299316	0.087*
N12	0.20637 (12)	0.22456 (14)	0.37071 (10)	0.0392 (3)
C14	0.12200 (18)	0.1612 (2)	0.40544 (16)	0.0538 (5)
H14A	0.071235	0.218979	0.420747	0.081*
H14B	0.147061	0.115724	0.464096	0.081*
H14C	0.091237	0.106630	0.354706	0.081*
C15	0.29981 (18)	0.1561 (2)	0.37811 (16)	0.0561 (5)
H15A	0.345116	0.191657	0.335874	0.084*
H15B	0.284447	0.073696	0.357751	0.084*
H15C	0.332793	0.156901	0.445679	0.084*
S21	0.47009 (4)	0.51223 (5)	0.15128 (3)	0.04435 (13)
C21	0.56218 (13)	0.43472 (14)	0.22564 (11)	0.0333 (3)
N21	0.57661 (12)	0.45344 (13)	0.32191 (10)	0.0369 (3)
C22	0.54437 (16)	0.56303 (18)	0.36544 (14)	0.0463 (4)
H22A	0.540529	0.627600	0.317434	0.069*
H22B	0.593316	0.584178	0.422032	0.069*
H22C	0.477595	0.550936	0.386096	0.069*
C23	0.60727 (17)	0.3590 (2)	0.39199 (12)	0.0507 (5)
H23A	0.610361	0.283021	0.357553	0.076*
H23B	0.557930	0.352888	0.438242	0.076*
H23C	0.674128	0.377561	0.427288	0.076*
N22	0.62202 (12)	0.35804 (13)	0.18656 (9)	0.0384 (3)

C24	0.72499 (16)	0.3301 (2)	0.23060 (14)	0.0509 (5)
H24A	0.745874	0.386147	0.283738	0.076*
H24B	0.771017	0.336746	0.181307	0.076*
H24C	0.727201	0.248577	0.256314	0.076*
C25	0.59760 (19)	0.3148 (2)	0.08646 (13)	0.0536 (5)
H25A	0.523941	0.309911	0.069608	0.080*
H25B	0.627351	0.235605	0.080900	0.080*
H25C	0.625178	0.370024	0.041890	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.03421 (15)	0.03936 (14)	0.03465 (14)	0.00045 (9)	0.00284 (9)	0.00153 (8)
N1	0.0544 (10)	0.0439 (9)	0.0433 (8)	−0.0005 (7)	0.0056 (7)	−0.0033 (6)
C1	0.0435 (10)	0.0433 (9)	0.0341 (8)	0.0064 (8)	0.0078 (7)	0.0016 (6)
S1	0.0532 (3)	0.0467 (3)	0.0576 (3)	−0.0074 (2)	0.0087 (2)	−0.0008 (2)
N2	0.0442 (9)	0.0477 (9)	0.0489 (9)	0.0033 (7)	−0.0017 (7)	0.0035 (7)
C2	0.0350 (9)	0.0444 (9)	0.0374 (8)	−0.0011 (7)	0.0049 (6)	−0.0005 (7)
S2	0.0516 (3)	0.0689 (4)	0.0587 (3)	0.0139 (3)	0.0055 (2)	0.0237 (3)
S11	0.0358 (3)	0.0584 (3)	0.0352 (2)	−0.00976 (19)	0.00353 (16)	−0.00086 (17)
C11	0.0327 (8)	0.0426 (8)	0.0288 (6)	0.0009 (7)	0.0053 (6)	−0.0055 (6)
N11	0.0335 (8)	0.0444 (8)	0.0446 (7)	0.0057 (6)	0.0036 (6)	−0.0023 (6)
C12	0.0537 (13)	0.0477 (11)	0.0659 (12)	0.0154 (9)	0.0155 (10)	0.0021 (9)
C13	0.0371 (11)	0.0755 (15)	0.0574 (11)	0.0002 (10)	−0.0080 (8)	−0.0021 (10)
N12	0.0382 (8)	0.0401 (8)	0.0395 (7)	0.0033 (6)	0.0056 (6)	−0.0009 (6)
C14	0.0545 (13)	0.0496 (11)	0.0571 (11)	−0.0128 (9)	0.0068 (9)	0.0030 (9)
C15	0.0566 (13)	0.0549 (12)	0.0573 (11)	0.0209 (10)	0.0096 (9)	0.0043 (9)
S21	0.0363 (3)	0.0573 (3)	0.0390 (2)	−0.00071 (19)	0.00352 (16)	0.01763 (18)
C21	0.0341 (9)	0.0352 (8)	0.0307 (7)	−0.0069 (6)	0.0048 (6)	0.0035 (6)
N21	0.0404 (8)	0.0407 (7)	0.0295 (6)	0.0014 (6)	0.0049 (5)	0.0007 (5)
C22	0.0430 (11)	0.0498 (10)	0.0477 (9)	−0.0052 (8)	0.0118 (8)	−0.0134 (8)
C23	0.0588 (13)	0.0611 (12)	0.0320 (8)	0.0063 (10)	0.0048 (7)	0.0106 (8)
N22	0.0468 (9)	0.0381 (7)	0.0303 (6)	−0.0006 (6)	0.0055 (5)	−0.0012 (5)
C24	0.0517 (12)	0.0556 (11)	0.0458 (9)	0.0138 (9)	0.0083 (8)	0.0007 (8)
C25	0.0690 (14)	0.0571 (11)	0.0355 (9)	−0.0105 (10)	0.0107 (8)	−0.0100 (8)

Geometric parameters (Å, º)

Co1—N1	1.9484 (17)	N11—C13	1.459 (3)
Co1—N2	1.9499 (17)	N11—C12	1.461 (3)
Co1—S11	2.3157 (5)	N12—C15	1.455 (3)
Co1—S21	2.3196 (6)	N12—C14	1.465 (3)
N1—C1	1.162 (3)	S21—C21	1.7282 (17)
C1—S1	1.613 (2)	C21—N22	1.336 (2)
N2—C2	1.160 (2)	C21—N21	1.339 (2)
C2—S2	1.6066 (18)	N21—C23	1.458 (2)
S11—C11	1.7411 (18)	N21—C22	1.459 (2)
C11—N12	1.327 (2)	N22—C24	1.460 (3)

C11—N11	1.335 (2)	N22—C25	1.464 (2)
N1—Co1—N2	106.56 (7)	C11—N11—C12	121.74 (17)
N1—Co1—S11	102.86 (5)	C13—N11—C12	114.72 (17)
N2—Co1—S11	121.40 (5)	C11—N12—C15	122.09 (17)
N1—Co1—S21	117.66 (5)	C11—N12—C14	123.28 (16)
N2—Co1—S21	97.67 (6)	C15—N12—C14	114.12 (17)
S11—Co1—S21	111.564 (19)	C21—S21—Co1	107.02 (6)
C1—N1—Co1	164.57 (16)	N22—C21—N21	119.39 (15)
N1—C1—S1	179.27 (18)	N22—C21—S21	119.81 (12)
C2—N2—Co1	175.96 (17)	N21—C21—S21	120.76 (13)
N2—C2—S2	178.70 (18)	C21—N21—C23	122.68 (15)
C11—S11—Co1	97.16 (5)	C21—N21—C22	122.21 (15)
N12—C11—N11	120.27 (16)	C23—N21—C22	114.11 (15)
N12—C11—S11	120.22 (13)	C21—N22—C24	123.21 (14)
N11—C11—S11	119.51 (14)	C21—N22—C25	121.86 (16)
C11—N11—C13	122.80 (17)	C24—N22—C25	113.75 (16)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C12—H12B⋯S1[i]	0.98	2.93	3.906 (2)	174
C14—H14A⋯S2[ii]	0.98	2.93	3.741 (2)	141
C22—H22C⋯S11	0.98	2.61	3.442 (2)	143
C24—H24A⋯S1[iii]	0.98	2.92	3.878 (2)	166

Symmetry codes: (i) $-x$, $y+1/2$, $-z+1/2$; (ii) $-x$, $y-1/2$, $-z+1/2$; (iii) $-x+1$, $y+1/2$, $-z+1/2$.