Synthesis, crystal structure and thermal properties of bis(1,3-dicyclohexylthiourea-κS)bis(isothiocyanato-κN)cobalt(II)

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Crystals of the title compound, [Co(NCS)₂(C₁₃H₂₄N₂S)₂], were obtained by the reaction of Co(NCS)₂ with 1,3-dicyclohexylthiourea in ethanol. Its crystal structure consists of discrete complexes that are located on twofold rotation axes, in which the CoII cations are tetrahedrally coordinated by two terminal N-bonded thiocyanate anions and two 1,3-dicyclohexylthiourea ligands. These complexes are linked via intermolecular N—H⋯C=S and C—H⋯S hydrogen bonding into chains, which elongate in the b-axis direction. These chains are closely packed in a pseudo-hexagonal manner. The CN stretching vibration of the thiocyanate anions located at 2038 cm⁻¹ is in agreement with only terminal bonded anionic ligands linked to metal cations in a tetrahedral coordination. TG–DTA measurements prove the decomposition of the compound at about 227°C. DSC measurements reveal a small endothermic signal before decomposition at about 174°C, which might correspond to melting.

1. Chemical context

Coordination polymers based on Co(NCS)₂ have been investigated for several years because they can show interesting magnetic properties due to the large magnetic anisotropy of CoII. This is the reason why we and others are especially interested in this class of compounds. In most cases, the CoII cations are octahedrally coordinated and linked by pairs of thiocyanate anions into chains, even if a few compounds with single thiocyanate bridges have been reported (Palion-Gazda et al., 2015). If the Co cations are all-trans or cis–cis–trans coordinated with the thiocyanate anions in the trans-position, the chains are linear and frequently show antiferromagnetic or ferromagnetic behavior or a slow relaxation of the magnetization indicative of single-chain magnetism (Wang et al., 2005; Shurda et al., 2013; Wöhler et al., 2014; Jin et al., 2007; Prananto et al., 2017; Mautner et al., 2018; Rams et al., 2020; Jochim et al., 2020a). In the case where the Co centers are cis–cis–trans coordinated with the thiocyanate anions in the cis-position, the chains are corrugated and the magnetic exchange is suppressed (Shi et al., 2007; Böhme et al., 2020). In some cases Co(NCS)₂ layers are observed, in which the Co cations are linked by single and double thiocyanate bridges or by single anionic ligands exclusively (Suckert et al., 2016; Werner et al., 2015a). These compounds usually show ferromagnetic behavior with low critical temperatures, which can be tuned by mixed crystal formation with NiII cations (Wellm et al., 2018, 2020; Neumann et al., 2018a).
In the case where monocoordinating co-ligands are used and the chains are linear, these compounds have the general composition Co(NCS)$_2$(L)$_2$ ($L =$ co-ligand) but for this composition a second structure exists, in which the Co cations are tetrahedrally coordinated and in this case, no cooperative magnetic exchange interactions can be observed. The reason why, dependent on the nature of the co-ligand, chains or complexes are formed is not clear. First of all, one can assume that the cobalt cations would prefer a tetrahedral coordination with bulky co-ligands because of steric crowding. On the other hand, we observed that strong N-donor co-ligands such as, for example, 4-(dimethylamino)pyridine would lead to the formation of tetrahedral complexes (Neumann et al., 2018b), whereas weaker donors such as 4-(4-chlorobenzyl)pyridine (Werner et al., 2015b) or 4-(3-phenylpropyl)pyridine (Werner et al., 2014; Ceglarska et al., 2021) lead to the formation of chains. In the case of intermediate donor ligands like 4-methoxypyridine, both isomers can be obtained, chains and discrete complexes (Mautner et al., 2018; Rams et al., 2020).

In the course of our systematic work, we became interested in S-donor co-ligands and with thiourea we obtained a compound with the desired chain structure showing antiferromagnetic ordering but no slow relaxation of the magnetization (Jochim et al., 2020a). In further work, we obtained two compounds with 1,3-dimethylthiourea (and 1,1,3,3-tetramethylthiourea) but in this case, tetrahedral discrete complexes were obtained (Jochim et al., 2020b,c). To investigate the influence of the co-ligand in more detail we used 1,3-dicyclohexylthiourea as the co-ligand and we obtained crystals of the title compound, which were characterized by single crystal X-ray diffraction, which proves the formation of a discrete complex even with this ligand. Investigations using X-ray powder diffraction show that the title compound was obtained as a pure phase (Fig. 1). The CN stretching vibration is observed at 2038 cm$^{-1}$, which is typical for thiocyanates that are only terminal bonded to metal cations in a tetrahedral coordination (Fig. S1). Measurements using simultaneously differential scanning calorimetry show a small endothermic event before the compound decomposes (Fig. S3). To check if this event corresponds to some transition, the residue formed after the endothermic signal (see point ‘x’ in Fig. S3) was isolated and investigated by XRPD measurements, which shows that the powder pattern is identical to that of the pristine material but of lower crystallinity (Fig. S4).

2. Structural commentary

The asymmetric unit of the title compound consists of one Co$^{II}$cation that is located on a twofold rotation axis, one thiocyanate anion, two sulfur atoms, two nitrogen atoms, and four carbon atoms. The CN stretching vibration is observed at 2038 cm$^{-1}$, which is typical for thiocyanates that are only terminal bonded to metal cations in a tetrahedral coordination (Fig. S1). Measurements using simultaneously differential scanning calorimetry show a small endothermic event before the compound decomposes (Fig. S3). To check if this event corresponds to some transition, the residue formed after the endothermic signal (see point ‘x’ in Fig. S3) was isolated and investigated by XRPD measurements, which shows that the powder pattern is identical to that of the pristine material but of lower crystallinity (Fig. S4).
cyanate anion and one 1,3-dicyclohexylthiourea ligand that occupies general positions. The Co $^{II}$ cations are fourfold coordinated by two terminal N-bonded thiocyanate anions and two sulfur atoms of 1,3-dicyclohexylthiourea ligands each (Fig. 2). The Co—N and Co—S distances are comparable to that observed in other Co(NCS)$_2$ compounds with thiourea derivatives (Table 1, Jochim et al., 2020a, b). The bond angles deviate from the ideal values, revealing that the tetrahedra are slightly distorted (see supporting information). Both hexane rings of the 1,3-dimethylthiourea ligand are in a chair conformation (Figs. 2 and 3). There are two symmetry-equivalent intramolecular N—H···N hydrogen bonds between the amino H atom of the 1,3-dicyclohexylthiourea ligand and the N atoms of the thiocyanate anions (Table 2 and Fig. 3). The N—H···N angle is close to linearity, indicating that this is a relatively strong interaction (Table 2).

3. Supramolecular features

In the crystal structure of the title compound the discrete complexes are linked into chains by two intermolecular N—H···S hydrogen bonds related by the twofold rotation axis between the N—H H atoms and the thiocyanate S atom of a neighboring complex (Fig. 4, Table 2). The discrete complexes are additionally linked by two symmetry-equivalent C—H···S hydrogen bonds, which might correspond to a weak interaction (Fig. 4, Table 2). These chains elongate along the b-axis direction and each chain is surrounded by six neighboring chains in a pseudo-hexagonal manner (Fig. 5).

4. Database survey

There are only ten crystal structures with this ligand reported in the Cambridge Structural Database (CSD version 5.42, last update November 2020; Groom et al., 2016). The most important for us is bis(1,3-dicyclohexylthiourea)bis(isothiocyanato)zinc(II), which is isotypic to the title compound (refcode: TINBIC; Jia et al., 2007). These authors also reported the structure of hexakis(1,3-dicyclohexylthiourea)lead(II)bis(isothiocyanate) ethanol solvate, which

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**Table 1**

| Bond                  | Distance (Å) | Error (Å) |
|-----------------------|--------------|-----------|
| Co1—N1                | 1.9516 (16)  |           |
| Co1—S11               | 2.3130 (5)   |           |
| N1—Co1—N1 $^\dagger$ | 113.00 (10)  |           |
| N1—Co1—S11 $^\dagger$| 106.00 (5)   |           |
| N1—Co1—S11 $^\dagger$| 109.67 (5)   |           |

Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$

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**Table 2**

| Bond                  | D—H (Å) | A—D···A (Å) | D···A (Å) | D—H···A (Å) |
|-----------------------|---------|-------------|-----------|-------------|
| N11—H11···N1         | 0.88    | 2.33        | 3.169 (2) | 160         |
| C12—H12···S1 $^\dagger$ | 1.00   | 2.93        | 3.774 (2) | 143         |
| N12—H12A···S1 $^\dagger$ | 0.88   | 2.84        | 3.6770 (16) | 159        |
| C19—H19B···S11       | 0.99    | 3.00        | 3.529 (2) | 114         |

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

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**Figure 3**

View of the discrete complex with intramolecular N—H···N hydrogen bonding shown as dashed lines.

**Figure 4**

Crystal structure of the title compound with a view of a chain formed by intermolecular N—H···S and C—H···S hydrogen bonding (dashed lines).

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**Figure 5**

Crystal structure of the title compound with a view in the direction of the crystallographic b-axis, showing the arrangement of the chains. Inter-molecular N—H···S and C—H···S hydrogen bonding is shown as dashed lines.
consists of discrete complexes, in which the Pb\textsuperscript{II} cations are octahedrally coordinated by six 1,3-dicyclohexylthiourea ligands (refcode: TINBUO; Jia et al., 2007). In that paper, the crystal structure of bis(1,3-dicyclohexylthiourea)dichlorocobalt(II) is also reported (refcode: TINBEY). The crystal structures of chlorobis(1,3-dicyclohexylthiourea)copper(I), of bromobis(1,3-dicyclohexylthiourea)copper(I) (refcodes: WODVER, WODVIV; Jia et al., 2008) and of chloro-tris(1,3-dicyclohexylthiourea)tellurium(II) chloride (refcode: OCAWUK, Husebye et al., 2001) also consist of discrete complexes. The crystal structure of 1,3-dicyclohexylthiourea was reported by Ramnathan et al. (1996) (refcode: ZIVGUG).

There are also several crystal structures with Co(NCS)\textsubscript{2} reported, in which the Co\textsuperscript{II} cations are tetrahedrally coordinated by two terminal N-bonded thiocyanate anions and two N-donor co-ligands, for example two polymorphic modifications of bis(4-dimethylaminopyridine)bis(isothiocyanato)cobalt(II) (refcode: GIOPEE, Neumann et al., 2018a; Krebs et al., 2021), bis(4-vinylpyridine)di(isothiocyanato)cobalt(II) (refcode: BOZJUW, Foxman & Mazurek, 1982), bis(2-chloropyridine)bis(isothiocyanato)cobalt(II), bis(2-bromopyridine)bis(isothiocyanato)cobalt(II), bis(2-methylpyridine)bis(isothiocyanato)cobalt(II) (refcodes: DEYDUI, DEYFIY and DEYGAR, Wöhler et al., 2013) and bis(4-methoxypyridine)bis(isothiocyanato)cobalt(II) (refcode: KIJQAY; Mautner et al., 2018).

Two structures have already been reported with thiourea derivatives and Co(NCS)\textsubscript{2}, viz. bis(1,3-dimethylthiourea)-bis(isothiocyanato)cobalt(II) (refcode: QUSZAI; Jochim et al., 2020b) and bis(1,1,3,3-tetramethylthiourea)bis(isothiocyanato)cobalt(II) (refcode: WUQTIO; Jochim et al., 2020c).

5. Synthesis and crystallization

Synthesis

Co(NCS)\textsubscript{2} was purchased from Merck. 1,3-Dicyclohexylthiourea was purchased from Alfa Aesar. All chemicals were used without further purification. Blue-colored single crystals suitable for single-crystal X-ray analysis were obtained after storage of 0.25 mmol Co(NCS)\textsubscript{2} (43.8 mg) and 0.50 mmol 1,3-dicyclohexylthiourea (120.2 mg) in 2.0 ml ethanol at 333 K over night.

Experimental details

The data collection for single crystal structure analysis was performed using an XtaLAB Synergy, Dualflex, HyPix diffractometer from Rigaku with Cu-Kα radiation.

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 Kα\textsubscript{1} radiation (\(\lambda = 1.540598\) Å) using a Stoe Transmission Powder Diffraction System (STADI P) equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator.

Thermogravimetry and differential thermoanalyis (TG-DTA) measurements were performed in a dynamic nitrogen atmosphere in Al\textsubscript{2}O\textsubscript{3} crucibles using a STA-PT 1000 ther-

| Table 3 |
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| **Experimental details.** |
| **Crystal data** |
| Chemical formula | [Co(NCS)\textsubscript{2}(C\textsubscript{13}H\textsubscript{24}N\textsubscript{2}S)\textsubscript{2}] |
| \(M_\text{r}\) | 655.89 |
| Crystal system, space group | Monoclinic, C2/c |
| Temperature (K) | 100 |
| \(a, b, c\) (Å) | 24.0667 (4), 8.8282 (1), 18.8910 (3) |
| \(\beta\) (°) | 125.619 (2) |
| \(V\) (Å\textsuperscript{3}) | 3262.76 (11) |
| \(Z\) | 4 |
| Radiation type | Cu Kα |
| \(\mu\) (mm\textsuperscript{-1}) | 6.73 |
| Crystal size (mm) | 0.15 × 0.08 × 0.03 |

| Data collection |
| Diffraction system | XtaLAB Synergy, Dualflex, HyPix |
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2021) |
| No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections | 20399, 3503, 3462 |
| \(R_{	ext{int}}\) | 0.025 |
| \(\text{sin} \theta/\lambda\) max. (Å\textsuperscript{-1}) | 0.639 |
| Refinement |
| \(R(F^2) > 2\sigma(F^2)\), \(wR(F^2)\), \(S\) | 0.035, 0.096, 1.05 |
| No. of reflections | 3503 |
| No. of parameters | 177 |
| H-atom treatment | H-atom parameters constrained |
| \(\Delta R_{	ext{max}}\), \(\Delta R_{	ext{free}}\) (e Å\textsuperscript{-1}) | 0.65, −0.36 |

Computer programs: CrysAlis PRO (Rigaku OD, 2021), SHELXT2016/5 (Sheldrick, 2015a), SHELXL2016/8 (Sheldrick, 2015b), DIAMOND (Brandenburg & Putz, 1999) and pubCIF (Westrip, 2010).

mobalance from Linseis. The instrument was calibrated using standard reference materials.

The DSC experiments were performed using a DSC 1 star system with STARE Excellence software from Mettler-Toledo AG under dynamic nitrogen flow in Al pans.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All non-hydrogen atoms were refined anisotropically. The C-bound H atoms were positioned with idealized geometry and were refined isotropically with \(U_{eq}(H) = 1.2\) \(U_{eq}(C)\) using a riding model.

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References

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Brandenburg, K. & Putz, H. (1999). DIAMOND. Crystal Impact GbR, Bonn, Germany.
Synthesis, crystal structure and thermal properties of bis(1,3-dicyclohexylthiourea-κS)bis(isothiocyanato-κN)cobalt(II)

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Computing details
Data collection: CrysAlis PRO (Rigaku OD, 2021); cell refinement: CrysAlis PRO (Rigaku OD, 2021); data reduction: CrysAlis PRO (Rigaku OD, 2021); program(s) used to solve structure: SHELXT2014/5 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2016/6 (Sheldrick, 2015b); molecular graphics: DIAMOND (Brandenburg & Putz, 1999); software used to prepare material for publication: pubCIF (Westrip, 2010).

Bis(1,3-dicyclohexylthiourea-κS)bis(isothiocyanato-κN)cobalt(II)

Crystal data
\[ \text{Co(NCS)}_2(C_{13}H_{24}N_2S)_2 \]
\[ M_r = 655.89 \]
Monoclinic, \( C2/c \)
a = 24.0667 (4) Å
b = 8.8282 (1) Å
c = 18.8910 (3) Å
\( \beta = 125.619 \, (2)° \)
\( V = 3262.76 \, (11) \, \text{Å}^3 \)
Z = 4

Data collection
XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm\(^{-1}\)
\( \theta \text{ scans} \)
Absorption correction: multi-scan
(\text{CrysAlisPro}; \text{Rigaku OD, 2021})

Refinement
Refinement on \( F^2 \)
Least-squares matrix: full
\( R[F^2 > 2\sigma(F^2)] = 0.035 \)
\( wR(F^2) = 0.096 \)
\( S = 1.05 \)
3503 reflections
177 parameters
0 restraints
Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
\( w = 1/[\sigma(F^2) + (0.054P)^2 + 5.0479P] \)
where \( P = (F^2 + 2F_c^2)/3 \)
\( \Delta(\sigma)_{	ext{max}} = 0.001 \)
\( \Delta \rho_{	ext{max}} = 0.65 \, \text{e Å}^{-3} \)
\( \Delta \rho_{	ext{min}} = -0.36 \, \text{e Å}^{-3} \)
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)**

| Atom | x   | y   | z   | Uiso/eq |
|------|-----|-----|-----|---------|
| Co1  | 0.500000 | 0.91248 (4) | 0.750000 | 0.02073 (12) |
| N1   | 0.57874 (8) | 1.03449 (18) | 0.78063 (11) | 0.0283 (3) |
| C1   | 0.62890 (10) | 1.1041 (2) | 0.82549 (13) | 0.0241 (4) |
| S1   | 0.69885 (2) | 1.19936 (6) | 0.88857 (3) | 0.02946 (13) |
| S11  | 0.53579 (2) | 0.76716 (5) | 0.87146 (3) | 0.02478 (12) |
| C11  | 0.59547 (9) | 0.6489 (2) | 0.87525 (12) | 0.0221 (3) |
| N11  | 0.63300 (8) | 0.70206 (18) | 0.84996 (11) | 0.0257 (3) |
| H11  | 0.628830 | 0.799458 | 0.837934 | 0.031* |
| C12  | 0.68063 (9) | 0.6182 (2) | 0.83960 (13) | 0.0250 (4) |
| H12  | 0.664260 | 0.511209 | 0.823464 | 0.030* |
| C13  | 0.67862 (11) | 0.6900 (3) | 0.76500 (14) | 0.0377 (5) |
| H13A  | 0.691074 | 0.798367 | 0.777936 | 0.045* |
| H13B  | 0.631610 | 0.683568 | 0.710954 | 0.045* |
| C14  | 0.72780 (12) | 0.6107 (3) | 0.75124 (15) | 0.0433 (6) |
| H14A  | 0.712524 | 0.504987 | 0.732404 | 0.052* |
| H14B  | 0.727319 | 0.662885 | 0.704507 | 0.052* |
| C15  | 0.80009 (11) | 0.6105 (3) | 0.83419 (15) | 0.0342 (5) |
| H15A  | 0.817123 | 0.715832 | 0.849578 | 0.041* |
| H15B  | 0.830355 | 0.553156 | 0.824289 | 0.041* |
| C16  | 0.80239 (10) | 0.5391 (2) | 0.90921 (14) | 0.0297 (4) |
| H16A  | 0.849393 | 0.546680 | 0.963165 | 0.036* |
| H16B  | 0.790582 | 0.430304 | 0.896754 | 0.036* |
| C17  | 0.75272 (10) | 0.6167 (2) | 0.92332 (13) | 0.0276 (4) |
| H17A  | 0.752748 | 0.562352 | 0.969193 | 0.033* |
| H17B  | 0.767965 | 0.721974 | 0.943308 | 0.033* |
| N12  | 0.60327 (7) | 0.50735 (18) | 0.90351 (10) | 0.0224 (3) |
| H12A  | 0.635837 | 0.452301 | 0.908415 | 0.027* |
| C18  | 0.56066 (9) | 0.4371 (2) | 0.92713 (12) | 0.0212 (3) |
| H18  | 0.550070 | 0.515812 | 0.955748 | 0.025* |
| C19  | 0.49330 (9) | 0.3789 (2) | 0.84687 (12) | 0.0244 (4) |
| H19A  | 0.502584 | 0.301113 | 0.817278 | 0.029* |
| H19B  | 0.468264 | 0.463403 | 0.805576 | 0.029* |
| C20  | 0.44955 (10) | 0.3106 (2) | 0.87343 (13) | 0.0262 (4) |
| H20A  | 0.437460 | 0.390552 | 0.898999 | 0.031* |
| H20B  | 0.406622 | 0.270325 | 0.821191 | 0.031* |
| C21  | 0.48772 (10) | 0.1834 (2) | 0.93957 (13) | 0.0281 (4) |
| H21A  | 0.495221 | 0.098353 | 0.911865 | 0.034* |
| H21B  | 0.459693 | 0.145614 | 0.958672 | 0.034* |
| C22  | 0.55656 (10) | 0.2392 (2) | 1.01863 (12) | 0.0256 (4) |
supporting information

H22A 0.581609 0.153099 1.058555 0.031*
H22B 0.548684 0.315490 1.050304 0.031*
C23 0.60031 (10) 0.3096 (2) 0.99230 (13) 0.0264 (4)
H23A 0.643242 0.349894 1.044513 0.032*
H23B 0.612306 0.231184 0.965832 0.032*

| Atomic displacement parameters (Å²) |
|-------------------------------------|
| $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
| Co1      | 0.0151 (2) | 0.0140 (2) | 0.0277 (2) | 0.000 | 0.00945 (17) | 0.000 |
| N1       | 0.0226 (8) | 0.0191 (8) | 0.0361 (9) | -0.0028 (6) | 0.0130 (7) | 0.0022 (7) |
| C1       | 0.0240 (9) | 0.0176 (8) | 0.0317 (9) | 0.0029 (7) | 0.0167 (8) | 0.0038 (7) |
| S1       | 0.0212 (2) | 0.0271 (2) | 0.0354 (2) | -0.00593 (17) | 0.0138 (2) | -0.00315 (18) |
| S11      | 0.0221 (2) | 0.0209 (2) | 0.0337 (2) | 0.00480 (16) | 0.01759 (19) | 0.00516 (17) |
| C11      | 0.0167 (8) | 0.0214 (9) | 0.0251 (8) | 0.0010 (7) | 0.0105 (7) | 0.0026 (7) |
| N11      | 0.0209 (7) | 0.0206 (8) | 0.0381 (9) | 0.0044 (6) | 0.0186 (7) | 0.0086 (6) |
| C12      | 0.0182 (8) | 0.0251 (9) | 0.0329 (9) | 0.0022 (7) | 0.0156 (8) | 0.0053 (8) |
| C13      | 0.0241 (10) | 0.0537 (14) | 0.0336 (10) | 0.0071 (9) | 0.0157 (9) | 0.0142 (10) |
| C14      | 0.0342 (12) | 0.0667 (17) | 0.0342 (11) | 0.0050 (11) | 0.0229 (10) | 0.0070 (11) |
| C15      | 0.0251 (10) | 0.0360 (11) | 0.0479 (12) | 0.0000 (8) | 0.0250 (10) | 0.0022 (9) |
| C16      | 0.0199 (9) | 0.0290 (10) | 0.0376 (10) | 0.0010 (8) | 0.0154 (8) | -0.0003 (8) |
| C17      | 0.0234 (9) | 0.0285 (9) | 0.0292 (9) | 0.0023 (7) | 0.0144 (8) | 0.0011 (8) |
| N12      | 0.0177 (7) | 0.0215 (7) | 0.0298 (7) | 0.0023 (6) | 0.0148 (6) | 0.0042 (6) |
| C18      | 0.0186 (8) | 0.0197 (8) | 0.0261 (9) | 0.0001 (7) | 0.0134 (7) | 0.0027 (7) |
| C19      | 0.0221 (9) | 0.0261 (9) | 0.0242 (8) | -0.0031 (7) | 0.0129 (7) | -0.0002 (7) |
| C20      | 0.0227 (9) | 0.0275 (10) | 0.0290 (9) | -0.0066 (7) | 0.0155 (8) | -0.0030 (7) |
| C21      | 0.0324 (10) | 0.0239 (9) | 0.0344 (10) | -0.0052 (8) | 0.0232 (9) | -0.0014 (8) |
| C22      | 0.0280 (9) | 0.0238 (9) | 0.0288 (9) | 0.0040 (7) | 0.0188 (8) | 0.0066 (7) |
| C23      | 0.0220 (9) | 0.0255 (9) | 0.0310 (9) | 0.0044 (7) | 0.0151 (8) | 0.0086 (7) |

Geometric parameters (Å, °)

Co1—N1 1.9516 (16)  
Co1—N1 1.9517 (16)  
Co1—S1 2.3130 (5)  
Co1—S1 2.3131 (5)  
N1—C1 1.167 (3)  
N1—C1 1.620 (2)  
S11—C11 1.7431 (18)  
C11—N11 1.330 (2)  
C11—N11 1.328 (2)  
N11—H11 0.8800  
N11—H11 0.8800  
N11—C12 1.470 (2)  
C12—H12 1.0000  
C12—C13 1.520 (3)  
C12—C17 1.522 (3)  
C13—H13A 0.9900  
C13—H13B 0.9900  
C16—H16B 0.9900  
C16—C17 1.530 (3)  
C17—H17A 0.9900  
C17—H17B 0.9900  
N12—H12A 0.8800  
N12—H12A 0.8800  
C18—H18 1.0000  
C18—C19 1.526 (2)  
C18—C23 1.525 (2)  
C19—H19A 0.9900  
C19—H19B 0.9900  
C20—H20A 0.9900  
C20—H20B 0.9900  
C21—H21A 0.9900  
C22—C21 1.526 (3)  
C23—H21A 0.9900  

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| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| C13—C14       | 1.522 (3)    | C21—H21B      | 0.9900       |
| C14—H14A      | 0.9900       | C21—C22       | 1.528 (3)    |
| C14—H14B      | 0.9900       | C22—H22A      | 0.9900       |
| C14—C15       | 1.519 (3)    | C22—C23       | 1.534 (3)    |
| C15—H15A      | 0.9900       | C23—H23A      | 0.9900       |
| C15—C16       | 1.522 (3)    | C23—H23B      | 0.9900       |
| C16—H16A      | 0.9900       |                |              |

| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| N1—Co1—N1i   | 113.00 (10)  | C12—C17—C16  | 110.88 (16)  |
| N1—Co1—S11i  | 109.67 (5)   | C12—C17—H17A | 109.5        |
| N1—Co1—S11   | 106.00 (5)   | C12—C17—H17B | 109.5        |
| N1—Co1—S11i  | 106.00 (5)   | C16—C17—H17A | 109.5        |
| N1—Co1—S11   | 109.67 (5)   | C16—C17—H17B | 109.5        |
| S11—Co1—S11  | 112.63 (3)   | H17A—C17—H17B| 108.1        |
| C1—N1—Co1    | 157.11 (17)  | C11—N12—H12A | 118.1        |
| N1—C1—S1     | 179.39 (19)  | C11—N12—C18  | 123.87 (15)  |
| C11—S11—Co1  | 101.24 (6)   | C18—N12—H12A | 118.1        |
| N11—C11—S11  | 119.32 (14)  | N12—C18—H18  | 108.3        |
| N12—C11—S11  | 120.02 (13)  | N12—C18—C19  | 111.41 (15)  |
| N12—C11—N11  | 120.67 (16)  | N12—C18—C23  | 109.67 (14)  |
| C11—N11—H11  | 116.0        | C19—C18—H18  | 108.3        |
| C11—N11—C12  | 127.98 (16)  | C23—C18—H18  | 108.3        |
| C12—N11—H11  | 116.0        | C23—C18—C19  | 110.89 (16)  |
| N11—C12—H12  | 108.5        | C18—C19—H19A | 109.7        |
| N11—C12—C13  | 107.87 (16)  | C18—C19—H19B | 109.7        |
| N11—C12—C17  | 111.80 (16)  | C18—C19—C20  | 110.05 (15)  |
| C13—C12—H12  | 108.5        | H19A—C19—H19B| 108.2        |
| C13—C12—C17  | 111.64 (16)  | C20—C19—H19A | 109.7        |
| C17—C12—H12  | 108.5        | C20—C19—H19B | 109.7        |
| C12—C13—H13A | 109.4        | C19—C20—H20A | 109.4        |
| C12—C13—H13B | 109.4        | C19—C20—H20B | 109.4        |
| C12—C13—C14  | 111.01 (18)  | H20A—C20—H20B| 108.0        |
| H13A—C13—H13B| 108.0        | C21—C20—C19  | 110.96 (16)  |
| C14—C13—H13A | 109.4        | C21—C20—H20A | 109.4        |
| C14—C13—H13B | 109.4        | C21—C20—H20B | 109.4        |
| C13—C14—H14A | 109.4        | C20—C21—H21A | 109.5        |
| C13—C14—H14B | 109.4        | C20—C21—H21B | 109.5        |
| H14A—C14—H14B| 108.0        | C20—C21—C22  | 110.86 (16)  |
| C15—C14—C13  | 111.2 (2)    | H21A—C21—H21B| 108.1        |
| C15—C14—H14A | 109.4        | C22—C21—H21A | 109.5        |
| C15—C14—H14B | 109.4        | C22—C21—H21B | 109.5        |
| C14—C15—H15A | 109.4        | C21—C22—H22A | 109.2        |
| C14—C15—H15B | 109.4        | C21—C22—H22B | 109.2        |
| C14—C15—C16  | 111.08 (17)  | C21—C22—C23  | 111.83 (16)  |
| H15A—C15—H15B| 108.0        | H22A—C22—H22B| 107.9        |
| C16—C15—H15A | 109.4        | C23—C22—H22A | 109.2        |
| C16—C15—H15B | 109.4        | C23—C22—H22B | 109.2        |
Symmetry code: (i) \(-x+1, y, -z+3/2\).

| Bond                        | Angle (°) | Bond                        | Angle (°) |
|-----------------------------|-----------|-----------------------------|-----------|
| C15—C16—H16A               | 109.3     | C18—C23—C22                | 109.6 (15) |
| C15—C16—H16B               | 109.3     | C18—C23—H23A               | 109.7     |
| C15—C16—C17                | 111.6 (17)| C18—C23—H23B               | 109.7     |
| H16A—C16—H16B              | 108.0     | C22—C23—H23A               | 109.7     |
| C17—C16—H16A               | 109.3     | C22—C23—H23B               | 109.7     |
| C17—C16—H16B               | 109.3     | H23A—C23—H23B              | 108.2     |

**Hydrogen-bond geometry (Å, †)**

| Bond            | D—H  | H···A | D···A      | D—H···A  |
|-----------------|------|-------|-----------|----------|
| N11—H11···N1    | 0.88 | 2.33  | 3.169 (2) | 160      |
| C12—H12···S1ii  | 1.00 | 2.93  | 3.774 (2) | 143      |
| N12—H12A···S1ii | 0.88 | 2.84  | 3.6770 (16)| 159     |
| C19—H19B···S11  | 0.99 | 3.00  | 3.529 (2) | 114      |

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