Crystal structures of two Co(NCS)₂  urotropine coordination compounds with different Co coordinations

Christoph Krebs, Inke Jess and Christian Näther*

Institute of Inorganic Chemistry, University of Kiel, Max-Eyth.-Str. 2, 24118 Kiel, Germany. *Correspondence e-mail: cnaether@ac.uni-kiel.de

The reaction of Co(NCS)₂ with urotropine in ethanol leads to the formation of two different compounds, namely, bis(ethanol-κO)bis(hexamethylenetetramine-κN)bis(thiocyanato-κN)cobalt(II)–diaqua-κ²O–bis(hexamethylenetetramine-κN)bis(thiocyanato-κN)cobalt(II)–ethanol–hexamethylenetetramine (1.2/0.8/1.6/4), [Co(NCS)₂(C₆H₁₂N₄)₂(C₂H₆O)₂]₁₂[Co(NCS)₂(C₆H₁₂N₄)₂(H₂O)₂]₀.₈⋅1.₆C₂H₆O⋅₄C₆H₁₂N₄, 1, and tris(ethanol-κO)(hexamethylenetetramine-κN)bis(thiocyanato-κN)cobalt(II). [Co(NCS)₂(C₆H₁₂N₄)(C₂H₆O)₃], 2. In the crystal structure of compound 1, two crystallographically independent discrete complexes are observed that are located on centres of inversion. In one of them, the Co cation is octahedrally coordinated to two terminal N-bonded thiocyanate anions, two urotropine ligands and two ethanol molecules, whereas in the second complex 80% of the coordinating ethanol is exchanged by water. Formally, compound 1 is a mixture of two different complexes, i.e. diaqua-dithiocyanato(urotropine)cobalt(II) and diethanoldithiocyanato(urotropine)cobalt(II), that contain additional ethanol and urotropine solvate molecules leading to an overall composition of [Co(NCS)₂(urotropine)₂(ethanol)₂(OH₂)]₀.₈⋅0.₈ethanol-4urotropine. Both discrete complexes are linked by intermolecular O−H⋯O and O−H⋯N hydrogen bonding and additional urotropine solvate molecules into chains, which are further connected into layers. These layers combine into a three-dimensional network by pairs of centrosymmetric intermolecular C−H⋯S hydrogen bonds. In the crystal structure of compound 2, dithiocyanato(urotropine)triethanolcobalt(II), the cobalt cation is octahedrally coordinated to two terminal N-bonded thiocyanate anions, one urotropine ligand and three ethanol molecules into discrete complexes, which are located in general positions. These complexes are linked by intermolecular O−H⋯N hydrogen bonding into layers, which are further connected into a three-dimensional network by intermolecular C−H⋯S hydrogen bonding.

1. Chemical context

Recently, we reported the crystal structure of two new coordination compounds with the composition [Co(NCS)₂(urotropine)₂(ethanol)₂] and [Co(NCS)₂(ethanol)₄](urotropine)₂ (Krebs et al., 2022). Both compounds consist of discrete complexes, in which the cobalt cations are octahedrally coordinated by four ethanol and two ethanol and two urotropine ligands, respectively. These investigations were performed to prepare precursors that on thermal decomposition transform into coordination polymers in which the cobalt cations are linked by μ-1,3 bridging thiocyanate anions into chains or layers (Näther et al., 2013). Several such compounds have been
reported in the literature and they are of interest because they show ferromagnetic or antiferromagnetic ordering or a slow relaxation of the magnetization, which is indicative for single-chain magnetism (Böhme et al., 2020; Shi et al., 2006; Jin et al., 2007; Jochim et al., 2020; Prananto et al., 2017; Mautner et al., 2018; Rams et al., 2020; Ceglarska et al., 2021; Werner et al., 2014, 2015; Suckert et al., 2016; Wellm et al., 2020). In this context, urotropine as a coligand was of interest because this ligand is able to form networks (Czubacka et al., 2012; Li et al., 2012), is magnetically silent and one compound with cadmium had already been reported in which the metal cations are linked by the anionic ligands into chains (Bai et al., 2009).

However, for the preparation of the two compounds mentioned above, cobalt thiocyanate was reacted with urotropine in ethanol and X-ray powder measurements show that none of these compounds can be prepared as a pure crystalline phase. Either the desired compounds were obtained as the minor phase or the experimental powder patterns were completely different from the calculated one. These investigations indicate that additional compounds are present and that the desired compounds are not very stable and transform in solution. Therefore, additional crystallization experiments were performed, which lead to the formation of single crystals of two new compounds that were identified by single crystal X-ray diffraction. Even these compounds contain ethanol as a ligand but in one compound one coordination site is simultaneously occupied by ethanol and water, which might originate from some residual water in the solvent used in the synthesis, whereas in the second compound the cobalt cations are coordinated by only one urotropine and three ethanol ligands. All this indicates that, for this system, different species are in equilibrium in solution and some phase crystallizes, presumably by kinetic control, which means that the synthesis is difficult to control.

2. Structural commentary
The asymmetric unit of compound 1 consists of two crystallographically independent Co cations that are located on centres of inversion as well as two thiocyanate anions, four urotropine ligands, three ethanol and one water molecule that occupy general positions (Fig. 1). One of the cobalt cations (Co1) is sixfold coordinated to two terminal N-bonded thiocyanate anions, two urotropine ligands and two ethanol molecules into discrete complexes (Fig. 1, top left). The methyl carbon atom of these ethanol molecules is disordered in two positions and was refined using a split model. The second cobalt cation is also sixfold coordinated, forming discrete complexes, to two terminal N-bonded thiocyanate anions, two urotropine ligands and two oxygen atoms, but the latter positions are mixed occupied by water and ethanol in a ratio of 8:2, leading to an overall composition for 1 of \([\text{Co(NCS)}_2(\text{urotropine})_2(\text{ethanol})_1.2(\text{H}_2\text{O})_0.8\text{ethanol}⋅4\text{urotropine}].\) In the case where it is occupied by water, an ethanol molecule is hydrogen bonded to this water molecule; if it is occupied by ethanol, this ethanol solvate molecule is not present (Fig. 1, top right). The position of the disordered O atoms of the water and ethanol molecule was resolved and all O—H H atoms were clearly located in the difference map and refined isotropically with reasonable displacement parameters, using restraints for the O—H distances (see Refinement). The Co—N bond lengths to the thiocyanate anions are similar in both complexes, which is also valid for the bond length to the urotropine ligands (Table 1). In contrast, the Co—O bond length to the water molecule is shorter than

![Crystal structure of compound 1 with labelling and displacement ellipsoids drawn at the 50% probability level. Symmetry code for the generation of equivalent atoms: (i) \(-x + 1, -y + 1, -z + 2\); (ii) \(-x + 2, -y + 1, -z + 1\).](image-url)
those to the ethanol molecules (Table 1), even if there might be some uncertainty in the distances because of the disorder.

The asymmetric unit of compound 2 consists of one crystallographically independent cobalt cation, one urotropine ligand and three ethanol molecules, all of them located in general positions (Fig. 2). In this compound the cobalt cations are sixfold coordinated to two terminal N-bonded thiocyanate anions, one urotropine ligand and three ethanol molecules. The Co—N and Co—O bond lengths are comparable to those in compound 1 and to similar ethanol complexes retrieved from the literature (Krebs et al., 2021a, Table 2). From the angles around the Co cations, it is obvious that in all compounds the octahedra are slightly distorted (see supporting information). It is noted that compound 2 completes the series of Co(NCS)₂-urotropine compounds with ethanol as an additional ligand, because in this compound the cobalt cations are coordinated to one urotropine and three ethanol ligands, whereas in the other compounds reported recently the cobalt cations are either coordinated to two urotropine and three ethanol ligands or to four ethanol ligands (Krebs et al., 2021a).

Table 1
Selected bond lengths (Å) for 1.

| Bond          | Length (Å) |
|---------------|------------|
| Co1—N1        | 2.0590 (16) |
| Co1—O1        | 2.1388 (13) |
| Co1—N11       | 2.2834 (15) |
| Co2—N2        | 2.0812 (16) |
| Co2—O2        | 2.029 (6)   |
| Co2—O4        | 2.21 (3)    |

Table 2
Selected bond lengths (Å) for 2.

| Bond          | Length (Å) |
|---------------|------------|
| Co1—N2        | 2.0615 (11) |
| Co1—N1        | 2.0624 (11) |
| Co1—O41       | 2.1021 (10) |

3. Supramolecular features

In the crystal structure of the title compound, extensive hydrogen bonding is observed (Table 3). The discrete complex around Co1 is linked to two urotropine solvate molecules via intermolecular O—H⋯N hydrogen bonding (Fig. 3 and Table 3). For the Co2 complex, two different surroundings are observed. In the case where this cation is coordinated to water, hydrogen bonding is observed (Table 3). The discrete complex built up of Co1, which is connected to two urotropine solvate molecules via intermolecular O—H⋯N hydrogen bonding (shown as dashed lines).
EtOH, the solvate ethanol molecule is not present and the surrounding is similar to that around Co1 with only hydrogen bonding to two urotropine ligands (compare Fig. 3 and Fig. 4, bottom). Both crystallographically independent complexes are linked into chains via intermolecular O—H—O hydrogen bonding (Fig. 5). The chains are further connected into layers by intermolecular C—H—O and C—H—N interactions. These layers are stacked onto each other and are linked by intermolecular centrosymmetric pairs of C—H···S hydrogen bonds, in which only the discrete complex built up of Co2 is involved (Fig. 6 and Table 3).

Table 4

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| C12—H12A···S2i | 0.99 | 2.87 | 3.6586 (13) | 137 |
| C12—H12B···S1vi | 0.99 | 2.92 | 3.8813 (13) | 164 |
| C15—H15A···S1iii | 0.99 | 2.99 | 3.9387 (13) | 161 |
| C15—H15B···S2v | 0.99 | 2.94 | 3.7110 (13) | 135 |
| C16—H16A···O21 | 0.99 | 2.54 | 3.1009 (16) | 116 |
| C16—H16B···N1 | 0.99 | 2.47 | 3.1083 (17) | 122 |
| O21—H21···N13 | 0.84 | 2.03 | 2.8424 (14) | 161 |
| C22—H22C···S1i | 0.98 | 3.02 | 3.9559 (16) | 161 |
| O31—H31···N12vi | 0.84 | 1.96 | 2.7969 (14) | 172 |
| O41—H41···S2vi | 0.84 | 2.37 | 3.2080 (10) | 174 |

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

Figure 4

View of the two different coordinations of Co2 in compound 1 with H2O (top) and ethanol (bottom) with intermolecular hydrogen bonding shown as dashed lines.

Figure 5

Part of the crystal structure of compound 1 showing the connection of the discrete complexes by the urotropine solvate molecules via intermolecular O—H···N hydrogen bonding (shown as dashed lines).

Figure 6

Crystal structure of compound 1 with a view along the crystallographic b axis and intermolecular hydrogen bonding shown as dashed lines.

Figure 7

Crystal structure of compound 2 with a view along the crystallographic a axis and intermolecular O—H···N hydrogen bonding shown as dashed lines.
In the crystal structure of compound 2, the discrete complexes are linked by strong intermolecular O—H···N hydrogen bonding between two of the three O—H hydrogen atoms of the ethanol ligands and two urotropine N atoms into layers that are parallel to the bc plane (Fig. 7 and Table 4). These layers are further linked by intermolecular O—H···S and C—H···S hydrogen bonding into a three-dimensional network (Table 4). Some of the O—H···S and C—H···S angles are close to linearity, indicating that these are relatively strong interactions (Table 4).

4. Database survey

In the Cambridge Structure Database (CSD version 5.42, last update November 2020; Groom et al., 2016) there are already several structures reported that contain cobalt thiocyanate and urotropine as a ligand, but only one of them contains additional ethanol (Krebs et al., 2021a). Most of them contain water as a ligand or solvate molecule. In [Co(NCS)2(H2O)4]2-2urotropine (Refcode: XILXOG; Li et al., 2007), the cobalt cations are octahedrally coordinated by two thiocyanate anions and four water ligands with two additional urotropine ligands acting as solvate molecules. [Co(NCS)2(urotropine)2(H2O)2][Co(NCS)2(H2O)4]:2H2O (Refcode: MOTNIS; Liu et al., 2002; MOTNIS01; Zhang et al., 1999, MOTNIS02; Chakraborty et al., 2006, MOTNIS03; Lu et al., 2010) consists of two crystallographically independent discrete complexes in which the cobalt cations are coordinated by two terminal N-bonded thiocyanate anions and four water or two water and two urotropine ligands with additional water as solvate molecules. There is also one complex with water and methanol as ligands with the composition [Co(NCS)2(urotropine)(CH3OH)2(H2O)] (Refcode: POFGAT; Shang et al., 2008), in which the cobalt cations are octahedrally coordinated by the N atoms of two thiocyanate anions, two methanol, one water and one urotropine ligand. Moreover, a compound with the composition [Co(NCS)2(urotropine)(CH3CN)2] that also consists of discrete complexes has been reported (Krebs et al., 2021). It is noted that even with other metal cations only discrete complexes are reported, such as, for example, with nickel (Refcode: XILROA; Bai et al., 2007, XILROA01; Lu et al., 2010), or zinc (Refcode: SIMXIY; Kruszynski et al., 2018). Finally, a crystal structure is reported with cadmium in which the Cd cations are linked by pairs of thiocyanate anions into chains, which are further linked by the urotropine ligand (Refcode: DOZZOI; Bai et al., 2009).

5. Synthesis and crystallization

**Synthesis** Co(NCS)2 and urotropine were purchased from Merck. All chemicals were used without further purification.
Crystals of compound 1 suitable for single-crystal X-ray diffraction were obtained after one day by the reaction of 0.15 mmol of Co(NCS)₂ (26.3 mg) with 0.60 mmol of urotropine (84.1 mg) in 1.0 mL of ethanol at room temperature. The reaction of 0.15 mmol of Co(NCS)₂ (26.3 mg) with 0.15 mmol of urotropine (21.0 mg) in 2.0 mL of ethanol at room temperature led to the formation of single crystals of compound 2.

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

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. All non-hydrogen atoms were refined anisotropically. The C—H hydrogen atoms were located in the difference map but positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined isotropically with $U_{	ext{iso}}(H) = 1.2U_{	ext{eq}}(C)$ (1.5 for methyl H atoms) using a riding model. The O—H hydrogen atoms were located in the difference map but positioned with idealized geometry allowed to rotate but not to tip and were refined isotropically with $U_{	ext{iso}}(H) = 1.5U_{	ext{eq}}(O)$ using a riding model. In compound 1, the methyl group of the EtOH molecule coordinated to Co1 is disordered and was refined using a split model. In this compound, Co2 is either coordinated to water or to EtOH. In this case the O atoms occupy nearly the same crystallographic positions but finally both O atoms can be refined separately with anisotropic displacement parameters. In the case where Co2 is coordinated to water, it is hydrogen bonded to one EtOH solvate molecule. If Co2 is coordinated to EtOH, the position of the EtOH solvate molecule cannot be occupied. Therefore, the site occupation factor (sof) of the EtOH solvate molecule must be identical to that of the coordinated water molecule. In the beginning the sof was refined, leading to values close to 0.8 for the water and 0.2 for the coordinated EtOH molecule but in the final refinements it was fixed at 0.8 and 0.2. The H-atom positions of both, water and EtOH, were clearly located and were refined with restraints and varying isotropic displacement parameters. This leads to comparable and reasonable values for the O—H distances as well as for the isotropic displacement parameters of the O—H hydrogen atoms.

Acknowledgements

This project was supported by the State of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft.

Funding information

Funding for this research was provided by: Deutsche Forschungsgemeinschaft (grant No. NA720/5-2).

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Computing details

For both structures, 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) for (1); SHELXT2014/4 (Sheldrick, 2015a) for (2). For both structures, program(s) used to refine structure: SHELXL2016/6 (Sheldrick, 2015b). Molecular graphics: DIAMOND (Brandenburg & Putz, 1999) for (1); OLEX2 (Dolomanov et al., 2009) for (2). Software used to prepare material for publication: publCIF (Westrip, 2010) for (1); OLEX2 (Dolomanov et al., 2009) for (2).

Bis(ethanol-κO)bis(hexamethylenetetramine-κN)bis(thiocyanato-κN)cobalt(II)–diaqua-κ$_2$O–bis(hexamethylenetetramine-κN)bis(thiocyanato-κN)cobalt(II)–ethanol–hexamethylenetetramine (1.2/0.8/1.6/4) (1)

Crystal data

[Co(NCS)$_2$(C$_6$H$_{12}$N$_4$)$_2$(C$_2$H$_6$O)$_2$]$_{1.2}$·[Co(NCS)$_2$(C$_6$H$_{12}$N$_4$)$_2$(H$_2$O)$_2$]$_{0.8}$·1.6C$_2$H$_6$O·4C$_6$H$_{12}$N$_4$

$M_r = 1684.84$

Triclinic, $P$

$a = 12.1536$ (2) Å

$b = 12.9256$ (3) Å

$c = 12.9374$ (3) Å

$\alpha = 76.629$ (2)°

$\beta = 80.395$ (2)°

$\gamma = 80.578$ (2)°

$V = 1932.91$ (7) Å$^3$

$Z = 1$

$F(000) = 898$

$D_x = 1.447$

Mg m$^{-3}$

radiation, $\lambda = 1.54178$ Å

Cell parameters from reflections

$\theta = 3.7−79.3°$

$\mu = 4.97$ mm$^{-1}$

$T = 100$ K

Plate, light colourless

$0.16 \times 0.12 \times 0.08$ mm
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\(^{-1}\)

ω scans
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2021)

\(T_{\text{min}} = 0.693, T_{\text{max}} = 1.000\)
25821 measured reflections
8226 independent reflections
7777 reflections with \(I > 2\sigma(I)\)

\(R_m = 0.024\)
\(\theta_{\text{max}} = 80.1^\circ, \theta_{\text{min}} = 3.5^\circ\)

\(h = -15\rightarrow15\)
\(k = -16\rightarrow13\)
\(l = -16\rightarrow16\)

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.040\)
\(wR(F^2) = 0.103\)
\(S = 1.09\)
8226 reflections
545 parameters
10 restraints

Primary atom site location: dual
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
\(w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 1.7899P]\)
where \(P = (F_o^2 + 2F_c^2)/3\)

\((\Delta/\sigma)_{\text{max}} = 0.001\)
\(\Delta\rho_{\text{max}} = 0.82\ e\ Å^{-3}\)
\(\Delta\rho_{\text{min}} = -0.69\ e\ Å^{-3}\)

Extinction correction: SHELXL2016/6
(Sheldrick 2015b),
\(F_c^* = kF_c[1+0.001xF_c^2/\sin(2\theta)]^{1/4}\)
Extinction coefficient: 0.00080 (10)

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 (Å\(^2\))

|   | x   | y   | z   | \(U_{eq}\)/Å\(^2\) | Occ. (<1) |
|---|-----|-----|-----|-------------------|-----------|
| Co1 | 0.500000 | 0.000000 | 1.000000 | 0.01667 (10) |
| Co2 | 1.000000 | 0.500000 | 0.500000 | 0.01929 (11) |
| N1  | 0.38177 (14) | -0.10448 (13) | 1.03166 (13) | 0.0209 (3) |
| C1  | 0.31474 (16) | -0.15722 (15) | 1.02515 (15) | 0.0219 (4) |
| S1  | 0.22329 (5) | -0.23250 (5) | 1.01546 (5) | 0.03988 (15) |
| N2  | 0.85107 (14) | 0.59836 (13) | 0.46671 (13) | 0.0238 (3) |
| C2  | 0.76974 (17) | 0.65684 (15) | 0.45319 (15) | 0.0226 (4) |
| S2  | 0.65758 (5) | 0.74450 (5) | 0.43091 (5) | 0.03506 (14) |
| O1  | 0.37719 (11) | 0.13161 (11) | 0.94616 (11) | 0.0216 (3) |
| H1  | 0.392 (3) | 0.1982 (16) | 0.927 (3) | 0.060 (10)* |
| C3  | 0.26483 (18) | 0.13151 (18) | 0.91942 (18) | 0.0294 (4) |
| H3AA| 0.250342 | 0.057923 | 0.930034 | 0.044* |
| H3AB| 0.262932 | 0.164417 | 0.844216 | 0.044* |
| H3BC| 0.250431 | 0.196444 | 0.865692 | 0.044* |
| H3BD| 0.271029 | 0.072225 | 0.883622 | 0.044* |
| C4  | 0.1725 (2) | 0.1909 (2) | 0.98618 (19) | 0.0200 (4) |
| H4A | 0.100686 | 0.185071 | 0.968034 | 0.030* |
| H4B | 0.183149 | 0.265097 | 0.971950 | 0.030* |
| H4C | 0.175324 | 0.160103 | 1.060858 | 0.030* |
| Atom | x       | y       | z       | Ueq  | Occupancy |
|------|---------|---------|---------|------|------------|
| C4'  | 0.1630 (6) | 0.1249 (14) | 0.9957 (8) | 0.047 (3) | 0.2        |
| H4'A | 0.1041 (3) | 0.1097 (5) | 0.9626 (11) | 0.071 (2) | 0.2        |
| H4'B | 0.1406 (3) | 0.1919 (5) | 1.0181 (11) | 0.071 (2) | 0.2        |
| H4'C | 0.1767 (3) | 0.0687 (5) | 1.0569 (11) | 0.071 (2) | 0.2        |
| O2   | 0.9172 (3) | 0.3693 (6) | 0.5467 (6) | 0.0215 (6) | 0.8        |
| H2'A | 0.939 (3) | 0.308 (3) | 0.588 (5) | 0.07 (3) | 0.8        |
| H2'B | 0.8447 (7) | 0.372 (4) | 0.548 (4) | 0.077 (18) | 0.8        |
| O3   | 0.69673 (15) | 0.37997 (14) | 0.54414 (15) | 0.0275 (4) | 0.8        |
| C5   | 0.6645 (2) | 0.2810 (2) | 0.5350 (2) | 0.0267 (5) | 0.8        |
| H5'A | 0.586260 | 0.291950 | 0.523215 | 0.032* | 0.8        |
| H5'B | 0.622275 | 0.228069 | 0.600949 | 0.032* | 0.8        |
| C6   | 0.7380 (2) | 0.2411 (2) | 0.4427 (2) | 0.0298 (5) | 0.8        |
| H6'A | 0.731836 | 0.294723 | 0.3780 (4) | 0.045* | 0.8        |
| H6'B | 0.714164 | 0.176471 | 0.4348 (3) | 0.045* | 0.8        |
| H6'C | 0.814805 | 0.226809 | 0.4565 (17) | 0.045* | 0.8        |
| H3   | 0.656 (3) | 0.406 (3) | 0.597 (2) | 0.054 (11)* | 0.8        |
| O4   | 0.8970 (16) | 0.367 (3) | 0.543 (3) | 0.0215 (6) | 0.2        |
| C7   | 0.7799 (8) | 0.3562 (8) | 0.5603 (9) | 0.026 (2) | 0.2        |
| H7'A | 0.736856 | 0.426993 | 0.5464 (7) | 0.032* | 0.2        |
| H7'B | 0.759133 | 0.323060 | 0.6348 (3) | 0.032* | 0.2        |
| C8   | 0.7500 (9) | 0.2899 (8) | 0.4899 (8) | 0.030 (2) | 0.2        |
| H8'A | 0.762768 | 0.326382 | 0.4162 (3) | 0.046* | 0.2        |
| H8'B | 0.672194 | 0.279629 | 0.5089 (2) | 0.046* | 0.2        |
| H8'C | 0.796095 | 0.221486 | 0.4996 (3) | 0.046* | 0.2        |
| H4   | 0.930 (14) | 0.306 (9) | 0.574 (17) | 0.02 (5)* | 0.2        |
| N11  | 0.53970 (13) | −0.0405 (12) | 0.8339 (4) | 0.0169 (3) |          |
| N12  | 0.59897 (13) | −0.1856 (13) | 0.7331 (6) | 0.0199 (3) |          |
| N13  | 0.46941 (13) | −0.0293 (13) | 0.6626 (2) | 0.0201 (3) |          |
| N14  | 0.66683 (13) | −0.0110 (12) | 0.6632 (2) | 0.0189 (3) |          |
| C11  | 0.57045 (16) | −0.1585 (9) | 0.8391 (14) | 0.0193 (4) |          |
| H11'A | 0.634285 | −0.1843 (9) | 0.8785 (16) | 0.023* |          |
| H11'B | 0.507809 | −0.1953 (6) | 0.8783 (6) | 0.023* |          |
| C12  | 0.63690 (15) | 0.0124 (15) | 0.7708 (4) | 0.0189 (4) |          |
| H12'A | 0.618761 | 0.0894 (4) | 0.7642 (9) | 0.023* |          |
| H12'B | 0.701533 | −0.0110 (12) | 0.8094 (14) | 0.023* |          |
| C13  | 0.56767 (16) | 0.0235 (15) | 0.6061 (15) | 0.0213 (4) |          |
| H13'A | 0.586413 | 0.0076 (4) | 0.5351 (2) | 0.026* |          |
| H13'B | 0.548205 | 0.1005 (6) | 0.5977 (3) | 0.026* |          |
| C14  | 0.50120 (16) | −0.1457 (16) | 0.6745 (15) | 0.0220 (4) |          |
| H14'A | 0.518813 | −0.1630 (3) | 0.6040 (6) | 0.026* |          |
| H14'B | 0.437746 | −0.181983 | 0.7125 (5) | 0.026* |          |
| C15  | 0.44349 (16) | −0.0043 (15) | 0.7698 (3) | 0.0205 (4) |          |
| H15'A | 0.378951 | −0.0386 (7) | 0.8083 (7) | 0.025* |          |
| H15'B | 0.423192 | 0.072471 | 0.7625 (9) | 0.025* |          |
| C16  | 0.69351 (16) | −0.1281 (15) | 0.6746 (15) | 0.0208 (4) |          |
| H16'A | 0.758527 | −0.1531 (8) | 0.7124 (5) | 0.025* |          |
| H16'B | 0.713010 | −0.1448 (6) | 0.6039 (3) | 0.025* |          |
| N21  | 0.96389 (13) | 0.5327 (12) | 0.6688 (12) | 0.0185 (3) |          |
| Atom | x     | y     | z     | Ueq |
|------|-------|-------|-------|-----|
| N22  | 1.03238 (14) | 0.51130 (13) | 0.84249 (13) | 0.0209 (3) |
| N23  | 0.83260 (14) | 0.50888 (13) | 0.83676 (13) | 0.0211 (3) |
| N24  | 0.91408 (14) | 0.67678 (13) | 0.77182 (13) | 0.0207 (3) |
| C21  | 0.86158 (16) | 0.48569 (15) | 0.72915 (15) | 0.0206 (4) |
| H21A | 0.798587 | 0.514069 | 0.689148 | 0.025* |
| H21B | 0.874416 | 0.408596 | 0.735116 | 0.025* |
| C22  | 0.81436 (16) | 0.62564 (15) | 0.82683 (16) | 0.0221 (4) |
| H22A | 0.794956 | 0.641618 | 0.897807 | 0.027* |
| H22B | 0.751325 | 0.655797 | 0.787314 | 0.027* |
| C23  | 1.00907 (16) | 0.62886 (15) | 0.83182 (16) | 0.0226 (4) |
| H23A | 0.992555 | 0.645241 | 0.902716 | 0.027* |
| H23B | 1.075775 | 0.660737 | 0.795445 | 0.027* |
| C24  | 1.05778 (16) | 0.48863 (15) | 0.73384 (15) | 0.0201 (4) |
| H24A | 1.073004 | 0.411640 | 0.739378 | 0.024* |
| H24B | 1.125119 | 0.519334 | 0.697337 | 0.024* |
| C25  | 0.94127 (16) | 0.65112 (14) | 0.66518 (15) | 0.0205 (4) |
| H25A | 1.007066 | 0.683951 | 0.627731 | 0.025* |
| H25B | 0.879088 | 0.681840 | 0.624686 | 0.025* |
| C26  | 0.92924 (16) | 0.46570 (15) | 0.89559 (15) | 0.0217 (4) |
| H26A | 0.942690 | 0.388452 | 0.902783 | 0.026* |
| H26B | 0.911220 | 0.480513 | 0.967089 | 0.026* |
| N31  | 0.41819 (13) | 0.34324 (13) | 0.86223 (13) | 0.0213 (3) |
| N32  | 0.34067 (15) | 0.51211 (14) | 0.75097 (14) | 0.0266 (4) |
| N33  | 0.47210 (17) | 0.51353 (15) | 0.87450 (15) | 0.0325 (4) |
| N34  | 0.53923 (15) | 0.44041 (15) | 0.71314 (14) | 0.0289 (4) |
| C31  | 0.31950 (17) | 0.40495 (16) | 0.81169 (17) | 0.0266 (4) |
| H31A | 0.299473 | 0.365307 | 0.763932 | 0.032* |
| H31B | 0.255972 | 0.411911 | 0.867126 | 0.032* |
| C32  | 0.3720 (2) | 0.56912 (17) | 0.82560 (18) | 0.0329 (5) |
| H32A | 0.386349 | 0.640567 | 0.787339 | 0.040* |
| H32B | 0.309371 | 0.576543 | 0.881808 | 0.040* |
| C33  | 0.56536 (19) | 0.50044 (19) | 0.78861 (19) | 0.0349 (5) |
| H33A | 0.631573 | 0.462773 | 0.820177 | 0.042* |
| H33B | 0.582728 | 0.570673 | 0.749263 | 0.042* |
| C34  | 0.51269 (18) | 0.33500 (16) | 0.77563 (16) | 0.0272 (4) |
| H34A | 0.578777 | 0.295933 | 0.806522 | 0.033* |
| H34B | 0.494052 | 0.294447 | 0.727982 | 0.033* |
| C35  | 0.43694 (18) | 0.49921 (17) | 0.66807 (17) | 0.0291 (4) |
| H35A | 0.452907 | 0.569471 | 0.627554 | 0.035* |
| H35B | 0.417450 | 0.460785 | 0.618972 | 0.035* |
| C36  | 0.44831 (19) | 0.40664 (17) | 0.93320 (16) | 0.0275 (4) |
| H36A | 0.386711 | 0.413627 | 0.990439 | 0.033* |
| H36B | 0.514013 | 0.368715 | 0.965490 | 0.033* |
| N41  | 0.98222 (14) | 0.16814 (13) | 0.66156 (13) | 0.0236 (3) |
| N42  | 1.07891 (16) | −0.00576 (15) | 0.62924 (17) | 0.0350 (4) |
| N43  | 1.09861 (17) | 0.05352 (15) | 0.79123 (17) | 0.0379 (5) |
| N44  | 0.92004 (15) | 0.00149 (14) | 0.77178 (14) | 0.0276 (4) |
| C41  | 1.04120 (19) | 0.10589 (18) | 0.58097 (18) | 0.0316 (5) |
Atomic displacement parameters ($\AA^2$)

|       | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|-------|------------|------------|------------|------------|------------|------------|
| Co1   | 0.0194 (2) | 0.0162 (2) | 0.0148 (2) | −0.00317 (15) | −0.00286 (15) | −0.00303 (15) |
| Co2   | 0.0223 (2) | 0.0144 (2) | 0.0185 (2) | 0.00176 (16)  | −0.00397 (16) | −0.00022 (16) |
| N1    | 0.0246 (8) | 0.0200 (7) | 0.0189 (7) | −0.00060 (6)  | −0.0018 (6)   | −0.0045 (6)   |
| C1    | 0.0258 (9) | 0.0193 (9) | 0.0184 (9) | −0.00040 (7)  | −0.0006 (7)   | −0.0029 (7)   |
| S1    | 0.0345 (3) | 0.0400 (3) | 0.0532 (4) | −0.0172 (2)   | 0.0012 (3)    | −0.0224 (3)   |
| N2    | 0.0247 (8) | 0.0206 (8) | 0.0232 (8) | 0.0042 (6)    | −0.0050 (6)   | −0.0025 (6)   |
| C2    | 0.0267 (10)| 0.0226 (9) | 0.0199 (9) | −0.0029 (8)   | −0.0031 (7)   | −0.0075 (7)   |
| S2    | 0.0283 (3) | 0.0407 (3) | 0.0403 (3) | 0.0136 (2)    | −0.0156 (2)   | −0.0217 (2)   |
| O1    | 0.0244 (7) | 0.0192 (6) | 0.0222 (6) | −0.0027 (5)   | −0.0082 (5)   | −0.0030 (5)   |
| C3    | 0.0272 (10)| 0.0309 (11)| 0.0322 (11)| −0.0013 (8)   | −0.0083 (8)   | −0.0091 (9)   |
| C4    | 0.0190 (11)| 0.0222 (12)| 0.0184 (11)| −0.0034 (10)  | −0.0006 (8)   | −0.0044 (10)  |
| C4'   | 0.042 (7)  | 0.059 (10) | 0.040 (7)  | −0.022 (7)    | −0.012 (6)    | 0.006 (7)     |
| O2    | 0.0187 (17)| 0.0192 (8) | 0.0251 (10)| 0.0002 (16)   | −0.0061 (15)  | −0.0012 (7)   |
| O3    | 0.0245 (10)| 0.0260 (9) | 0.0324 (10)| −0.0041 (7)   | −0.0003 (7)   | −0.0087 (7)   |
| C5    | 0.0244 (13)| 0.0246 (12)| 0.0298 (13)| −0.0041 (10)  | −0.0060 (10)  | −0.0004 (10)  |
| C6    | 0.0291 (13)| 0.0293 (13)| 0.0308 (14)| −0.0040 (11)  | −0.0050 (11)  | −0.0052 (11)  |
| O4    | 0.0187 (17)| 0.0192 (8) | 0.0251 (10)| 0.0002 (16)   | −0.0061 (15)  | −0.0012 (7)   |
| C7    | 0.013 (5)  | 0.028 (5)  | 0.035 (5)  | 0.003 (4)     | 0.002 (4)     | −0.008 (4)    |
| C8    | 0.032 (6)  | 0.024 (5)  | 0.028 (5)  | −0.001 (4)    | −0.006 (4)    | 0.007 (4)     |
| N11   | 0.0173 (7) | 0.0173 (7) | 0.0149 (7) | −0.0003 (6)   | −0.0035 (5)   | −0.0016 (6)   |
| N12   | 0.0233 (8) | 0.0198 (7) | 0.0168 (7) | 0.0004 (6)    | −0.0046 (6)   | −0.0051 (6)   |
| N13   | 0.0207 (8) | 0.0226 (8) | 0.0175 (7) | 0.0011 (6)    | −0.0057 (6)   | −0.0060 (6)   |
| N14   | 0.0203 (7) | 0.0204 (8) | 0.0154 (7) | −0.0004 (6)   | −0.0030 (6)   | −0.0041 (6)   |
| C11   | 0.0247 (9) | 0.0165 (8) | 0.0163 (8) | −0.0009 (7)   | −0.0039 (7)   | −0.0033 (7)   |
| C12   | 0.0204 (9) | 0.0208 (9) | 0.0152 (8) | −0.0024 (7)   | −0.0023 (7)   | −0.0033 (7)   |
| C13   | 0.0233 (9) | 0.0225 (9) | 0.0165 (8) | 0.0017 (7)    | −0.0057 (7)   | −0.0022 (7)   |
| C14   | 0.0227 (9) | 0.0242 (9) | 0.0214 (9) | −0.0016 (7)   | −0.0064 (7)   | −0.0076 (7)   |
C15 0.0193 (9) 0.0237 (9) 0.0188 (9) 0.0012 (7) -0.0044 (7) -0.0067 (7)
C16 0.0194 (9) 0.0222 (9) 0.0199 (9) 0.0026 (7) -0.0042 (7) -0.0053 (7)
N21 0.0185 (7) 0.0153 (7) 0.0200 (7) -0.0003 (6) -0.0041 (6) -0.0004 (6)
N22 0.0226 (8) 0.0189 (7) 0.0209 (8) 0.0001 (6) -0.0060 (6) -0.0031 (6)
N23 0.0215 (8) 0.0212 (8) 0.0197 (8) -0.0026 (6) -0.0032 (6) -0.0024 (6)
N24 0.0226 (8) 0.0186 (7) 0.0198 (8) -0.0002 (6) -0.0033 (6) -0.0032 (6)
C21 0.0208 (9) 0.0192 (9) 0.0210 (9) -0.0024 (7) -0.0036 (7) -0.0023 (7)
C22 0.0197 (9) 0.0217 (9) 0.0232 (9) 0.0012 (7) -0.0032 (7) -0.0041 (7)
C23 0.0232 (9) 0.0202 (9) 0.0251 (9) -0.0020 (7) -0.0073 (7) -0.0041 (7)
C24 0.0192 (8) 0.0188 (8) 0.0210 (9) 0.0008 (7) -0.0044 (7) -0.0028 (7)
C25 0.0246 (9) 0.0154 (8) 0.0197 (9) -0.0004 (7) -0.0031 (7) -0.0014 (7)
C26 0.0239 (9) 0.0197 (9) 0.0196 (9) -0.0017 (7) -0.0049 (7) 0.0003 (7)
N31 0.0206 (8) 0.0206 (8) 0.0227 (8) -0.0029 (6) -0.0045 (6) -0.0032 (6)
N32 0.0251 (8) 0.0217 (8) 0.0312 (9) -0.0001 (7) -0.0056 (7) -0.0025 (7)
N33 0.0441 (11) 0.0273 (9) 0.0303 (9) -0.0127 (8) -0.0096 (8) -0.0056 (7)
N34 0.0246 (8) 0.0307 (9) 0.0258 (9) -0.0009 (7) -0.0019 (7) 0.0022 (7)
C31 0.0219 (9) 0.0241 (10) 0.0332 (11) -0.0022 (8) -0.0071 (8) -0.0027 (8)
C32 0.0431 (13) 0.0203 (10) 0.0345 (11) -0.0020 (9) -0.0035 (9) -0.0068 (8)
C33 0.0317 (11) 0.0337 (11) 0.0385 (12) -0.0148 (9) -0.0111 (9) 0.0056 (9)
C34 0.0277 (10) 0.0249 (10) 0.0251 (10) 0.0040 (8) -0.0026 (8) -0.0031 (8)
C35 0.0299 (11) 0.0288 (10) 0.0247 (10) 0.0005 (8) -0.0057 (8) 0.0007 (8)
C36 0.0343 (11) 0.0281 (10) 0.0221 (9) -0.0087 (8) -0.0045 (8) -0.0054 (8)
N41 0.0239 (8) 0.0223 (8) 0.0236 (8) -0.0054 (6) -0.0049 (6) 0.0000 (6)
N42 0.0301 (10) 0.0273 (9) 0.0417 (11) 0.0018 (7) 0.0013 (8) -0.0037 (8)
N43 0.0397 (11) 0.0287 (10) 0.0452 (11) -0.0112 (8) -0.0241 (9) 0.0100 (8)
N44 0.0273 (9) 0.0219 (8) 0.0310 (9) -0.0063 (7) -0.0025 (7) 0.0009 (7)
C41 0.0304 (11) 0.0307 (11) 0.0281 (10) -0.0011 (9) 0.0019 (8) -0.0010 (9)
C42 0.0240 (11) 0.0309 (12) 0.0623 (17) -0.0016 (9) -0.0088 (10) 0.0084 (11)
C43 0.0447 (13) 0.0295 (11) 0.0302 (11) -0.0087 (10) -0.0126 (10) 0.0075 (9)
C44 0.0246 (10) 0.0231 (9) 0.0276 (10) -0.0028 (8) -0.0034 (8) -0.0004 (8)
C45 0.0420 (13) 0.0243 (10) 0.0404 (12) -0.0122 (9) -0.0219 (10) 0.0056 (9)
C46 0.0343 (11) 0.0199 (10) 0.0434 (13) -0.0050 (8) -0.0042 (10) -0.0059 (9)

Geometric parameters (Å, °)

Co1—N1i 2.0590 (16)  C16—H16B 0.9700
Co1—N1 2.0590 (16)  N21—C21 1.493 (2)
Co1—O1i 2.1388 (13)  N21—C24 1.490 (2)
Co1—O1 2.1388 (13)  N21—C25 1.500 (2)
Co1—N11i 2.2834 (15)  N22—C23 1.478 (2)
Co1—N11 2.2834 (15)  N22—C24 1.474 (2)
Co2—N2ii 2.0812 (16)  N22—C26 1.469 (2)
Co2—N2 2.0812 (16)  N23—C21 1.465 (2)
Co2—O2 2.029 (6)  N23—C22 1.468 (2)
Co2—O2ii 2.029 (6)  N23—C26 1.469 (2)
Co2—O4ii 2.029 (6)  N24—C22 1.473 (2)
Co2—O4 2.029 (6)  N24—C23 1.470 (2)
Co2—N21 2.2788 (16)  N24—C25 1.465 (2)
| Bond       | Distance (Å)    | Bond       | Distance (Å)    |
|------------|-----------------|------------|-----------------|
| Co2—N21a   | 2.2788 (16)     | C21—H21A  | 0.9700          |
| N1—C1      | 1.169 (3)       | C21—H21B  | 0.9700          |
| C1—S1      | 1.629 (2)       | C22—H22A  | 0.9700          |
| N2—C2      | 1.154 (3)       | C22—H22B  | 0.9700          |
| C2—S2      | 1.643 (2)       | C23—H23A  | 0.9700          |
| O1—H1      | 0.880 (18)      | C23—H23B  | 0.9700          |
| O1—C3      | 1.464 (2)       | C24—H24A  | 0.9700          |
| C3—H3AA    | 0.9700          | C24—H24B  | 0.9700          |
| C3—H3AB    | 0.9700          | C25—H25A  | 0.9700          |
| C3—H3BC    | 0.9700          | C25—H25B  | 0.9700          |
| C3—H3BD    | 0.9700          | C26—H26A  | 0.9700          |
| C3—C4      | 1.515 (3)       | C26—H26B  | 0.9700          |
| C3—C4'     | 1.4495 (10)     | N31—C31   | 1.486 (2)       |
| C4—H4A     | 0.9600          | N31—C34   | 1.474 (3)       |
| C4—H4B     | 0.9600          | N31—C36   | 1.486 (2)       |
| C4—H4C     | 0.9600          | N32—C31   | 1.466 (3)       |
| C4′—H4′A   | 0.9600          | N32—C32   | 1.471 (3)       |
| C4′—H4′B   | 0.9600          | N32—C35   | 1.465 (3)       |
| C4′—H4′C   | 0.9600          | N33—C32   | 1.469 (3)       |
| O2—H2A     | 0.872 (19)      | N33—C33   | 1.467 (3)       |
| O2—H2B     | 0.871 (19)      | N33—C36   | 1.463 (3)       |
| O3—C5      | 1.433 (3)       | N34—C33   | 1.480 (3)       |
| O3—H3      | 0.871 (19)      | N34—C34   | 1.470 (3)       |
| C5—H5A     | 0.9700          | N34—C35   | 1.480 (3)       |
| C5—H5B     | 0.9700          | C31—H31A  | 0.9700          |
| C5—C6      | 1.505 (4)       | C31—H31B  | 0.9700          |
| C6—H6A     | 0.9600          | C32—H32A  | 0.9700          |
| C6—H6B     | 0.9600          | C32—H32B  | 0.9700          |
| C6—H6C     | 0.9600          | C33—H33A  | 0.9700          |
| O4—C7      | 1.427 (17)      | C33—H33B  | 0.9700          |
| O4—H4      | 0.87 (2)        | C34—H34A  | 0.9700          |
| C7—H7A     | 0.9700          | C34—H34B  | 0.9700          |
| C7—H7B     | 0.9700          | C35—H35A  | 0.9700          |
| C7—C8      | 1.507 (13)      | C35—H35B  | 0.9700          |
| C8—H8A     | 0.9600          | C36—H36A  | 0.9700          |
| C8—H8B     | 0.9600          | C36—H36B  | 0.9700          |
| C8—H8C     | 0.9600          | N41—C41   | 1.483 (3)       |
| N11—C11    | 1.499 (2)       | N41—C44   | 1.482 (2)       |
| N11—C12    | 1.488 (2)       | N41—C45   | 1.475 (3)       |
| N11—C15    | 1.496 (2)       | N42—C41   | 1.465 (3)       |
| N12—C11    | 1.465 (2)       | N42—C42   | 1.469 (3)       |
| N12—C14    | 1.472 (2)       | N42—C46   | 1.464 (3)       |
| N12—C16    | 1.476 (2)       | N43—C42   | 1.479 (4)       |
| N13—C13    | 1.474 (2)       | N43—C43   | 1.473 (3)       |
| N13—C14    | 1.470 (2)       | N43—C45   | 1.469 (3)       |
| N13—C15    | 1.468 (2)       | N44—C43   | 1.465 (3)       |
| N14—C12    | 1.467 (2)       | N44—C44   | 1.467 (3)       |
| N14—C13    | 1.472 (2)       | N44—C46   | 1.463 (3)       |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| N14—C16              | 1.473 (2)    | C41—H41A             | 0.9700       |
| C11—H11A             | 0.9700       | C41—H41B             | 0.9700       |
| C11—H11B             | 0.9700       | C42—H42A             | 0.9700       |
| C12—H12A             | 0.9700       | C42—H42B             | 0.9700       |
| C12—H12B             | 0.9700       | C43—H43A             | 0.9700       |
| C13—H13A             | 0.9700       | C43—H43B             | 0.9700       |
| C13—H13B             | 0.9700       | C44—H44A             | 0.9700       |
| C14—H14A             | 0.9700       | C44—H44B             | 0.9700       |
| C14—H14B             | 0.9700       | C45—H45A             | 0.9700       |
| C15—H15A             | 0.9700       | C45—H45B             | 0.9700       |
| C15—H15B             | 0.9700       | C46—H46A             | 0.9700       |
| C16—H16A             | 0.9700       | C46—H46B             | 0.9700       |

| Bond                  | Angle (°)    | Bond                  | Angle (°)    |
|----------------------|--------------|----------------------|--------------|
| N1'—Co1—N1           | 180.0        | N14—C16—H16A         | 109.1        |
| N1—Co1—O1i           | 89.16 (6)    | N14—C16—H16B         | 109.1        |
| N1'—Co1—O1           | 89.16 (6)    | H16A—C16—H16B        | 107.9        |
| N1—Co1—O1            | 90.84 (6)    | C21—N21—Co2          | 110.79 (11)  |
| N1'—Co1—N1i          | 90.84 (6)    | C21—N21—C25          | 106.97 (14)  |
| N1—Co1—N11           | 93.90 (6)    | C24—N21—Co2          | 113.66 (11)  |
| N1—Co1—N11i          | 93.90 (6)    | C24—N21—C21          | 107.30 (14)  |
| N1—Co1—N11i          | 93.90 (6)    | C24—N21—C25          | 107.16 (14)  |
| N1—Co1—N11i          | 93.90 (6)    | C25—N21—Co2          | 110.66 (11)  |
| O1—Co1—O1i           | 180.00 (7)   | C24—N21—C23          | 108.01 (14)  |
| O1—Co1—N11i          | 91.57 (5)    | C26—N22—C23          | 107.79 (15)  |
| O1—Co1—N11           | 91.57 (5)    | C26—N22—C24          | 108.16 (15)  |
| O1—Co1—N11i          | 88.43 (5)    | C26—N22—C22          | 108.62 (14)  |
| O1—Co1—N11i          | 88.43 (5)    | C26—N22—C26          | 108.13 (15)  |
| N11—Co1—N11i         | 180.0        | C22—N23—C26          | 107.86 (15)  |
| N2—Co2—N2ii          | 180.0        | C23—N24—C22          | 108.30 (14)  |
| N2—Co2—O4            | 85.7 (7)     | C25—N24—C22          | 107.77 (15)  |
| N2ii—Co2—O4ii         | 85.7 (7)     | C25—N24—C23          | 107.98 (15)  |
| N2—Co2—O4ii          | 94.3 (7)     | N21—C21—H21A         | 109.1        |
| N2ii—Co2—O4ii         | 94.3 (7)     | N21—C21—H21B         | 109.1        |
| N2—Co2—N21ii         | 91.78 (6)    | N23—C21—N21          | 112.54 (15)  |
| N2ii—Co2—N21ii       | 88.22 (6)    | N23—C21—H21A         | 109.1        |
| N2ii—Co2—N21         | 91.78 (6)    | N23—C21—H21B         | 109.1        |
| N2—Co2—N22           | 88.22 (6)    | H21A—C21—H21B        | 107.8        |
| O2ii—Co2—N2           | 89.20 (16)   | N23—C22—N24          | 112.53 (15)  |
| O2—Co2—N2ii          | 89.20 (16)   | N23—C22—H22A         | 109.1        |
| O2ii—Co2—N2ii         | 90.80 (16)   | N23—C22—H22B         | 109.1        |
| O2ii—Co2—N2           | 90.80 (16)   | N24—C22—H22A         | 109.1        |
| O2ii—Co2—O2           | 180.0        | N24—C22—H22B         | 109.1        |
| O2—Co2—O4ii          | 174.6 (9)    | H22A—C22—H22B        | 107.8        |
| O2ii—Co2—O4ii         | 5.4 (9)      | N22—C23—H23A         | 109.1        |
| O2—Co2—N21           | 91.3 (2)     | N22—C23—H23B         | 109.1        |
| O2—Co2—N21ii         | 88.7 (2)     | N24—C23—N22          | 112.47 (15)  |
| O2ii—Co2—N21ii        | 91.3 (2)     | N24—C23—H23A         | 109.1        |
| O2ii—Co2—N21         | 88.7 (2)     | N24—C23—H23B         | 109.1        |
O4ii—Co2—O4 180.0  H23A—C23—H23B 107.8
O4ii—Co2—N21ii 92.9 (9)  N21—C24—H24A 109.1
O4—Co2—N21 92.9 (9)  N21—C24—H24B 109.1
O4ii—Co2—N21 87.1 (9)  N22—C24—N21 112.52 (15)
O4—Co2—N21ii 87.1 (9)  N22—C24—H24A 109.1
N21ii—Co2—N21 180.0  N22—C24—H24B 109.1
C1—N1—Co1 164.85 (15)  H24A—C24—H24B 107.8
N1—C1—S1 178.89 (18)  N21—C25—H25A 109.0
C2—N2—Co2 175.29 (16)  N21—C25—H25B 109.0
N2—C2—S2 177.31 (19)  N24—C25—N21 112.98 (14)
Co1—O1—H1 122 (2)  N22—C26—H26A 109.0
C3—O1—Co1 129.54 (12)  N22—C26—H26B 109.0
C3—O1—H1 107 (2)  N23—C26—N22 112.80 (15)
H3AA—C3—H3AB 107.8  N23—C26—H26A 109.0
H3BC—C3—H3BD 113.01 (18)  N23—C26—H26B 109.0
O1—C3—H3AA 109.0  N22—C26—H26A 109.0
O1—C3—H3AB 109.0  N22—C26—H26B 109.0
O1—C3—H3BC 106.0  N23—C26—N22 112.80 (15)
O1—C3—H3BD 106.0  N23—C26—H26A 109.0
O1—C3—C4 113.01 (18)  N23—C26—H26B 109.0
H3AA—C3—H3AB 107.8  H26A—C26—H26B 107.8
H3BC—C3—H3BD 106.3  C34—N31—C31 107.28 (15)
C4—C3—H3AA 109.0  C34—N31—C36 107.97 (16)
C4—C3—H3AB 109.0  C36—N31—C31 107.86 (16)
C4—C3—H3BC 125.1 (6)  C31—N32—C32 107.40 (17)
C4—C3—H3BD 106.0  C35—N32—C31 108.44 (17)
C3—C4—H4A 109.5  C33—N33—C32 108.52 (17)
C3—C4—H4B 109.5  C36—N33—C32 108.32 (17)
C3—C4—H4C 109.5  C36—N33—C33 108.1 (18)
C4—C4′—H4′A 109.5  N31—C31—H31A 109.0
C4—C4′—H4′B 109.5  N31—C31—H31B 109.0
C4—C4′—H4′C 109.5  N31—C31—H31B 112.86 (16)
C3—C4′—H4′B 109.5  N32—C31—N31 110.90
C3—C4′—H4′C 109.5  N32—C31—H31A 109.0
C4′—C4′—H4′A 109.5  N32—C31—H31B 109.0
C4′—C4′—H4′B 109.5  N32—C31—H31B 109.0
C4′—C4′—H4′C 109.5  N32—C31—H31B 109.0
H4A—C4—H4B 109.5  N32—C31—N31 112.86 (16)
H4A—C4—H4C 109.5  N32—C31—H31A 109.0
H4B—C4—H4C 109.5  N32—C31—H31B 109.0
C3—C4′—H4′A 109.5  C31—C31—H31A 109.0
C3—C4′—H4′B 109.5  C31—C31—H31B 109.0
C3—C4′—H4′C 109.5  C31—C31—N31 110.90
C3—C4′—H4′B 109.5  N32—C31—N31 112.86 (16)
C3—C4′—H4′C 109.5  N32—C31—H31A 109.0
Co2—O2—H2A 127 (4)  N32—C32—H32A 109.1
Co2—O2—H2B 127 (3)  N32—C32—H32B 109.1
H2A—O2—H2B 106 (4)  N33—C32—N32 111.80 (17)
C5—O3—H3 112 (3)  N33—C32—H32A 109.1
O3—C5—H5A 109.8  N33—C32—H32A 109.1
O3—C5—H5B 109.8  H32A—C32—H32B 107.8
O3—C5—C6 109.6 (2)  N33—C33—N34 112.55 (17)
H5A—C5—H5B 108.2  N33—C33—H33A 109.1
C6—C5—H5A 109.8  N33—C33—H33B 109.1
C6—C5—H5B 109.8  N34—C33—H33A 109.1
C5—C6—H6A 109.5  N34—C33—H33B 109.1
C5—C6—H6B  109.5  H33A—C33—H33B  107.8
C5—C6—H6C  109.5  N31—C34—H34A  109.1
H6A—C6—H6B  109.5  N31—C34—H34B  109.1
H6A—C6—H6C  109.5  N34—C34—N31  112.62 (16)
H6B—C6—H6C  109.5  N34—C34—H34A  109.1
Co2—O4—H4  115 (10)  N34—C34—H34B  109.1
C7—O4—Co2  137 (2)  H34A—C34—H34B  107.8
C7—O4—H4  106 (10)  N32—C35—N34  112.61 (16)
O4—C7—H7A  109.1  N32—C35—H35A  109.1
O4—C7—H7B  109.1  N32—C35—H35B  109.1
O4—C7—H7C  112.4 (15)  N33—C36—N31  111.87 (16)
H7A—C7—H7B  107.9  N33—C36—H36A  109.2
H7A—C7—H7C  109.1  N33—C36—H36B  109.2
C8—C7—H7A  109.1  H35A—C35—H35B  107.8
C8—C7—H7B  109.1  N31—C36—H36A  109.2
C8—C7—H7C  109.5  N31—C36—H36B  109.2
C7—C8—H8A  109.5  N33—C36—H36B  109.2
C7—C8—H8B  109.5  N33—C36—H36B  109.2
H8A—C8—H8C  109.5  N33—C36—H36B  109.2
H8A—C8—H8C  109.5  N33—C36—H36B  109.2
H8B—C8—H8C  109.5  N33—C36—H36B  109.2
C11—N11—Co1  112.38 (10)  C44—N41—C41  107.46 (16)
C12—N11—Co1  110.45 (11)  C45—N41—C41  108.17 (18)
C12—N11—C11  106.96 (14)  C45—N41—C44  108.76 (19)
C12—N11—C15  106.95 (13)  C46—N42—C41  108.79 (17)
C15—N11—Co1  112.93 (11)  C46—N42—C42  107.80 (19)
C15—N11—C11  106.83 (14)  C46—N43—C42  107.73 (19)
C11—N12—C14  108.22 (14)  C45—N43—C42  108.42 (19)
C11—N12—C16  108.09 (14)  C45—N43—C43  107.99 (19)
C14—N12—C16  108.03 (14)  C43—N44—C42  108.03 (17)
C14—N13—C13  107.97 (15)  C46—N44—C43  108.19 (18)
C15—N13—C13  107.82 (14)  C46—N44—C44  107.81 (16)
C15—N13—C14  108.50 (14)  N41—C41—H41A  109.1
C12—N14—C13  108.45 (14)  N41—C41—H41B  109.1
C12—N14—C16  108.30 (14)  N42—C41—N41  112.64 (17)
C13—N14—C16  107.44 (14)  N42—C41—H41A  109.1
N11—C11—H11A  109.0  N42—C41—H41B  109.1
N11—C11—H11B  109.0  H41A—C41—H41B  107.8
N12—C11—N11  113.01 (14)  N42—C42—N43  112.48 (18)
N12—C11—H11A  109.0  N42—C42—H42A  109.1
N12—C11—H11B  109.0  N42—C42—H42B  109.1
H11A—C11—H11B  107.8  N43—C42—H42A  109.1
N11—C12—H12A  109.0  N43—C42—H42B  109.1
N11—C12—H12B  109.0  H42A—C42—H42B  107.8
N14—C12—N11  112.97 (15)  N43—C43—H43A  109.1
N14—C12—H12A  109.0  N43—C43—H43B  109.1
N14—C12—H12B  109.0  N44—C43—N43  112.46 (18)
H12A—C12—H12B  107.8  N44—C43—H43A  109.1
N13—C13—H13A  109.1  N44—C43—H43B  109.1
### Supporting Information

| Bond          | Angle (°) | Bond          | Angle (°) |
|---------------|-----------|---------------|-----------|
| N13—C13—H13B | 109.1     | H43A—C43—H43B| 107.8     |
| N14—C13—N13  | 112.61 (14) | N41—C44—H44A | 109.1     |
| N14—C13—H13A | 109.1     | N41—C44—H44B | 109.1     |
| N14—C13—H13B | 109.1     | N44—C44—N41  | 112.30 (16) |
| H13A—C13—H13B | 107.8    | N44—C44—H44A | 109.1     |
| N12—C14—H14A | 109.1     | N44—C44—H44B | 109.1     |
| N12—C14—H14B | 109.1     | H44A—C44—H44B | 107.9     |
| N13—C14—N12  | 112.35 (15) | N41—C45—H45A | 109.2     |
| N13—C14—H14A | 109.1     | N41—C45—H45B | 109.2     |
| N13—C14—H14B | 109.1     | N43—C45—N41  | 112.17 (17) |
| H14A—C14—H14B | 107.9    | N43—C45—H45A | 109.2     |
| N11—C15—H15A | 109.0     | N42—C46—H46A | 108.9     |
| N11—C15—H15B | 109.0     | N42—C46—H46B | 108.9     |
| N13—C15—N11  | 112.95 (14) | N44—C46—N42  | 113.21 (17) |
| N13—C15—H15A | 109.0     | N44—C46—H46A | 108.9     |
| N13—C15—H15B | 109.0     | N44—C46—H46B | 108.9     |
| N11—C16—H16A | 109.1     | H46A—C46—H46B | 107.7     |
| N12—C16—H16B | 109.1     | C31—N31—C34—N34 | 57.9 (2) |
| N14—C16—N12  | 112.42 (15) | C31—N31—C36—N33 | −57.3 (2) |
| Co1—O1—C3—C4 | 121.56 (18) | C31—N31—C34—N34 | 57.9 (2) |
| Co1—O1—C3—C4' | 85.5 (9)   | C31—N31—C36—N33 | 58.3 (2) |
| Co1—N11—C11—N12 | −178.62 (11) | C32—N32—C33—N33 | 57.9 (2) |
| Co1—N11—C12—N14 | 179.71 (11) | C32—N32—C34—N34 | 58.0 (2) |
| Co1—N11—C15—N13 | 179.36 (12) | C32—N32—C35—N35 | 58.0 (2) |
| Co2—O4—C7—C8 | 125 (2)    | C32—N32—C36—N36 | 58.5 (2) |
| Co2—N21—C21—N23 | −177.58 (11) | C32—N32—C37—N37 | 57.9 (2) |
| Co2—N21—C24—N22 | 179.79 (11) | C32—N32—C38—N38 | 58.0 (2) |
| C11—N11—C12—N14 | 178.24 (12) | C32—N32—C39—N39 | 58.0 (2) |
| C11—N11—C15—N13 | 57.12 (18) | C32—N34—C35—N35 | 58.0 (2) |
| C11—N12—C14—C18 | 125 (2)    | C32—N34—C36—N36 | 58.0 (2) |
| C11—N12—C16—N14 | −57.24 (18) | C32—N35—C36—N37 | 58.0 (2) |
| C12—N11—C11—N12 | −57.43 (18) | C32—N35—C37—N38 | 57.9 (2) |
| C12—N11—C15—N13 | 57.65 (19) | C32—N35—C38—N39 | 58.0 (2) |
| C12—N14—C13—N13 | −58.23 (19) | C32—N35—C39—N40 | 58.0 (2) |
| C12—N14—C16—N12 | 58.46 (19) | C34—N31—C35—N35 | 57.9 (2) |
| C13—N13—C14—N12 | 58.01 (19) | C34—N31—C36—N36 | 58.0 (2) |
| C13—N13—C15—N11 | −58.61 (19) | C34—N34—C35—N35 | 57.9 (2) |
| C13—N14—C12—N11 | 57.91 (19) | C34—N34—C36—N36 | 58.0 (2) |
| C13—N14—C16—N12 | −58.50 (19) | C35—N32—C33—N33 | 57.9 (2) |
| C14—N12—C11—N11 | −58.54 (19) | C35—N32—C34—N34 | 58.0 (2) |
| C14—N12—C16—N14 | 58.45 (19) | C35—N34—C35—N35 | 57.9 (2) |
| C14—N13—C13—N14 | −58.58 (19) | C36—N31—C32—N32 | 57.9 (2) |
| C14—N13—C15—N11 | 58.09 (19) | C36—N31—C33—N33 | 58.0 (2) |
| C15—N11—C11—N12 | 57.00 (19) | C36—N31—C34—N34 | 58.1 (2) |
| C15—N11—C12—N14 | −57.03 (18) | C36—N33—C32—N32 | 59.6 (2) |

*Acta Cryst.* (2022), E78, 264-269
C15—N13—C13—N14 58.46 (19)  
C15—N13—C14—N12 −58.6 (2)  
C16—N12—C11—N11 58.22 (19)  
C16—N12—C14—N13 −58.04 (19)  
C16—N14—C12—N11 −58.39 (19)  
C16—N14—C13—N13 58.63 (19)  
C21—N21—C24—N22 −57.37 (19)  
C21—N21—C25—N24 57.47 (19)  
C21—N23—C22—N24 −58.9 (2)  
C22—N21—C21—N23 57.83 (19)  
C22—N24—C25—N21 −58.47 (19)  
C23—N22—C24—N21 −58.54 (19)  
C23—N22—C25—N23 58.2 (2)  
C23—N23—C22—N24 −58.8 (2)  
C23—N24—C25—N21 58.31 (19)  
C24—N21—C21—N23 57.83 (19)  
C24—N21—C25—N24 −57.34 (19)  
C24—N22—C23—N22 59.1 (2)  
C24—N22—C26—N22 −58.31 (19)  
C24—N22—C26—N23 58.2 (2)  
C24—N22—C26—N24 −58.6 (2)  
C24—N23—C22—N23 58.72 (2)  
C24—N23—C26—N23 −58.31 (19)  
C25—N21—C21—N23 −56.89 (18)  
C25—N21—C24—N22 57.21 (19)  
C25—N24—C22—N23 58.72 (19)  
C25—N24—C22—N22 −58.9 (2)  

Symmetry codes: (i) −x+1, −y, −z+2; (ii) −x+2, −y+1, −z+1.

Hydrogen-bond geometry (Å, °)

| D—H···A         | D—H  | H···A | D···A   | D—H···A |
|-----------------|------|------|--------|--------|
| O1—H1···N31     | 0.88 (2) | 1.92 (2) | 2.793 (2) | 170 (3) |
| C4′—H4′···N43   | 0.96  | 2.50  | 3.243 (14) | 134    |
| C4′—H4′···N44   | 0.96  | 2.38  | 3.161 (10) | 138    |
| O2—H2···N41     | 0.87 (2) | 1.88 (2) | 2.743 (7) | 173 (7) |
| O2—H2B···O3     | 0.87 (2) | 1.80 (2) | 2.665 (4) | 177 (5) |
| C5—H5···S2      | 0.97  | 3.02  | 3.925 (3) | 156    |
| O3—H3···N34     | 0.87 (2) | 1.97 (2) | 2.821 (3) | 167 (4) |
| O4—H4···N41     | 0.87 (2) | 1.94 (5) | 2.81 (3) | 170 (19)|
| C11—H1A···O1    | 0.97  | 2.49  | 3.058 (2) | 117    |
| C11—H1B···N1    | 0.97  | 2.67  | 3.213 (2) | 116    |
| C12—H1B···N44   | 0.97  | 2.64  | 3.423 (3) | 138    |
| C13—H13···N13   | 0.97  | 2.70  | 3.563 (2) | 149    |
| C13—H13B···S2   | 0.97  | 2.95  | 3.7150 (19) | 136 |
| C14—H14···S2    | 0.97  | 2.93  | 3.840 (2) | 156    |
| C15—H15B···O1   | 0.97  | 2.61  | 3.118 (2) | 113    |
| C22—H22B···N12  | 0.97  | 2.58  | 3.448 (2) | 149    |
C25—H25A···O2ii 0.97 2.50 3.026 (7) 114
C25—H25A···O4ii 0.97 2.49 3.08 (3) 119
C25—H25B···N2 0.97 2.61 3.202 (3) 119
C26—H26A···S1i 0.97 2.98 3.655 (2) 128
C26—H26B···N22viii 0.97 2.69 3.581 (3) 152
C33—H33A···N23 0.97 2.66 3.431 (3) 137
C45—H45A···S2ii 0.97 3.01 3.959 (3) 165
Symmetry codes: (i) −x+1, −y, −z+2; (ii) −x+2, −y+1, −z+1; (iii) x−1, y, z; (iv) −x+1, −y+1, −z+1; (v) −x+1, −y, −z+1; (vi) x, y+1, z; (vii) x, y+1, z; (viii) −x+2, −y+1, −z+2.

Tris(ethanol-κO)(hexamethylenetetramine-κN)bis(thiocyanato-κN)cobalt(II) (2)

Crystal data

[Co(NCS)2(C6H12N4)(C2H6O)3]  
M_r = 453.49  
Monoclinic, P2_1/n  
a = 11.1463 (1) Å  
b = 15.7705 (1) Å  
c = 12.1824 (1) Å  
β = 103.886 (1)°  
V = 2078.87 (3) Å³  
Z = 4

F(000) = 956  
D_x = 1.449 Mg m⁻³

Cell parameters from 23697 reflections

θ = 4.7–78.0°  
µ = 8.57 mm⁻¹  
T = 100 K

Block, intense orange  
0.2 × 0.18 × 0.03 mm

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  
ω scans  
Absorption correction: multi-scan  
(CrysAlisPro; Rigaku OD, 2021)

Refinement

Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.025  
wR(F²) = 0.068  
S = 1.08  
4431 reflections  
242 parameters  
1 restraint

Primary atom site location: dual  
Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained

H-atom parameters constrained

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          | \(U_{eq}^*/U_{eq}\) |
|-------|------------|------------|------------|----------------------|
| Co1   | 0.51335(2) | 0.27266(2) | 0.57458(2) | 0.01059(7)           |
| N1    | 0.67247(10)| 0.34371(7) | 0.62465(9) | 0.0153(2)            |
| C1    | 0.76466(12)| 0.38035(8) | 0.65618(11)| 0.0141(2)            |
| S1    | 0.89474(3) | 0.43141(2) | 0.70092(3) | 0.02407(10)          |
| N2    | 0.35462(10)| 0.20093(7) | 0.52823(9) | 0.0153(2)            |
| C2    | 0.25674(12)| 0.17255(8) | 0.49267(11)| 0.0134(2)            |
| S2    | 0.11817(3) | 0.13335(2) | 0.44031(3) | 0.01552(8)           |
| N11   | 0.48544(9) | 0.32562(7) | 0.39886(9) | 0.0110(2)            |
| N12   | 0.35142(10)| 0.34740(7) | 0.20867(9) | 0.0131(2)            |
| N13   | 0.49385(10)| 0.45980(7) | 0.29661(9) | 0.0127(2)            |
| N14   | 0.57416(10)| 0.32908(7) | 0.23263(9) | 0.0137(2)            |
| C11   | 0.36212(11)| 0.30856(8) | 0.32095(10)| 0.0123(2)            |
| H11A  | 0.349734   | 0.246546   | 0.312045   | 0.015*               |
| H11B  | 0.296401   | 0.331440   | 0.354686   | 0.015*               |
| C12   | 0.37105(12)| 0.44001(8) | 0.22303(11)| 0.0140(2)            |
| H12A  | 0.363639   | 0.466531   | 0.148044   | 0.017*               |
| H12B  | 0.306101   | 0.464431   | 0.256487   | 0.017*               |
| C13   | 0.58915(12)| 0.42110(8) | 0.24547(11)| 0.0147(2)            |
| H13A  | 0.583835   | 0.446900   | 0.170375   | 0.018*               |
| H13B  | 0.672136   | 0.433681   | 0.293783   | 0.018*               |
| C14   | 0.58124(11)| 0.29098(8) | 0.34359(11)| 0.0130(2)            |
| H14A  | 0.664260   | 0.301634   | 0.393063   | 0.016*               |
| H14B  | 0.570316   | 0.228850   | 0.334757   | 0.016*               |
| C15   | 0.45097(12)| 0.31188(8) | 0.15994(11)| 0.0147(2)            |
| H15A  | 0.439358   | 0.249853   | 0.150305   | 0.018*               |
| H15B  | 0.445047   | 0.337046   | 0.084374   | 0.018*               |
| C16   | 0.50169(12)| 0.41931(8) | 0.40684(11)| 0.0126(2)            |
| H16A  | 0.437357   | 0.443759   | 0.441062   | 0.015*               |
| H16B  | 0.583193   | 0.432292   | 0.457605   | 0.015*               |
| O21   | 0.41718(8) | 0.37678(6) | 0.62519(8) | 0.01481(19)          |
| H21   | 0.458750   | 0.419051   | 0.654234   | 0.022*               |
| C21   | 0.31119(12)| 0.36740(9) | 0.67299(12)| 0.0174(3)            |
| H21A  | 0.320943   | 0.404600   | 0.740012   | 0.021*               |
| H21B  | 0.306126   | 0.308048   | 0.697966   | 0.021*               |
| C22   | 0.19389(14)| 0.39014(12)| 0.58774(14)| 0.0295(3)            |
| H22A  | 0.181805   | 0.351233   | 0.523285   | 0.044*               |
| H22B  | 0.199742   | 0.448405   | 0.561561   | 0.044*               |
| H22C  | 0.123733   | 0.385578   | 0.622869   | 0.044*               |
| O31   | 0.62924(8) | 0.17312(6) | 0.54561(8) | 0.01390(18)          |
| H31   | 0.695985   | 0.172350   | 0.595461   | 0.021*               |
| C31   | 0.59743(13)| 0.08809(8) | 0.50586(12)| 0.0172(3)            |
| H31A  | 0.508810   | 0.085995   | 0.466374   | 0.021*               |
| H31B  | 0.610588   | 0.049076   | 0.571334   | 0.021*               |
| C32   | 0.67444(14)| 0.05882(9) | 0.42600(12)| 0.0210(3)            |
| H32A  | 0.658634   | 0.095774   | 0.359399   | 0.032*               |
|     | U11  | U22  | U33  | U12  | U13  | U23  |
|-----|------|------|------|------|------|------|
| Co1 | 0.00865 (11) | 0.01120 (12) | 0.01104 (12) | -0.00058 (7) | 0.00060 (8) | -0.00032 (7) |
| N1  | 0.0121 (5) | 0.0164 (5) | 0.0155 (5) | -0.0011 (4) | -0.0003 (4) | -0.0007 (4) |
| C1  | 0.0149 (6) | 0.0116 (6) | 0.0154 (6) | 0.0034 (5) | 0.0029 (5) | 0.0009 (5) |
| S1  | 0.01192 (16) | 0.01850 (17) | 0.0400 (2) | -0.00438 (12) | 0.00274 (14) | -0.00662 (14) |
| N2  | 0.0143 (5) | 0.0149 (5) | 0.0157 (5) | -0.0015 (4) | 0.0016 (4) | 0.0008 (4) |
| C2  | 0.0157 (6) | 0.0123 (6) | 0.0122 (5) | 0.0019 (5) | 0.0035 (5) | 0.0015 (4) |
| S2  | 0.01174 (15) | 0.01751 (16) | 0.01595 (15) | -0.00302 (11) | 0.00064 (11) | -0.00024 (11) |
| N11 | 0.0099 (5) | 0.0110 (5) | 0.0114 (5) | -0.0007 (4) | 0.0014 (4) | -0.0008 (4) |
| N12 | 0.0133 (5) | 0.0133 (5) | 0.0117 (5) | -0.0004 (4) | 0.0015 (4) | 0.0004 (4) |
| N13 | 0.0117 (5) | 0.0125 (5) | 0.0132 (5) | -0.0006 (4) | 0.0018 (4) | 0.0005 (4) |
| N14 | 0.0135 (5) | 0.0143 (5) | 0.0137 (5) | -0.0003 (4) | 0.0038 (4) | 0.0003 (4) |
| C11 | 0.0101 (5) | 0.0146 (6) | 0.0111 (6) | -0.0015 (4) | 0.0006 (4) | 0.0010 (4) |
| C12 | 0.0117 (6) | 0.0128 (6) | 0.0156 (6) | 0.0005 (4) | -0.0003 (5) | 0.0017 (5) |
| C13 | 0.0126 (6) | 0.0150 (6) | 0.0169 (6) | -0.0014 (5) | 0.0044 (5) | 0.0002 (5) |
| C14 | 0.0116 (6) | 0.0145 (6) | 0.0134 (6) | 0.0029 (5) | 0.0037 (5) | 0.0006 (5) |
| C15 | 0.0157 (6) | 0.0157 (6) | 0.0127 (6) | -0.0009 (5) | 0.0037 (5) | -0.0018 (5) |
| C16 | 0.0131 (6) | 0.0115 (6) | 0.0124 (5) | -0.0006 (4) | 0.0017 (5) | -0.0010 (4) |
| O21 | 0.0123 (4) | 0.0142 (4) | 0.0191 (5) | -0.0019 (3) | 0.0062 (4) | -0.0027 (3) |
| C21 | 0.0156 (6) | 0.0202 (7) | 0.0183 (6) | -0.0013 (5) | 0.0078 (5) | -0.0025 (5) |
| C22 | 0.0155 (7) | 0.0410 (9) | 0.0313 (8) | 0.0045 (6) | 0.0044 (6) | -0.0042 (7) |
| O31 | 0.0114 (4) | 0.0129 (4) | 0.0148 (4) | 0.0013 (3) | -0.0020 (3) | -0.0017 (3) |
| C31 | 0.0169 (6) | 0.0139 (6) | 0.0190 (6) | -0.0001 (5) | 0.0007 (5) | -0.0031 (5) |
| C32 | 0.0215 (7) | 0.0214 (7) | 0.0175 (6) | 0.0063 (5) | -0.0008 (5) | -0.0041 (5) |
| O41 | 0.0230 (5) | 0.0156 (5) | 0.0122 (4) | -0.0048 (3) | 0.0022 (4) | -0.0001 (3) |
| C41 | 0.0209 (7) | 0.0159 (6) | 0.0192 (6) | -0.0026 (5) | -0.0011 (5) | 0.0040 (5) |
| C42 | 0.0219 (8) | 0.0392 (9) | 0.0434 (10) | -0.0028 (7) | 0.0103 (7) | 0.0176 (8) |

**Geometric parameters (Å, °)**

| Bond | Distance (Å) | Angle (°) |
|------|--------------|-----------|
| Co1—N2 | 2.0615 (11) | C14—H14B | 0.9900 |
| Co1—N1 | 2.0624 (11) | C15—H15A | 0.9900 |
| Co1—O41 | 2.1021 (10) | C15—H15B | 0.9900 |
| Co1—O31 | 2.1157 (9) | C16—H16A | 0.9900 |
| Bond | Length (Å)          | Bond         | Angle (°)    |
|------|---------------------|--------------|--------------|
| Co1—O21 | 2.1314 (9)        | C16—H16B | 0.9900       |
| Co1—N11 | 2.2489 (11)       | O21—C21   | 1.4446 (15)  |
| N1—C1  | 1.1610 (18)        | O21—H21   | 0.8400       |
| C1—S1  | 1.6335 (13)        | C21—C22   | 1.505 (2)    |
| N2—C2  | 1.1625 (18)        | C21—H21A  | 0.9900       |
| C2—S2  | 1.6437 (13)        | C21—H21B  | 0.9900       |
| N11—C16 | 1.4889 (16)       | C22—H22A  | 0.9800       |
| N11—C11 | 1.4955 (15)       | C22—H22B  | 0.9800       |
| N11—C14 | 1.4957 (15)       | C22—H22C  | 0.9800       |
| N12—C11 | 1.4771 (15)       | C31—C31   | 1.4409 (16)  |
| N12—C12 | 1.4810 (16)       | O31—C31   | 0.8400       |
| N12—C15 | 1.4878 (16)       | C31—C32   | 1.5157 (19)  |
| N13—C16 | 1.4705 (16)       | C31—H31A  | 0.9900       |
| N13—C12 | 1.4783 (16)       | C31—H31B  | 0.9900       |
| N13—C13 | 1.4855 (16)       | C32—H32A  | 0.9800       |
| N14—C14 | 1.4640 (16)       | C32—H32B  | 0.9800       |
| N14—C13 | 1.4648 (17)       | C32—H32C  | 0.9800       |
| N14—C15 | 1.4695 (16)       | O41—C41   | 1.4339 (16)  |
| C11—H11A | 0.9900          | O41—H41   | 0.8400       |
| C11—H11B | 0.9900          | C41—C42   | 1.504 (2)    |
| C12—H12A | 0.9900          | C41—H41A  | 0.9900       |
| C12—H12B | 0.9900          | C41—H41B  | 0.9900       |
| C13—H13A | 0.9900          | C42—H42A  | 0.9800       |
| C13—H13B | 0.9900          | C42—H42B  | 0.9800       |
| C14—H14A | 0.9900          | C42—H42C  | 0.9800       |

N2—Co1—N1 178.73 (4) N14—C15—N12 111.62 (10)
N2—Co1—O41 90.12 (4) N14—C15—H15A 109.3
N1—Co1—O41 88.61 (4) N12—C15—H15A 109.3
N2—Co1—O31 93.75 (4) N14—C15—H15B 109.3
N1—Co1—O31 86.35 (4) N12—C15—H15B 109.3
O41—Co1—O31 88.09 (4) H15A—C15—H15B 108.0
N2—Co1—O21 92.51 (4) N13—C16—N11 113.06 (10)
N1—Co1—O21 87.27 (4) N13—C16—H16A 109.0
O41—Co1—O21 86.42 (4) N11—C16—H16A 109.0
O31—Co1—O21 171.68 (4) N11—C16—H16B 109.0
N2—Co1—N11 91.69 (4) N11—C16—H16B 109.0
N1—Co1—N11 89.57 (4) H16A—C16—H16B 107.8
O41—Co1—N11 177.25 (4) C21—O21—Co1 123.67 (8)
O31—Co1—N11 93.85 (4) C21—O21—H21 109.5
O21—Co1—N11 91.43 (4) Co1—O21—H21 117.9
C1—N1—Co1 176.60 (11) O21—C21—C22 110.89 (12)
N1—C1—N1 179.67 (14) N2—O21—Co1 109.5
C2—N2—Co1 168.63 (11) C22—C21—H21A 109.5
N2—C2—S2 179.00 (12) C22—C21—H21B 109.5
C16—N11—C11 107.39 (9) C22—C21—H21B 109.5
C16—N11—C14 107.64 (10) H21A—C21—H21B 108.0
C11—N11—C14 107.18 (10) C21—C22—H22A 109.5
| Bond                  | Distance (Å) | Angle (°) |
|-----------------------|--------------|-----------|
| C16—N11—Co1          | 108.63 (7)   |           |
| C11—N11—Co1          | 115.68 (7)   |           |
| C14—N11—Co1          | 110.02 (7)   |           |
| C11—N12—C12          | 108.83 (10)  |           |
| C11—N12—C15          | 108.14 (10)  |           |
| C12—N12—C15          | 108.38 (10)  |           |
| C16—N13—C12          | 107.78 (10)  |           |
| C16—N13—C13          | 108.23 (10)  |           |
| C12—N13—C13          | 108.07 (10)  |           |
| C14—N14—C13          | 109.17 (10)  |           |
| C14—N14—C15          | 108.43 (10)  |           |
| C13—N14—C15          | 108.26 (10)  |           |
| N12—C11—N11          | 111.76 (10)  |           |
| N12—C11—H11A         | 109.3        |           |
| N11—C11—H11A         | 109.3        |           |
| N12—C11—H11B         | 109.3        |           |
| N11—C11—H11B         | 109.3        |           |
| H11A—C11—H11B        | 107.9        |           |
| N13—C12—N12          | 111.64 (10)  |           |
| N13—C12—H12A         | 109.3        |           |
| N12—C12—H12A         | 109.3        |           |
| N12—C12—H12B         | 109.3        |           |
| H12A—C12—H12B        | 108.0        |           |
| N14—C13—N13          | 112.16 (10)  |           |
| N14—C13—H13A         | 109.2        |           |
| N13—C13—H13A         | 109.2        |           |
| N14—C13—H13B         | 109.2        |           |
| N13—C13—H13B         | 109.2        |           |
| H13A—C13—H13B        | 107.9        |           |
| N14—C14—N11          | 112.31 (10)  |           |
| N14—C14—H14A         | 109.1        |           |
| N11—C14—H14A         | 109.1        |           |
| N14—C14—H14B         | 109.1        |           |
| N11—C14—H14B         | 109.1        |           |
| H14A—C14—H14B        | 107.9        |           |

**Hydrogen-bond geometry (Å, °)**

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|-------|-------|---------|
| C12—H12A···S2i | 0.99 | 2.87  | 3.6586 (13) | 137 |
| C12—H12B···S1ii | 0.99 | 2.92  | 3.8813 (13) | 164 |
| C15—H15A···S1iii | 0.99 | 2.99  | 3.9387 (13) | 161 |
| C15—H15B···S2iv | 0.99 | 2.94  | 3.7110 (13) | 135 |
| C16—H16A···O21 | 0.99 | 2.54  | 3.1009 (16) | 116 |
| C16—H16B···N1 | 0.99 | 2.47  | 3.1083 (17) | 122 |
| O21—H21···N13ii | 0.84 | 2.03  | 2.8424 (14) | 161 |
| C22—H22C···S1v | 0.98 | 3.02  | 3.9559 (16) | 161 |
|      |     |     |          |     |
|------|-----|-----|----------|-----|
| O31—H31···N12\textsuperscript{vi} | 0.84 | 1.96 | 2.7969 (14) | 172 |
| O41—H41···S2\textsuperscript{vi} | 0.84 | 2.37 | 3.2080 (10) | 174 |

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