Crystal structure of diethanolbis(thiocyanato)bis-(urotropine)cobalt(II) and tetraethanolbis(thiocyanato)cobalt(II)—urotropine (1/2)

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The reaction of one equivalent Co(NCS)2 with four equivalents of urotropine (hexamethylenetetramine) in ethanol leads to the formation of two compounds, namely, bis(ethanol-kO)bis(thiocyanato-kN)bis(urotropine-kN)cobalt(II), [Co(NCS)2(C2H12N4)2(C2H6O)2] (1), and tetrakis(ethanol-kO)bis(thiocyanato-kN)cobalt(II)—urotropine (1/2), [Co(NCS)2(C2H6O)4]2C6H12N4 (2). In 1, the Co cations are located on centers of inversion and are sixfold coordinated by two terminal N-bonded thiocyanate anions, two ethanol and two urotropine ligands whereas in 2 the cobalt cations occupy position Wyckoff position c and are sixfold coordinated by two anionic ligands and four ethanol ligands. Compound 2 contains two additional urotropine solvate molecules per formula unit, which are hydrogen bonded to the complexes. In both compounds, the building blocks are connected via intermolecular O—H···N (1 and 2) and C—H···S (1) hydrogen bonding to form three-dimensional networks.

1. Chemical context

Thiocyanate anions are versatile ligands that exhibit a variety of coordination modes, leading to rich structural chemistry (Nätber et al., 2013). For less chalcophilic metal cations such as MnII, FeII, CoII or NiII, most compounds contain terminal N-bonded thiocyanate anions, whereas for chalcophilic metal cations such as for example CdII, the μ-1,3-bridging mode is preferred. Therefore, the synthesis of bridging compounds with the former cations is sometimes difficult to achieve, which is a pity, because such compounds are of interest due to their magnetic properties (Mautner et al., 2018; Mekuimemba et al., 2018; Mousavi et al., 2020; Palion-Gazda et al., 2015; Suckert et al., 2016). This is especially the case with cobalt, which frequently exhibits interesting behavior due to its large magnetic anisotropy, so we and others have been studying such compounds for several years (Shi et al., 2006; Jin et al., 2007; Wellm et al., 2020; Prananto et al., 2017). Within this project we are interested for example in the influence of the co-ligand on the magnetic anisotropy and the magnetic behavior of compounds, in which the cations are linked by thiocyanate anions into chains (Böhme et al., 2020; Rams et al., 2020; Ceglarska et al., 2021; Werner et al., 2014, 2015).

In the course of our systematic work, we became interested in urotropine as a co-ligand. Therefore, we reacted Co(NCS)2 with urotropine in acetonitrile, which leads to the formation of a compound with the composition [Co(NCS)2(H2O)2(urotropine)2]2(urotropine)2(MeCN)2 consisting of discrete
complexes, which are linked by urotropine and acetonitrile solvate molecules into a hydrogen-bonded network (Krebs et al., 2021). In principle, the formation of discrete solvato complexes would be no problem because in several cases such complexes can be transformed by thermal decomposition into the desired compounds with a bridging coordination of the anionic ligands (Näther et al., 2013), but XRPD measurements proved that this crystalline phase was not obtained pure.

In further work, we used ethanol as a solvent leading to the formation of two different crystals in the same batch that were characterized by single-crystal X-ray diffraction. The crystals in this batch were crushed and investigated by XRPD. Comparison of the experimental pattern with that calculated for 1 and 2 reveal that only 1 can be detected together with at least one additional and unknown crystalline phase. The reason for this observation is unclear, but it might be that 2 is unstable and transforms into a new phase on grinding.

2. Structural commentary

The asymmetric unit of 1, Co(NCS)$_2$(urotropine)$_2$(EtOH)$_2$, consists of one crystallographically independent Co cation, located on a center of inversion, as well as one thiocyanate anion, one urotropine ligand and one ethanol molecule occupying general positions (Fig. 1). In 2, [Co(NCS)$_2$(EtOH)$_4$](urotropine)$_2$, the asymmetric unit contains one cobalt cation on position of site symmetry 222 (Wyckoff position c), one thiocyanate anion that is located on a twofold rotation axis and one urotropine molecule on an inversion axis (Fig. 2). The Co—N distance to the thiocyanate anions in 1 is slightly shorter than in 2, whereas the Co—O bond length to the ethanol ligand is longer (compare Tables 1 and 2). The former can be traced back to the fact that in 2 the Co cation is exclusively coordinated by ethanol, whereas in 1 this cation is additionally coordinated by a urotropine ligand, which is a stronger donor than ethanol, transferring additional charge to the Co center. This leads to a strengthening of the Co—N thiocyanate bond and therefore this bond length is shorter. This is also supported by previous investigations when discrete complexes with an N$_6$ (four N atoms of N-donor co-

ligands) or N$_4$O$_2$ (two N-donor co-ligands and two e.g. water molecules) coordination were compared. For N$_4$O$_2$ coordination, the CN stretching vibration of the thiocyanate anions is significantly shifted to higher values, which indicates that the C—N bond becomes stronger, leading to a weakening of the
Co—N bond (Böhme et al., 2020). The angles around the Co
cations deviate from the ideal octahedral values, which shows
that the octahedra are slightly distorted (see supporting
information). The octahedron in 2 is more distorted than in 1,
which is obvious from the octahedral angle variance (1.8138
for 1 and 8.1624 for 2) and the mean octahedral quadratic
elongation (1.0062 for 1 and 1.0023 for 2) calculated by the
method of Robinson et al. (1971).

3. Supramolecular features
In the crystal structures of both compounds, intermolecular
hydrogen bonding is observed (Tables 3 and 4). In 1, the
discrete complexes are linked via intermolecular O—H···N
hydrogen bonding between the hydroxyl H atoms of one
complex and the N atoms of neighboring complexes into
chains extending in the a-axis direction (Fig. 3 and Table 3).
These chains are further linked into a three-dimensional
network by C—H···S hydrogen bonding between the thio-
cyanate S atoms and each one H atom of urotropine ligands
(Fig. 4). There are additional C—H···N and C—H···O
contacts but from the distances and angles it is indicated that
these are very weak interactions (Table 3).

Table 1
Selected bond lengths (Å) for 1.

| Bond         | Length (Å) |
|--------------|------------|
| Co1—N1       | 2.037 (2)  |
| Co1—N11      | 2.321 (2)  |

Table 2
Selected bond lengths (Å) for 2.

| Bond         | Length (Å) |
|--------------|------------|
| Co1—N1       | 2.078 (2)  |
| Co1—O1       | 2.0894 (15)|

Table 3
Hydrogen-bond geometry (Å, °) for 1.

| D—H···A     | D—H | H···A | D···A | D—H···A |
|-------------|------|-------|-------|---------|
| C13—H13B···S1i | 0.99 | 2.81  | 3.781 (3) | 168 |
| C14—H14A···S1ii | 0.99 | 2.98  | 3.816 (3) | 143 |
| C16—H16B···N1iii | 0.99 | 2.57  | 3.166 (3) | 119 |
| O1—H1···N1iv | 0.84 (2) | 2.05 (3) | 2.870 (3) | 165 (4) |
| C22—H22B···S1v | 0.98 | 3.02  | 3.989 (3) | 169 |

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

Table 4
Hydrogen-bond geometry (Å, °) for 2.

| D—H···A     | D—H | H···A | D···A | D—H···A |
|-------------|------|-------|-------|---------|
| O1—H1···N11 | 0.87 (2) | 1.95 (2) | 2.799 (3) | 163 (4) |
| C2—H2B···N1i | 0.99 | 2.68  | 3.211 (3) | 114 |

Symmetry code: (i) −x+1, −y+2, z.

Figure 3
Crystal structure of compound 1 with a view of a chain formed by
intermolecular O—H···N hydrogen bonding along the crystallographic
a-axis. Intermolecular hydrogen bonding is shown as dashed lines.

Figure 4
Crystal structure of compound 1 with a view along the crystallographic a-
axis with intermolecular C—H···S hydrogen bonding shown as dashed lines.

Figure 5
Crystal structure of compound 2 with a view along the crystallographic a-
axis with intermolecular O—H···N hydrogen bonding shown as dashed lines.
In the crystal structure of 2, each complex is linked to neighboring complexes via intermolecular O—H···N hydrogen bonds between the four O—H hydrogen atoms of one complex and the N atoms of the urotropine molecules of four neighboring complexes to form a three-dimensional network (Fig. 5 and Table 4). From the H···N distance and the O—H···N angle it is obvious that this corresponds to a strong interaction. In contrast to 1, no C—H···S hydrogen bonding is observed and the additional C—H···N contact represents a weak interaction (Table 4).

4. Database survey

The Cambridge structure Database (CSD version 5.42, last update November 2020; Groom et al., 2016) already contains some structures of transition-metal thio cyanate coordination compounds with urotropine as a co-ligand. This includes a mixed complex with the composition [Co(NCS)2(C6H12N4)2(CH3OH)(H2O)2] (Refcode: XILXOG; Li et al., 1999), which the cobalt cations are coordinated by water, ethanol, urotropine and N-bonded thio cyanate anions (Refcode: POFGAT; Shang et al., 2008). It also contains two compounds with the composition [Co(NCS)2(C6H12N4)2(H2O)2](H2O)2 (Refcode: XILXOG; Li et al., 2007) and [Co(NCS)2(C6H12N4)2(H2O)4][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), that also form discrete complexes with terminal N-bonded thio cyanate anions. The structure of thio cyanates including, for example, nickel (Refcode: XILROA; Bai et al., 2007, XILROA01; Liu et al., 2010) and zinc (Refcode: SIMXY; Kruszynski & Swiatkowski, 2018), but none of them contains ethanol as a co-ligand. The latter structure with the composition [Zn(NCS)2(urotropine)(H2O)2]·(H2O)2 contains two different complexes, one of them similar to 1 and the second similar to 2 with the difference that the EtOH is exchanged by water.

Finally, it is noted that with cadmium and mercury a crystal structure with urotropine is reported in which the Cd cations are linked by pairs of thiocyanate anions into chains (Refcode: DIJSIY; Mak & Wu, 1985). The formation of such a compound can be traced back to the fact that cadmium and mercury are much more chalcophilic than cobalt. There is one additional structure with cadmium similar to that mentioned above. In this structure, the cadmium cations are linked by pairs of thiocyanate anions into chains that are either connected by two EtOH molecules or urotro-
pine ligands, which connect neighboring chains (FEWZ0Y; Barszcz et al., 2013).

5. Synthesis and crystallization

**Synthesis** Co(NCS)$_2$ and urotropine were purchased from Merck. All chemicals were used without further purification.

Single crystals of 1 and 2 were obtained by reacting 0.15 mmol of Co(NCS)$_2$ (26.3 mg) with 0.6 mmol of urotropine (84.1 mg) in 1 mL of ethanol after one day.

**Experimental details**

The data collection for single crystal structure analysis was performed using a Rigaku XtaLAB Synergy Dualflex kappa-diffractometer equipped with HyPix hybrid photon counting HPC detector, using Cu-Kα radiation from a PhotonJet micro-focus X-ray source.

The PXRD measurements were performed with Cu Kα$_1$ 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.

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 positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined isotropically with $U_{	ext{iso}}$(H) = 1.2$U_{	ext{eq}}$(C) (1.5 for methyl H atoms). The O—H hydrogen atoms were located in the difference map and were refined with restraints for the O—H distance (DFIX) and varying isotropic displacement parameters. The crystal of 1 was twinned by non-merohedry and therefore, a twin refinement using data in HKLF-5 format was performed where all equivalents were merged [BASF parameter = 0.309 (1)].

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Crystal structure of diethanolbis(thiocyanato)bis(urotropine)cobalt(II) and tetra-ethanolbis(thiocyanato)cobalt(II)–urotropine (1/2)

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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); program(s) used to refine structure: SHELXL2016/6 (Sheldrick, 2015b); molecular graphics: DIAMOND (Brandenburg & Putz, 1999); software used to prepare material for publication: publCIF (Westrip, 2010).

Bis(ethanol-κO)bis(thiocyanato-κN)bis(urotropine-κN)cobalt(II) (1)

Crystal data
[Co(NCS)₂(C₆H₁₂N₄)(C₂H₆O)₂]
Mr = 547.62
Monoclinic, P2₁/n
a = 7.73205 (19) Å
b = 11.5092 (3) Å
c = 13.6693 (3) Å
β = 95.376 (2)°
V = 1211.08 (5) Å³
Z = 2

F(000) = 578
Dₐ = 1.502 Mg m⁻³
Cu Kα radiation, λ = 1.54184 Å

Cell parameters from 16954 reflections
θ = 5.0–79.3°
µ = 7.48 mm⁻¹
T = 100 K
Needle, light pink
0.12 × 0.03 × 0.02 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)

Tmin = 0.586, Tmax = 1.000
4731 measured reflections
4731 independent reflections
4504 reflections with I > 2σ(I)
θmax = 80.3°, θmin = 5.0°
h = −9→9
k = −14→14
l = −16→17

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.044
wR(F²) = 0.124
S = 1.06
4731 reflections
157 parameters
1 restraint
Primary atom site location: dual

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(Fo²) + (0.0719P)² + 0.7955P]
where P = (Fo² + 2Fc²)/3
(D/σ)max < 0.001
Δρmax = 0.63 e Å⁻³
Δρmin = −0.43 e Å⁻³

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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.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| Atom | x   | y   | z   | Uiso*/Ueq |
|------|-----|-----|-----|-----------|
| Co1  | 0.500000 | 0.500000 | 0.500000 | 0.01842 (17) |
| N1   | 0.3761 (3) | 0.35322 (18) | 0.44802 (17) | 0.0228 (4) |
| C1   | 0.3160 (3) | 0.2624 (2) | 0.43241 (18) | 0.0227 (5) |
| S1   | 0.23069 (10) | 0.13371 (6) | 0.41163 (5) | 0.0324 (2) |
| N11  | 0.6678 (3) | 0.50619 (16) | 0.36795 (16) | 0.0187 (4) |
| C11  | 0.6534 (3) | 0.3991 (2) | 0.30608 (19) | 0.0225 (5) |
| H11A | 0.682796 | 0.330698 | 0.348296 | 0.027* |
| H11B | 0.531562 | 0.390244 | 0.277616 | 0.027* |
| N12  | 0.7674 (3) | 0.40116 (19) | 0.22623 (16) | 0.0240 (5) |
| C12  | 0.9479 (4) | 0.4157 (2) | 0.2689 (2) | 0.0244 (5) |
| H12A | 1.025654 | 0.417629 | 0.215328 | 0.029* |
| H12B | 0.981359 | 0.348202 | 0.311347 | 0.029* |
| N13  | 0.9718 (3) | 0.52416 (19) | 0.32779 (16) | 0.0216 (4) |
| C13  | 0.9175 (3) | 0.6229 (2) | 0.2625 (2) | 0.0226 (5) |
| H13A | 0.930800 | 0.696067 | 0.300510 | 0.027* |
| H13B | 0.994929 | 0.627096 | 0.208895 | 0.027* |
| N14  | 0.7371 (3) | 0.61247 (18) | 0.21969 (16) | 0.0211 (4) |
| C14  | 0.6256 (3) | 0.6071 (2) | 0.30005 (19) | 0.0203 (5) |
| H14A | 0.503020 | 0.600855 | 0.272245 | 0.024* |
| H14B | 0.637958 | 0.680151 | 0.338260 | 0.024* |
| C15  | 0.7207 (4) | 0.5030 (2) | 0.1637 (2) | 0.0244 (6) |
| H15A | 0.797350 | 0.505963 | 0.109629 | 0.029* |
| H15B | 0.599568 | 0.494447 | 0.134039 | 0.029* |
| C16  | 0.8536 (3) | 0.5178 (2) | 0.40565 (19) | 0.0199 (5) |
| H16A | 0.867948 | 0.588774 | 0.446484 | 0.024* |
| H16B | 0.886778 | 0.450435 | 0.448420 | 0.024* |
| O1   | 0.2998 (2) | 0.60272 (15) | 0.41991 (14) | 0.0217 (4) |
| H1   | 0.215 (4) | 0.570 (4) | 0.389 (3) | 0.058 (13)* |
| C21  | 0.2958 (3) | 0.7251 (2) | 0.3965 (2) | 0.0248 (5) |
| H21A | 0.257744 | 0.734961 | 0.325847 | 0.030* |
| H21B | 0.414779 | 0.757096 | 0.408512 | 0.030* |
| C22  | 0.1752 (4) | 0.7938 (2) | 0.4565 (2) | 0.0287 (6) |
| H22A | 0.056867 | 0.763078 | 0.444535 | 0.043* |
| H22B | 0.176250 | 0.875727 | 0.437066 | 0.043* |
| H22C | 0.214619 | 0.786813 | 0.526478 | 0.043* |
### Atomic displacement parameters (Å²)

|     | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|
| Co  | 0.0184 (3)| 0.0121 (3)| 0.0244 (3)| −0.00104 (19)| 0.0005 (2)| −0.0001 (2)|
| N1  | 0.0221 (10)| 0.0161 (10)| 0.0303 (11)| −0.0029 (8)| 0.0037 (8)| −0.0025 (8)|
| C1  | 0.0216 (11)| 0.0232 (12)| 0.0236 (11)| 0.0011 (9)| 0.0038 (9)| −0.0023 (10)|
| S1  | 0.0378 (4)| 0.0239 (3)| 0.0362 (4)| −0.0115 (3)| 0.0076 (3)| −0.0050 (3)|
| N11 | 0.0193 (10)| 0.0150 (10)| 0.0215 (10)| −0.0013 (7)| 0.0006 (8)| 0.0007 (7)|
| C11 | 0.0262 (12)| 0.0160 (11)| 0.0250 (12)| −0.0013 (9)| 0.0008 (10)| −0.0009 (10)|
| N12 | 0.0314 (12)| 0.0179 (10)| 0.0229 (10)| 0.0009 (8)| 0.0031 (9)| −0.0016 (8)|
| C12 | 0.0269 (13)| 0.0199 (12)| 0.0270 (13)| 0.0040 (10)| 0.0050 (10)| 0.0012 (10)|
| N13 | 0.0219 (10)| 0.0193 (10)| 0.0239 (10)| 0.0014 (8)| 0.0028 (8)| 0.0016 (9)|
| C13 | 0.0220 (12)| 0.0196 (11)| 0.0264 (13)| −0.0003 (9)| 0.0034 (10)| 0.0031 (10)|
| N14 | 0.0235 (10)| 0.0172 (9)| 0.0225 (10)| 0.0006 (8)| 0.0013 (8)| 0.0019 (8)|
| C14 | 0.0214 (11)| 0.0153 (11)| 0.0240 (12)| 0.0018 (9)| 0.0007 (10)| 0.0010 (9)|
| C15 | 0.0303 (14)| 0.0210 (13)| 0.0216 (13)| 0.0005 (9)| 0.0006 (11)| 0.0007 (9)|
| C16 | 0.0194 (11)| 0.0181 (10)| 0.0221 (12)| 0.0001 (9)| 0.0009 (9)| 0.0016 (9)|
| O1  | 0.0210 (8)| 0.0143 (8)| 0.0297 (9)| 0.0002 (6)| 0.0009 (7)| 0.0034 (7)|
| C21 | 0.0248 (12)| 0.0171 (11)| 0.0328 (13)| 0.0001 (9)| 0.0036 (10)| 0.0033 (10)|
| C22 | 0.0333 (14)| 0.0217 (12)| 0.0305 (13)| 0.0027 (10)| 0.0005 (11)| −0.0029 (11)|

### Geometric parameters (Å, °)

| Bond/Angle | Distance/Angle |
|------------|---------------|
| Co1—N1 | 2.037 (2) |
| Co1—N1 | 2.037 (2) |
| Co1—N1 | 2.321 (2) |
| Co1—N1 | 2.321 (2) |
| Co1—O1 | 2.1620 (18) |
| Co1—O1 | 2.1620 (18) |
| N1—C1 | 1.156 (3) |
| C1—S1 | 1.635 (3) |
| N11—C11 | 1.493 (3) |
| N11—C14 | 1.503 (3) |
| N11—C16 | 1.486 (3) |
| C11—H11A | 0.9900 |
| C11—H11B | 0.9900 |
| C11—N12 | 1.466 (3) |
| N12—C12 | 1.471 (4) |
| N12—C15 | 1.475 (3) |
| C12—H12A | 0.9900 |
| C12—H12B | 0.9900 |
| C12—N13 | 1.487 (3) |
| N13—C13 | 1.481 (3) |
| N1—Co1—N1 | 180.0 |
| N1—Co1—N11 | 91.89 (8) |
| N1—Co1—N11 | 91.89 (8) |
| N1—Co1—N11 | 91.89 (8) |

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| Bond                  | Angle (°)       | Bond                  | Angle (°)       |
|----------------------|-----------------|----------------------|-----------------|
| N1—Co1—N11i          | 88.11 (8)       | N14—C13—H13B        | 109.1           |
| N1i—Co1—O1i          | 89.19 (8)       | C13—N14—C15         | 108.0 (2)       |
| N1—Co1—O1            | 89.19 (8)       | C14—N14—C13         | 108.1 (2)       |
| N1—Co1—O1i           | 90.81 (8)       | N11—C14—H14A        | 109.0           |
| N1i—Co1—N11i         | 180.0           | N11—C14—H14B        | 109.0           |
| O1—Co1—N11           | 90.87 (7)       | N14—C14—N11         | 112.8 (2)       |
| O1i—Co1—N11i         | 89.13 (7)       | N14—C14—H14A        | 109.0           |
| O1—Co1—N11i          | 90.87 (7)       | H14A—C14—H14B       | 107.8           |
| O1i—Co1—O1           | 89.13 (7)       | N12—C15—H15A        | 109.2           |
| C1—N1—Co1            | 169.3 (2)       | N12—C15—H15B        | 109.2           |
| N1—C1—S1             | 179.4 (3)       | N14—C15—N12         | 111.9 (2)       |
| C11—N11—Co1          | 113.44 (15)     | N14—C15—H15A        | 109.2           |
| C11—N11—C14          | 106.7 (2)       | N14—C15—H15B        | 109.2           |
| C14—N11—Co1          | 113.53 (15)     | H15A—C15—H15B       | 107.9           |
| C16—N11—Co1          | 109.01 (16)     | N11—C16—H16A        | 108.8           |
| C16—N11—C11          | 106.79 (19)     | N11—C16—H16B        | 108.8           |
| C16—N11—C14          | 106.96 (19)     | N13—C16—N11         | 113.6 (2)       |
| N11—C11—H11A         | 109.0           | N13—C16—H16A        | 108.8           |
| N11—C11—H11B         | 109.0           | N13—C16—H16B        | 108.8           |
| H11A—C11—H11B        | 107.8           | H16A—C16—H16B       | 107.7           |
| N12—C11—N11          | 113.0 (2)       | Co1—O1—Co1          | 130.16 (16)     |
| N12—C11—H11A         | 109.0           | C21—O1—Co1          | 109 (3)         |
| N12—C11—H11B         | 109.0           | C21—O1—H1           | 109.0           |
| C11—N12—C12          | 108.7 (2)       | O1—C21—H21A         | 109.0           |
| C11—N12—C15          | 108.2 (2)       | O1—C21—H21B         | 109.0           |
| C12—N12—C15          | 108.1 (2)       | O1—C21—C22          | 112.9 (2)       |
| N12—C12—H12A         | 109.2           | H21A—C21—H21B       | 107.8           |
| N12—C12—H12B         | 109.2           | C22—C21—H21A        | 109.0           |
| N12—C12—N13          | 112.0 (2)       | C22—C21—H21B        | 109.0           |
| H12A—C12—H12B        | 107.9           | C21—C22—H22A        | 109.5           |
| N13—C12—H12A         | 109.2           | C21—C22—H22B        | 109.5           |
| N13—C12—H12B         | 109.2           | C21—C22—H22C        | 109.5           |
| C13—N13—C12          | 107.7 (2)       | H22A—C22—H22B       | 109.5           |
| C16—N13—C12          | 107.3 (2)       | H22A—C22—H22C       | 109.5           |
| C16—N13—C13          | 108.4 (2)       | H22B—C22—H22C       | 109.5           |
| N13—C13—H13A         | 109.1           |                     |                 |
| Co1—N11—C11—N12      | −176.71 (16)    | C12—N13—C16—N11    | −59.2 (3)       |
| Co1—N11—C14—N14      | 177.58 (15)     | N13—C13—N14—C14    | 59.1 (3)        |
| Co1—N11—C16—N13      | −179.20 (15)    | N13—C13—N14—C15    | −58.7 (3)       |
| Co1—O1—C21—C22       | −107.1 (2)      | C13—N13—C16—N11    | 56.8 (3)        |
| N11—C11—N12—C12      | 58.0 (3)        | C13—N14—C14—N11    | −59.3 (3)       |
| N11—C11—N12—C15      | −59.2 (3)       | C13—N14—C15—N12    | 59.0 (3)        |
| C11—N11—C14—N14      | −56.7 (3)       | C14—N11—C11—N12    | 57.5 (3)        |
| C11—N11—C16—N13      | 57.9 (3)        | C14—N11—C16—N13    | −56.1 (3)       |
| C11—N12—C12—N13      | −58.6 (3)       | C14—N14—C15—N12    | −58.2 (3)       |
C11—N12—C15—N14  58.4 (3)  C15—N12—C12—N13  58.7 (3)
N12—C12—N13—C13  −57.9 (3)  C15—N14—C14—N11  57.9 (3)
N12—C12—N13—C16  58.6 (3)  C16—N11—C14—N14  57.3 (3)
C12—N12—C15—N14  −59.2 (3)  C16—N13—C13—N14  −57.7 (3)
N12—C12—N13—C16  58.6 (3)  C15—N14—C14—N11  57.9 (3)
C12—N12—C15—N14  −59.2 (3)  C16—N11—C14—N14  57.3 (3)
Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H  | H···A  | D···A  | D—H···A |
|-----------|-------|--------|--------|---------|
| C13—H13B···S1ii | 0.99  | 2.81   | 3.781 (3) | 168     |
| C14—H14A···S1ii | 0.99  | 2.98   | 3.816 (3) | 143     |
| C16—H16A···N1i  | 0.99  | 2.57   | 3.166 (3) | 119     |
| C16—H16B···O1i  | 0.99  | 2.49   | 3.090 (3) | 119     |
| O1—H1···N13iv   | 0.84 (2) | 2.05 (3) | 2.870 (3) | 165 (4) |
| C22—H22B···S1v  | 0.98  | 3.02   | 3.989 (3) | 169     |

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

Tetrakis(ethanol-κO)bis(thiocyanato-κN)cobalt(II)–urotropine (1/2) (2)

Crystal data

[Co(NCS)2(C2H6O)4]·2C6H12N4
Mr = 499.56
Tetragonal, P4n2
a = 9.69601 (6) Å
c = 12.94912 (14) Å
V = 1217.38 (2) Å³
Z = 2
F(000) = 530

Data collection

XtaLAB Synergy, Dualflex, HyPix
diffraclor
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)] = 0.024
wR(F²) = 0.064
S = 1.08
1343 reflections
75 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

Refinement on F²

w = 1/[σ²(F²) + (0.0326P)² + 0.587P]
where P = (F² + 2F Gibson)

(Δ/σ)max < 0.001
Δρmax = 0.20 e Å⁻³
Δρmin = −0.37 e Å⁻³

Extinction correction: SHELXL-2016/6
(Sheldrick 2016),
Fc = kFc[1+0.001xFc²/sin(2θ)]¹/⁴
Extinction coefficient: 0.0019 (4)
Absolute structure: $F([F^+]-[F^-])/[F^+]+[F^-]$ lack $x$ determined using 573 quotients
(Parsons et al., 2013)
Absolute structure parameter: 0.0070 (19)

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 ($\AA^2$)

|           | x        | y        | z        | $U_{\text{iso}}/U_{\text{eq}}$ | Occ. (<1) |
|-----------|----------|----------|----------|-----------------------------|-----------|
| Co1       | 0.500000 | 1.000000 | 0.750000 | 0.01833 (18)                |           |
| N1        | 0.34847 (17) | 0.84847 (17) | 0.750000 | 0.0233 (5)                  |           |
| C1        | 0.2634 (2) | 0.7634 (2) | 0.750000 | 0.0212 (5)                  |           |
| S1        | 0.14431 (5) | 0.64431 (5) | 0.750000 | 0.0340 (2)                  |           |
| O1        | 0.5977 (2) | 0.88742 (18) | 0.86662 (13) | 0.0275 (4)                |           |
| H1        | 0.587 (4) | 0.799 (2) | 0.875 (3) | 0.048 (10)*                |           |
| C2        | 0.7177 (3) | 0.9247 (3) | 0.9237 (2) | 0.0361 (6)                  |           |
| H2A       | 0.709202 | 0.890137 | 0.995411 | 0.043*                      |           |
| H2B       | 0.725516 | 1.026420 | 0.926484 | 0.043*                      |           |
| C3        | 0.8444 (3) | 0.8658 (4) | 0.8752 (3) | 0.0557 (10)                |           |
| H3A       | 0.852958 | 0.900109 | 0.804352 | 0.084*                      |           |
| H3B       | 0.837857 | 0.764901 | 0.874324 | 0.084*                      |           |
| H3C       | 0.925615 | 0.893581 | 0.915212 | 0.084*                      |           |
| N11       | 0.54520 (19) | 0.61785 (19) | 0.93312 (14) | 0.0186 (4)                |           |
| C11       | 0.500000 | 0.500000 | 0.8688 (2) | 0.0197 (6)                  |           |
| H11A      | 0.577109 | 0.470426 | 0.823830 | 0.024*                      | 0.5       |
| H11B      | 0.422888 | 0.529574 | 0.823832 | 0.024*                      | 0.5       |
| C12       | 0.6597 (2) | 0.5713 (2) | 0.99965 (16) | 0.0195 (4)                |           |
| H12A      | 0.690997 | 0.649175 | 1.043227 | 0.023*                      |           |
| H12B      | 0.738159 | 0.542300 | 0.955816 | 0.023*                      |           |

Atomic displacement parameters ($\AA^2$)

|        | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|--------|----------|----------|----------|----------|----------|----------|
| Co1    | 0.0176 (2) | 0.0176 (2) | 0.0198 (3) | −0.0025 (2) | 0.000 | 0.000 |
| N1     | 0.0229 (7) | 0.0229 (7) | 0.0241 (11) | −0.0033 (9) | 0.0000 (9) | 0.0000 (9) |
| C1     | 0.0203 (8) | 0.0203 (8) | 0.0230 (12) | 0.0031 (10) | −0.0012 (10) | 0.0012 (10) |
| S1     | 0.0265 (3) | 0.0265 (3) | 0.0488 (5) | −0.0090 (3) | −0.0070 (3) | 0.0070 (3) |
| O1     | 0.0293 (9) | 0.0198 (8) | 0.0332 (8) | −0.0061 (6) | −0.0102 (7) | 0.0058 (7) |
| C2     | 0.0442 (16) | 0.0289 (12) | 0.0352 (13) | −0.0127 (11) | −0.0183 (12) | 0.0089 (11) |
| C3     | 0.0286 (14) | 0.074 (2) | 0.064 (2) | −0.0106 (15) | −0.0070 (15) | 0.0378 (19) |
| N11    | 0.0164 (8) | 0.0185 (8) | 0.0210 (8) | 0.0007 (7) | 0.0006 (7) | 0.0021 (7) |
| C11    | 0.0193 (14) | 0.0198 (14) | 0.0199 (14) | 0.0005 (11) | 0.000 | 0.000 |
| C12    | 0.0164 (10) | 0.0194 (11) | 0.0226 (10) | −0.0016 (8) | −0.0021 (8) | 0.0016 (8) |
### Geometric parameters (Å, °)

| Bond/Angle/Distance | Value 1 | Value 2 | Value 3 |
|---------------------|---------|---------|---------|
| Co1—NI1             | 2.078 (2) | C2—C3  | 1.494 (5) |
| Co1—N1              | 2.078 (2) | C3—H3A | 0.9800 |
| Co1—O1              | 2.0894 (15) | C3—H3B | 0.9800 |
| Co1—O1i             | 2.0894 (15) | C3—H3C | 0.9800 |
| Co1—O1ii            | 2.0894 (15) | N11—C11 | 1.481 (2) |
| Co1—O1iii           | 2.0894 (15) | N11—C12iv | 1.483 (3) |
| N1—C1               | 1.166 (4) | N11—C12 | 1.476 (3) |
| C1—S1               | 1.633 (3) | C11—H11A | 0.9900 |
| O1—H1               | 0.87 (2) | C11—H11B | 0.9900 |
| O1—C2               | 1.426 (3) | C12—H12A | 0.9900 |
| C2—H2A              | 0.9900 | C12—H12B | 0.9900 |
| C2—H2B              | 0.9900 | |
| Ni1—Co1—N1          | 180.0 | C3—C2—H2A | 109.5 |
| Ni1—Co1—O1i         | 92.80 (6) | C3—C2—H2B | 109.5 |
| Ni1—Co1—O1iii       | 92.80 (6) | C2—C3—H3A | 109.5 |
| Ni1—Co1—O1ii        | 92.80 (6) | C2—C3—H3B | 109.5 |
| Ni1—Co1—O1iii       | 87.20 (6) | C2—C3—H3C | 109.5 |
| Ni1—Co1—O1ii        | 87.20 (6) | H3A—C3—H3B | 109.5 |
| Ni1—Co1—O1          | 87.20 (6) | H3A—C3—H3C | 109.5 |
| Ni1—Co1—O1i         | 87.20 (6) | H3B—C3—H3C | 109.5 |
| Ni1—Co1—O1          | 92.80 (6) | C11—N11—C12v | 108.42 (15) |
| O1i—Co1—O1i         | 174.40 (11) | C12—N11—C11 | 108.38 (16) |
| O1i—Co1—O1ii        | 87.54 (9) | C12—N11—C12v | 108.31 (13) |
| O1i—Co1—O1i         | 87.53 (9) | N11—C11—N11v | 111.5 (2) |
| O1i—Co1—O1i         | 92.74 (9) | N11v—C11—H11A | 109.3 |
| O1i—Co1—O1i         | 174.40 (11) | N11—C11—H11A | 109.3 |
| O1i—Co1—O1           | 92.74 (10) | N11—C11—H11B | 109.3 |
| C1—N1—Co1           | 180.00 (18) | N11v—C11—H11B | 109.3 |
| N1—C1—S1            | 180.0 (2) | H11A—C11—H11B | 108.0 |
| Co1—O1—H1           | 123 (2) | N11—C12—N11v | 111.70 (19) |
| C2—O1—Co1           | 127.80 (16) | N11—C12—H12A | 109.3 |
| C2—O1—H1            | 107 (2) | N11v—C12—H12A | 109.3 |
| O1—C2—H2A           | 109.5 | N11—C12—H12B | 109.3 |
| O1—C2—H2B           | 109.5 | N11v—C12—H12B | 109.3 |
| O1—C2—C3            | 110.8 (3) | H12A—C12—H12B | 107.9 |
| H2A—C2—H2B          | 108.1 | |

| Angle/Distance       | Value 1  | Value 2  | Value 3  |
|----------------------|-----------|-----------|-----------|
| Co1—O1—C2—C3        | −94.0 (2) | C12v—N11—C11—N11v | −58.55 (12) |
| C11—N11—C12—N11v    | −58.9 (2) | C12v—N11—C12—N11v | 58.52 (16) |
| C12—N11—C11—N11v    | 58.80 (12) | |

Symmetry codes: (i) −x+1, −y+2, z; (ii) y−1/2, x+1/2, −z+3/2; (iii) −y+3/2, −x+3/2, −z+3/2; (iv) −y+1, x, −z+2; (v) −x+1, −y+1, z; (vi) y, −x+1, −z+2.
**Hydrogen-bond geometry (Å, °)**

|        | D—H   | H···A | D···A | D—H···A |
|--------|-------|-------|-------|---------|
| O1—H1···N11 | 0.87 (2) | 1.95 (2) | 2.799 (3) | 163 (4) |
| C2—H2B···N1i | 0.99  | 2.68  | 3.211 (3) | 114     |

Symmetry code: (i) −x+1, −y+2, z.