Comparison of the crystal structures of the low- and high-temperature forms of bis[4-(dimethylamino)pyridine]dithiocyanatocobalt(II)

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Single crystals of the high-temperature form I of [Co(NCS)₂(DMAP)₂] (DMAP = 4-dimethylaminopyridine, C₇H₁₀N₂) were obtained accidentally by the reaction of Co(NCS)₂ with DMAP at slightly elevated temperatures under kinetic control. This modification crystallizes in the monoclinic space group P₂₁/m and is isotypic with the corresponding Zn compound. The asymmetric unit consists of one crystallographically independent Co cation and two crystallographically independent thiocyanate anions that are located on a crystallographic mirror plane and one DMAP ligand (general position). In its crystal structure the discrete complexes are linked by C—H···S hydrogen bonds into a three-dimensional network. For comparison, the crystal structure of the known low-temperature form II, which is already thermodynamically stable at room temperature, was redetermined at the same temperature. In this polymorph the complexes are connected by C—H···S and C—H···N hydrogen bonds into a three-dimensional network. At 100 K the density of the high-temperature form I (ρ = 1.462 g cm⁻³) is higher than that of the low-temperature form II (ρ = 1.457 g cm⁻³), which is in contrast to the values determined by XRPD at room temperature. Therefore, these two forms represent an exception to the Kitaigorodskii density rule, for which extensive intermolecular hydrogen bonding in form II might be responsible.

1. Chemical context

Polymorphism and isomerism is a widespread phenomenon in coordination chemistry (Braga & Grepioni, 2000; Moulton & Zaworotko, 2001; Batten et al., 1998; Zhang et al., 2009). On one hand, these phenomena are a disadvantage for rational crystal design, but on the other hand they are of advantage for studying structure–property relationships (Braga et al., 2001; Tao et al., 2012; Ossinger et al., 2020; Sheu et al., 2009). Because in such a case the composition of the different forms is identical, all changes in the physical properties can be directly correlated with the structural changes. One class of compounds in which polymorphism and especially isomerism is observed are coordination compounds based on transition-metal thiocyanates, because this anionic ligand shows several different coordination modes leading to a large structural variability (Böhme et al., 2020; Jochim et al., 2020; Mautner et al., 2018; Neumann et al., 2020a; Wellin et al., 2020a; Werner et al., 2015; Buckingham, 1994; Barnett et al., 2002).

In this context, we have recently reported the crystal structure of form II of Co(NCS)₂(DMAP)₂ (DMAP = 4-dimethylaminopyridine, C₇H₁₀N₂), which crystallizes as discrete complexes in which the cobalt cations are tetrahedrally coor-
This modification can directly be obtained from the reaction of Co(NCS)_2 and 4-dimethylaminopyridine in aqueous solution or by thermal decomposition of Co(NCS)_2(DMAP)_2(H_2O)_2-dihydrate (Neumann et al., 2018a). In contrast, if the methanol complex Co(NCS)_2(DMAP)_2(MeOH)_2 is thermally decomposed, a new polymorphic modification of Co(NCS)_2(DMAP)_2 (form I) is obtained. Because we were not able to prepare single crystals of this form, the corresponding Zn complex was prepared and XRPD indicates that it is isotypic to form I of the Co compound (Neumann et al., 2018b). Solvent-mediated conversion experiments reveal that form II is the thermodynamically stable form at room temperature and transforms into form I upon heating. Both forms are related by enantiotropism and the thermodynamic transition temperature was determined to be above 135°C. The metastability of form I at room temperature might be the reason why no single crystals were obtained. It is noted that in contrast to the Co modification I, the corresponding Zn form is already thermodynamically stable at room temperature, which might be the reason that single crystals of this form can easily be prepared from solution (Neumann et al., 2020a,b).

Later on, we investigated whether the physical properties of thiocyanate coordination compounds can be influenced by mixed crystal formation and we found out that, for example, the critical temperature in layered thiocyanate networks can be tuned by preparing mixed crystals with Co(NCS)_2 and Ni(NCS)_2 where a linear increase of T_c with increasing Co content was observed (Neumann et al., 2018b; Wellm et al., 2018, 2020b). In the course of our systematic work, we are currently investigating whether mixed crystals of Ni(NCS)_2(DMAP)_2 and Co(NCS)_2(DMAP)_2 can be prepared. As already noted, the Co compound forms discrete complexes whereas the Ni compound shows a chain structure (Jochim et al., 2018). Preliminary XRPD investigations indicate that, in those cases where more than 50% Co(NCS)_2 is used in the synthesis, a very small amount of form I of Co(NCS)_2(DMAP)_2 is formed as a side phase. This is in agreement with crystallization experiments to obtain single crystals where Co(NCS)_2 and Ni(NCS)_2 were used in a 90:10 ratio, because block-shaped and needle-like crystal are visible. Both of them were identified by single crystal X-ray diffraction, which proves that the block-like crystals correspond to the unit cell of the Ni compound, whereas the needle-like crystals correspond to the metastable form I of Co(NCS)_2(DMAP)_2, which was obviously obtained accidentally under kinetic control. To exclude the possibility that mixed crystals of form I have formed, the crystallization reaction was repeated with only Co(NCS)_2 and in this case the same crystalline phase was obtained. As mentioned above, its single-crystal structure is unknown and it is therefore presented here for the first time. For better comparison, we also present the structure of form II at 100 K, because in our previous work it was measured at 170 K (Neumann et al., 2018b).

2. Structural commentary

Form I of Co(NCS)_2(DMAP)_2 crystallizes in the monoclinic space group P2_1/m with Z = 2 and the Co cation as well as the thiocyanate anions are located on a crystallographic mirror

Figure 1
Crystal structure of form I with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: (i) = x, 3/2 – y, z.

Figure 2
Crystal structure of form II with labeling and displacement ellipsoids drawn at the 50% probability level.
plane, whereas the known form II crystallizes in space group $P2_1/c$ with $Z = 4$ with all atoms in general positions. In both modifications, the Co$^{II}$ cations are fourfold coordinated by two terminal N-bonded thiocyanate anions and two DMAP ligands within slightly distorted tetrahedral environments (Figs. 1 and 2 and Table 1). In form I, the two Co—N bond lengths to the thiocyanate anions are slightly different, which is not the case in form II (Table 2). Usually this is reflected in the values of the CN stretching vibrations but this is not the case for form I, because two bands are expected but only one is visible in its IR spectrum (Neumann et al., 2018b). Moreover, the Co—N bond lengths to the DMAP ligands are slightly longer in form I compared to form II (Table 2). From the N—Co—N bond angles, it is obvious that both tetrahedra are slightly distorted (Table 1). In both modifications, the Co—N—C bond angle is close to linear. Finally, it is noted that the density of form I at 100 K of 1.462 g cm$^{-3}$ is significantly greater than that of form II (1.457 g cm$^{-3}$). This is surprising because form I was proven to be thermodynamically stable at a lower temperature and should have the higher density according to the density rule (Kitaigorodskii, 1961). This was determined from a Pawley fit of a powder pattern measured at room temperature (Neumann et al., 2018b) and therefore, the current findings are somehow in contradiction to the previous findings. Other exceptions to this rule are known if the crystal structure is dominated by intermolecular hydrogen bonding, as already discussed in the literature (Burger & Ramberger, 1979).

3. Supramolecular features

In the crystal structure of form I, the discrete complexes are linked by C—H···S hydrogen bonds between one of the DMAP methyl H atoms and the thiocyanate S atoms into layers that lie parallel to the $bc$ plane (Fig. 3). In this arrangement, each of the two S atoms acts as an acceptor for two hydrogen bonds to two symmetry-equivalent DMAP ligands (Fig. 3). The C—H···S angles are close to 180°, indicating a relatively strong interaction (Table 3). These layers are further connected by weaker C—H···S contacts involving the thiocyanate S atom S1 and the methyl H atoms of the DMAP ligands (Fig. 4).

![Figure 3](image-url)  
Crystal structure of form I with a view of a layer in the direction of the crystallographic $a$-axis. Intermolecular C—H···S hydrogen bonding is shown as dashed lines.
In contrast to form I, both hydrogen bonds, C—H···S and C—H···N, are present in form II. In this modification, the molecules are linked by pairs of C—H···N hydrogen bonds between the thiocyanate N atoms and the H atoms of the DMAP ligands into chains that propagate along the crystallographic c-axis direction (Fig. 5). These chains are further linked into a complicated three-dimensional network by four different C—H···S hydrogen bonds between the hydrogen atoms of the DMAP ligands and the thiocyanate S atoms (Fig. 6 and Table 4). For three of these hydrogen bonds, the C—H···S angle is close to linearity, which indicates that it is a relatively strong interaction. This extensive intermolecular hydrogen bonding might be responsible for the fact that the density of the low-temperature form II at 100 K is lower than that of the high-temperature form I, which is an exception to the density rule.

4. Database survey
As mentioned in the Chemical context section, the single-crystal structure of form II and the thermodynamic relations between form I and form II have already been reported (Neumann et al., 2018b). Also related are the corresponding Zn(NCS)$_2$ modifications, but in contrast to Co, three different forms were observed with Zn (Neumann et al., 2018a,b).

However, compounds with DMAP and other transition-metal thiocyanates also exist. This includes the compound Zn(NCS)$_2$(DMAP)$_2$:chlorobenzene (Cambridge Structural Database refcode: QIPXES; Secondo et al., 2000), where the metal center is tetrahedrally coordinated. In addition, some octahedral complexes are known in the literature. Cu(NCS)$_2$(DMAP)$_2$(dimethylformamide)$_2$ (HIVZAO; Chen et al., 2007); Mn(NCS)$_2$(DMAP)$_2$(CH$_3$OH)$_2$ (NUKCON; Suckert et al., 2015) and Cd(NCS)$_2$(DMAP)$_2$(DMSO)$_2$ (QIPXOC; Secondo et al., 2000) all consist of a metal center with two thiocyanate anions, two DMAP co-ligands and two additional identical co-ligands each.

In [Cd(NCS)$_2$(DMAP)$_2$)$_n$ (QIPXW; Secondo et al., 2000) and [Ni(NCS)$_2$(DMAP)$_2$]$_n$ (GIQQOP; Jochim et al., 2018), two non-isotypical linear chains are reported, in which the cations have an all-trans MN$_4$S$_2$ octahedral coordination of two N-bonded and two S-bonded bridging thiocyanate anions and two DMAP co-ligands.

Figure 4
Crystal structure of form I viewed in the direction of the crystallographic c-axis. Intermolecular C—H···S hydrogen bonding is shown as dashed lines.

Figure 5
Crystal structure of form II with a view of a chain with intermolecular C—H···S hydrogen bonding shown as dashed lines.

Figure 6
Crystal structure of form II with a view in the direction of the crystallographic b-axis. Intermolecular C—H···S and C—H···N hydrogen bonds are shown as dashed lines.
5. Synthesis and crystallization

Co(NCS)2 and DMAP were purchased from Merck. All chemicals were used without further purification.

Blue single crystals of form I suitable for single crystal X-ray analysis were obtained three days after storing 0.15 mmol Co(NCS)2 (26.3 mg) and 0.30 mmol DMAP (36.6 mg) in 1.0 ml H2O at 333 K followed by slow cooling.

Single crystals of form II were obtained as described in the literature (Neumann et al., 2018a).

6. Refinement

The C-bound H atoms were located in the difference map but positioned with idealized geometry (C—H = 0.95–0.98 Å; methyl H atoms allowed to rotate but not to tip) and were refined isotropically with

Form I Form II

\[ \Delta \rho_{\text{max}} \text{ (e Å}^{-3}\text{)} \] 0.25, −0.37 0.29, −0.35

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Comparison of the crystal structures of the low- and high-temperature forms of bis[4-(dimethylamino)pyridine]dithiocyanatocobalt(II)

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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[4-(dimethylamino)pyridine]dithiocyanatocobalt(II) (Form_I)

Crystal data

[Co(NCS)₂(C₇H₁₀N₂)₂]  
\( M_r = 419.43 \)  
Monoclinic, \( P1_2_1/\text{m}1 \)  
\( a = 5.3708 (1) \ \text{Å} \)  
\( b = 15.2200 (2) \ \text{Å} \)  
\( c = 11.8014 (1) \ \text{Å} \)  
\( \beta = 99.076 (1)^\circ \)  
\( V = 952.61 (2) \ \text{Å}^3 \)  
\( Z = 2 \)  

\( F(000) = 434 \)  
\( D_r = 1.462 \ \text{Mg} \ \text{m}^{-3} \)  
Cu Kα radiation, \( \lambda = 1.54184 \ \text{Å} \)  
Cell parameters from 13880 reflections  
\( \theta = 3.8 \text{–} 77.3^\circ \)  
\( \mu = 9.20 \ \text{mm}^{-1} \)  
\( T = 100 \ \text{K} \)  
Block, light blue  
0.2 × 0.12 × 0.04 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\(^{-1}\) \( \omega \) scans  
Absorption correction: multi-scan  
(CrystalisPro; Rigaku OD, 2021)

\( T_{\text{min}} = 0.311, \ T_{\text{max}} = 1.000 \)  
16411 measured reflections  
2100 independent reflections  
2081 reflections with \( I > 2\sigma(I) \)  
\( R_{\text{int}} = 0.025 \)  
\( \theta_{\text{max}} = 78.1^\circ, \ \theta_{\text{min}} = 3.8^\circ \)  
\( h = -6 \rightarrow 5 \)  
\( k = -19 \rightarrow 19 \)  
\( l = -14 \rightarrow 14 \)

Refinement

Refinement on \( F^2 \)  
Least-squares matrix: full  
\( R[F^2 > 2\sigma(F^2)] = 0.024 \)  
\( wR(F^2) = 0.067 \)  
\( S = 1.14 \)  
2100 reflections  
126 parameters  
0 restraints  
Primary atom site location: dual

\( \Delta f/\sigma \) max = 0.001  
\( \Delta f_{\text{max}} = 0.25 \ \text{e} \ \text{Å}^{-3} \)  
\( \Delta f_{\text{min}} = -0.37 \ \text{e} \ \text{Å}^{-3} \)

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

\( w = 1/[(\sigma F^2) + (0.0348P)^2 + 0.4033P] \)  
where \( P = (F^2 + 2F_E^2)/3 \)

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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.

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

|      | x       | y       | z       | Uiso*/Ueq |
|------|---------|---------|---------|-----------|
| Co1  | 0.93113 (6) | 0.750000 | 0.27609 (3) | 0.01820 (10) |
| N1   | 1.1349 (3)  | 0.750000 | 0.15392 (15) | 0.0236 (4)    |
| C1   | 1.2586 (4)  | 0.750000 | 0.08142 (17) | 0.0197 (4)    |
| S1   | 1.43347 (10)| 0.750000 | −0.01905 (4) | 0.02516 (13)  |
| N2   | 1.1055 (3)  | 0.750000 | 0.43574 (15) | 0.0228 (4)    |
| C2   | 1.2525 (4)  | 0.750000 | 0.52018 (17) | 0.0202 (4)    |
| S2   | 1.46184 (10)| 0.750000 | 0.63528 (4)  | 0.02618 (13)  |
| N11  | 0.7113 (2)  | 0.64220 (8)| 0.26788 (10)| 0.0186 (2)    |
| C11  | 0.5802 (3)  | 0.62788 (9)| 0.35490 (12)| 0.0194 (3)    |
| H11  | 0.614076    | 0.664879 | 0.420344   | 0.023*       |
| C12  | 0.4021 (3)  | 0.56372 (9)| 0.35509 (12)| 0.0197 (3)    |
| H12  | 0.318372    | 0.556780 | 0.419671   | 0.024*       |
| C13  | 0.3428 (3)  | 0.50769 (9)| 0.25904 (12)| 0.0196 (3)    |
| C14  | 0.4861 (3)  | 0.52099 (10)| 0.16919 (12)| 0.0216 (3)    |
| H14  | 0.460807    | 0.483952 | 0.103587   | 0.026*       |
| C15  | 0.6609 (3)  | 0.58727 (9)| 0.17704 (12)| 0.0203 (3)    |
| H15  | 0.752119    | 0.595055 | 0.115020   | 0.024*       |
| N12  | 0.1612 (2)  | 0.44622 (8)| 0.25328 (11)| 0.0229 (3)    |
| C16  | 0.0279 (3)  | 0.43142 (10)| 0.34987 (14)| 0.0265 (3)    |
| H16A | 0.147210    | 0.410913 | 0.416077   | 0.040*       |
| H16B | −0.103220   | 0.386937 | 0.329058   | 0.040*       |
| H16C | −0.049866   | 0.486459 | 0.369491   | 0.040*       |
| C17  | 0.1036 (3)  | 0.38967 (11)| 0.15329 (15)| 0.0320 (4)    |
| H17A | 0.053675    | 0.425800 | 0.084731   | 0.048*       |
| H17B | −0.034880   | 0.349998 | 0.163508   | 0.048*       |
| H17C | 0.253102    | 0.355095 | 0.144230   | 0.048*       |

**Atomic displacement parameters (Å²)**

|      | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|------|-----|-----|-----|-----|-----|-----|
| Co1  | 0.01752 (17) | 0.01727 (17) | 0.02091 (17) | 0.000 | 0.00643 (12) | 0.000 |
| N1   | 0.0219 (8)    | 0.0256 (9)   | 0.0246 (9)   | 0.000 | 0.0077 (7)    | 0.000 |
| C1   | 0.0170 (9)    | 0.0193 (9)   | 0.0220 (9)   | 0.000 | 0.0007 (7)    | 0.000 |
| S1   | 0.0251 (3)    | 0.0307 (3)   | 0.0215 (2)   | 0.000 | 0.00917 (19)  | 0.000 |
| N2   | 0.0225 (8)    | 0.0226 (9)   | 0.0246 (9)   | 0.000 | 0.0076 (7)    | 0.000 |
| C2   | 0.0223 (9)    | 0.0160 (9)   | 0.0248 (10)  | 0.000 | 0.0108 (8)    | 0.000 |
| S2   | 0.0249 (3)    | 0.0292 (3)   | 0.0237 (2)   | 0.000 | 0.00158 (19)  | 0.000 |
| N11  | 0.0187 (5)    | 0.0172 (5)   | 0.0203 (5)   | 0.0012 (4) | 0.0043 (4)    | 0.0012 (4) |
| C11  | 0.0211 (6)    | 0.0187 (6)   | 0.0190 (6)   | 0.0022 (5) | 0.0047 (5)    | −0.0010 (5) |
Geometric parameters (Å, °)

| Bond/Distance | Value (Å)  |
|---------------|-----------|
| Co1—N1        | 1.9429 (18) |
| Co1—N2        | 1.9672 (19) |
| Co1—N1i       | 2.0148 (12) |
| N1—C1         | 1.163 (3)   |
| C1—S1         | 1.621 (2)   |
| N2—C2         | 1.170 (3)   |
| C2—S2         | 1.621 (2)   |
| N11—C11       | 1.3512 (17) |
| N11—C15       | 1.3529 (18) |
| C11—H11       | 0.9500      |
| C12—C13       | 1.414 (2)   |
| N1—Co1—N2     | 118.16 (8)  |
| N1—Co1—N11    | 111.03 (4)  |
| N1—Co1—N11i   | 111.03 (4)  |
| N2—Co1—N11    | 103.47 (4)  |
| N2—Co1—N11i   | 103.47 (4)  |
| N11—Co1—N11i  | 109.04 (7)  |
| C1—N1—Co1     | 179.48 (17) |
| N1—C1—S1      | 179.51 (19) |
| C2—N2—Co1     | 166.24 (16) |
| N2—C2—S2      | 178.57 (18) |
| C11—N11—Co1   | 117.81 (9)  |
| C11—N11—C15   | 116.08 (12) |
| C15—N11—Co1   | 125.71 (9)  |
| N11—C11—H11   | 117.8       |
| N11—C11—C12   | 124.41 (13) |
| C12—C11—H11   | 117.8       |
| C12—C12—H12   | 120.0       |
| C12—C12—C13   | 119.91 (13) |
| C13—C12—H12   | 120.0       |
| C12—C13—C14   | 115.63 (13) |

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N12—C13—C12  121.99 (13)  H17B—C17—H17C  109.5
N12—C13—C14  122.38 (13)

Symmetry code: (i) x, −y+3/2, z.

Hydrogen-bond geometry (Å, °)

\[
\begin{array}{cccccc}
D—H···A & D—H & H···A & D···A & D—H···A \\
C16—H16B···S2^ii & 0.98 & 2.91 & 3.8367 (15) & 158 \\
C17—H17B···S1^iii & 0.98 & 2.94 & 3.7291 (16) & 138 \\
C17—H17C···S1^iv & 0.98 & 2.89 & 3.8018 (18) & 155 \\
\end{array}
\]

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

(Form_II)

Crystal data

\[
\begin{array}{l}
C_{16}H_{20}CoN_{6}S_{2} \\
Mr = 419.43 \\
Monoclinic, P2_1/c \\
a = 13.9171 (1) Å \\
b = 9.5114 (1) Å \\
c = 14.4487 (1) Å \\
\beta = 90.489 (1)° \\
V = 1912.52 (3) Å^3 \\
Z = 4 \\
F(000) = 868 \\
D_x = 1.457 Mg m^{-3} \\
Cu K\alpha radiation, \lambda = 1.54184 Å \\
Cell parameters from 41675 reflections \\
\theta = 3.2–79.4° \\
\mu = 9.17 mm^{-1} \\
T = 100 K \\
Block, dark blue \\
0.18 \times 0.1 \times 0.03 mm
\end{array}
\]

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}

\omega scans

Absorption correction: multi-scan

(CrystalClear; Rigaku OD, 2021)

Refinement

Refinement on F^2

Least-squares matrix: full

R[F^2 > 2\sigma(F^2)] = 0.026

wR(F^2) = 0.073

S = 1.13

4151 reflections

231 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\[w = 1/\sigma^2(F_o^2) + (0.0406P)^2 + 0.8179P\] where \(P = (F_o^2 + 2F_c^2)/3\)

(\(\Delta/\sigma\))_{max} = 0.002

\(\Delta\rho_{\text{max}} = 0.29\) e Å^{-3}

\(\Delta\rho_{\text{min}} = -0.35\) e Å^{-3}

Extinction correction: SHELXL2016/6

(Sheldrick, 2015b),

Fc = kFc[1+0.001xFc^2/\sin(2\theta)]^{-1/4}

Extinction coefficient: 0.0076 (11)
**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     | Uiso*/Ueq  |
|----|-------|-------|-------|------------|
| Co1 | 0.77328 (2) | 0.36737 (2) | 0.79003 (2) | 0.01802 (8) |
| N1  | 0.89733 (9)  | 0.40269 (14) | 0.84966 (9)  | 0.0228 (3)   |
| C1  | 0.97734 (11) | 0.42519 (15) | 0.87028 (9)  | 0.0203 (3)   |
| S1  | 1.08865 (3)  | 0.45439 (4)  | 0.89675 (3)  | 0.02797 (10) |
| N2  | 0.72639 (9)  | 0.17383 (14) | 0.78687 (9)  | 0.0249 (3)   |
| C2  | 0.69467 (10) | 0.06052 (16) | 0.79023 (10) | 0.0225 (3)   |
| S2  | 0.64780 (3)  | −0.09564 (4) | 0.79675 (3)  | 0.02997 (10) |
| N11 | 0.67807 (8)  | 0.48667 (13) | 0.85774 (8)  | 0.0203 (2)   |
| C11 | 0.69896 (10) | 0.53200 (16) | 0.94415 (10) | 0.0213 (3)   |
| H11 | 0.759338     | 0.506648     | 0.970392     | 0.026*       |
| C12 | 0.63811 (11) | 0.61250 (16) | 0.99628 (10) | 0.0218 (3)   |
| H12 | 0.656100     | 0.639410     | 1.057333     | 0.026*       |
| C13 | 0.54861 (10) | 0.65531 (15) | 0.95897 (10) | 0.0199 (3)   |
| C14 | 0.52571 (10) | 0.60389 (16) | 0.86934 (10) | 0.0222 (3)   |
| H14 | 0.465517     | 0.625731     | 0.841373     | 0.027*       |
| C15 | 0.59106 (10) | 0.52243 (16) | 0.82332 (10) | 0.0213 (3)   |
| H15 | 0.573977     | 0.489080     | 0.763427     | 0.026*       |
| N12 | 0.48862 (9)  | 0.74021 (14) | 1.00607 (9)  | 0.0241 (3)   |
| C16 | 0.51936 (12) | 0.80309 (19) | 1.09350 (12) | 0.0303 (3)   |
| H16A| 0.577275     | 0.859533     | 1.083572     | 0.045*       |
| H16B| 0.533416     | 0.728603     | 1.138480     | 0.045*       |
| H16C| 0.468041     | 0.863388     | 1.117198     | 0.045*       |
| C17 | 0.40047 (11) | 0.79162 (19) | 0.96272 (12) | 0.0309 (3)   |
| H17A| 0.360713     | 0.711636     | 0.943368     | 0.046*       |
| H17B| 0.416451     | 0.848679     | 0.908512     | 0.046*       |
| H17C| 0.364953     | 0.849121     | 1.007120     | 0.046*       |
| N21 | 0.78919 (8)  | 0.42769 (13) | 0.65835 (8)  | 0.0189 (2)   |
| C21 | 0.82983 (10) | 0.33442 (16) | 0.59926 (10) | 0.0196 (3)   |
| H21 | 0.834119     | 0.238949     | 0.618167     | 0.024*       |
| C22 | 0.86504 (11) | 0.36954 (15) | 0.51404 (10) | 0.0209 (3)   |
| H22 | 0.891632     | 0.299061     | 0.475335     | 0.025*       |
| C23 | 0.86172 (10) | 0.51100 (16) | 0.48379 (9)  | 0.0200 (3)   |
| C24 | 0.81437 (11) | 0.60652 (16) | 0.54359 (11) | 0.0227 (3)   |
| H24 | 0.805027     | 0.701424     | 0.525107     | 0.027*       |
| C25 | 0.78214 (10) | 0.56180 (15) | 0.62799 (10) | 0.0211 (3)   |
| H25 | 0.753116     | 0.629049     | 0.667518     | 0.025*       |
| N22 | 0.90343 (9)  | 0.55389 (14) | 0.40487 (8)  | 0.0231 (3)   |
| C26 | 0.95644 (11) | 0.45537 (17) | 0.34714 (10) | 0.0248 (3)   |
| H26A| 0.911620     | 0.406459     | 0.305536     | 0.037*       |
### Atomic displacement parameters (Å$^2$)

|   | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|---|------------|------------|------------|------------|------------|------------|
| Co1 | 0.01610 (13) | 0.02028 (13) | 0.01770 (13) | -0.00148 (8) | 0.00179 (9) | -0.00024 (8) |
| N1  | 0.0219 (6)  | 0.0263 (6)  | 0.0202 (6)  | -0.0016 (5)  | 0.0008 (5)  | 0.0020 (5)  |
| C1  | 0.0247 (7)  | 0.0197 (7)  | 0.0166 (6)  | -0.0006 (5)  | 0.0008 (5)  | 0.0013 (5)  |
| S1  | 0.02121 (18) | 0.0317 (2)  | 0.03093 (19) | -0.00319 (14) | -0.00599 (14) | 0.00401 (15) |
| N2  | 0.0239 (6)  | 0.0224 (6)  | 0.0284 (6)  | -0.0016 (5)  | 0.0022 (5)  | 0.0000 (5)  |
| C2  | 0.0175 (6)  | 0.0262 (8)  | 0.0238 (7)  | 0.0019 (6)   | -0.0009 (5) | 0.0005 (6)  |
| S2  | 0.02535 (19) | 0.02148 (19) | 0.0430 (2)  | -0.00320 (14) | -0.00451 (16) | 0.00357 (16) |
| N11 | 0.0187 (6)  | 0.0227 (6)  | 0.0196 (5)  | -0.0013 (5)  | 0.0015 (4)  | -0.0004 (5) |
| C11 | 0.0166 (6)  | 0.0262 (7)  | 0.0211 (6)  | -0.00004 (5) | -0.0011 (5) | -0.0012 (6) |
| C12 | 0.0195 (7)  | 0.0248 (7)  | 0.0210 (7)  | -0.0013 (5)  | -0.0012 (5) | -0.0016 (5) |
| C13 | 0.0170 (6)  | 0.0193 (6)  | 0.0235 (7)  | -0.0026 (5)  | 0.0022 (5)  | 0.0020 (5)  |
| C14 | 0.0170 (6)  | 0.0259 (7)  | 0.0236 (7)  | -0.0009 (5)  | -0.0034 (5) | 0.0031 (6)  |
| C15 | 0.0210 (7)  | 0.0243 (7)  | 0.0187 (6)  | -0.0019 (5)  | -0.0015 (5) | 0.0002 (5)  |
| N12 | 0.0187 (6)  | 0.0264 (6)  | 0.0270 (6)  | 0.0034 (5)   | 0.0012 (5)  | -0.0015 (5) |
| C16 | 0.0245 (7)  | 0.0333 (9)  | 0.0332 (8)  | 0.0023 (6)   | 0.0030 (6)  | -0.0107 (7) |
| C17 | 0.0224 (7)  | 0.0324 (8)  | 0.0378 (8)  | 0.0089 (6)   | -0.0004 (6) | 0.0007 (7)  |
| N21 | 0.0170 (5)  | 0.0212 (6)  | 0.0185 (5)  | -0.0003 (4)  | 0.0010 (4)  | -0.0005 (4) |
| C21 | 0.0188 (6)  | 0.0193 (6)  | 0.0207 (6)  | -0.0009 (5)  | 0.0007 (5)  | -0.0015 (5) |
| C22 | 0.0183 (7)  | 0.0241 (7)  | 0.0203 (7)  | -0.0007 (5)  | 0.0003 (5)  | -0.0034 (5) |
| C23 | 0.0153 (6)  | 0.0253 (7)  | 0.0194 (6)  | -0.0031 (5)  | -0.0016 (5) | -0.0005 (5) |
| C24 | 0.0215 (7)  | 0.0210 (7)  | 0.0257 (7)  | 0.0010 (5)   | 0.0004 (6)  | 0.0025 (6)  |
| C25 | 0.0195 (6)  | 0.0208 (7)  | 0.0228 (7)  | 0.0024 (5)   | 0.0014 (5)  | -0.0022 (5) |
| N22 | 0.0226 (6)  | 0.0262 (7)  | 0.0205 (6)  | -0.0024 (5)  | 0.0029 (5)  | 0.0018 (5)  |
| C26 | 0.0016 (7)  | 0.0333 (8)  | 0.0195 (7)  | -0.0043 (6)  | 0.0037 (5)  | -0.0005 (6) |
| C27 | 0.0308 (8)  | 0.0293 (8)  | 0.0269 (7)  | -0.0040 (6)  | 0.0021 (6)  | 0.0076 (6)  |

### Geometric parameters (Å, °)

|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| Co1—N1 | 1.9521 (13) | C16—H16C | 0.9800 |
| Co1—N2 | 1.9535 (14) | C17—H17A | 0.9800 |
| Co1—N11 | 2.0057 (12) | C17—H17B | 0.9800 |
| Co1—N21 | 2.0013 (12) | C17—H17C | 0.9800 |
| N1—C1 | 1.170 (2) | N21—C21 | 1.3579 (18) |
| C1—S1 | 1.6164 (15) | N21—C25 | 1.3522 (19) |
| N2—C2 | 1.166 (2) | C21—H21 | 0.9500 |
| C2—S2 | 1.6253 (16) | C21—C22 | 1.371 (2) |
| N11—C11 | 1.3502 (18) | C22—H22 | 0.9500 |
| N11—C15 | 1.3488 (19) | C22—C23 | 1.415 (2) |
| Bond         | Length (Å) | Bond          | Length (Å) |
|--------------|------------|---------------|------------|
| C11—H11      | 0.9500     | C23—C24      | 1.420 (2)  |
| C11—C12      | 1.372 (2)  | C23—N22      | 1.3472 (18)|
| C12—H12      | 0.9500     | C24—H24      | 0.9500     |
| C12—C13      | 1.413 (2)  | C24—C25      | 1.370 (2)  |
| C13—C14      | 1.418 (2)  | C25—H25      | 0.9500     |
| C13—N12      | 1.3498 (19)| N22—C26      | 1.4590 (19)|
| C14—H14      | 0.9500     | N22—C27      | 1.461 (2)  |
| C14—C15      | 1.371 (2)  | C26—H26A     | 0.9800     |
| C15—H15      | 0.9500     | C26—H26B     | 0.9800     |
| N12—C16      | 1.459 (2)  | C26—H26C     | 0.9800     |
| N12—C17      | 1.457 (2)  | C27—H27A     | 0.9800     |
| C16—H16A     | 0.9800     | C27—H27B     | 0.9800     |
| C16—H16B     | 0.9800     | C27—H27C     | 0.9800     |

| Angle        |                  |                  |            |
|--------------|------------------|------------------|------------|
| N1—Co1—N2   | 117.81 (6)       | N12—C17—H17B    | 109.5      |
| N1—Co1—N11  | 105.83 (5)       | N12—C17—H17C    | 109.5      |
| N1—Co1—N21  | 105.41 (5)       | H17A—C17—H17B   | 109.5      |
| N2—Co1—N11  | 108.82 (5)       | H17A—C17—H17C   | 109.5      |
| N2—Co1—N21  | 106.71 (5)       | H17B—C17—H17C   | 109.5      |
| N21—Co1—N11 | 112.36 (5)       | C21—N21—Co1     | 117.41 (10)|
| C1—N1—Co1   | 168.56 (12)      | C25—N21—Co1     | 124.79 (10)|
| N1—C1—S1    | 178.72 (14)      | C25—N21—C21     | 116.22 (12)|
| C2—N2—Co1   | 175.34 (13)      | N21—C21—H21     | 118.0      |
| N2—C2—S2    | 178.29 (15)      | N21—C21—C22     | 124.03 (14)|
| C11—N11—Co1 | 119.59 (10)      | C22—C21—H21     | 118.0      |
| C15—N11—Co1 | 123.89 (10)      | C22—C21—H22     | 120.1      |
| C15—N11—C11 | 116.49 (12)      | C21—C22—C23     | 119.87 (13)|
| N11—C11—H11 | 118.1            | C23—C22—H22     | 120.1      |
| N11—C11—C12 | 123.84 (13)      | C22—C23—C24     | 115.75 (13)|
| C12—C11—H11 | 118.1            | N22—C23—C22     | 122.41 (13)|
| C11—C12—H12 | 120.1            | N22—C23—C24     | 121.80 (14)|
| C11—C12—C13 | 119.85 (14)      | C23—C24—H24     | 120.0      |
| C13—C12—H12 | 120.1            | C25—C24—C23     | 120.00 (14)|
| C12—C13—C14 | 116.08 (13)      | C25—C24—H24     | 120.0      |
| N12—C13—C12 | 121.80 (14)      | N21—C25—C24     | 123.92 (13)|
| N12—C13—C14 | 122.12 (14)      | N21—C25—H25     | 118.0      |
| C13—C14—H14 | 120.2            | C24—C25—H25     | 118.0      |
| C15—C14—C13 | 119.54 (13)      | C23—N22—C26     | 120.87 (13)|
| C15—C14—H14 | 120.2            | C23—N22—C27     | 121.07 (13)|
| N11—C15—C14 | 124.11 (13)      | C26—N22—C27     | 118.06 (12)|
| N11—C15—H15 | 117.9            | N22—C26—H26A    | 109.5      |
| C14—C15—H15 | 117.9            | N22—C26—H26B    | 109.5      |
| C13—N12—C16 | 120.26 (13)      | N22—C26—H26C    | 109.5      |
| C13—N12—C17 | 120.40 (13)      | H26A—C26—H26B   | 109.5      |
| C17—N12—C16 | 118.32 (13)      | H26A—C26—H26C   | 109.5      |
| N12—C16—H16A| 109.5            | H26B—C26—H26C   | 109.5      |
| N12—C16—H16B| 109.5            | N22—C27—H27A    | 109.5      |
| N12—C16—H16C| 109.5            | N22—C27—H27B    | 109.5      |
### Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H | H···A | D···A | D—H···A |
|-----------|-----|-------|-------|---------|
| C11—H11···S1<sup>i</sup> | 0.95 | 2.87  | 3.7312 (15) | 152 |
| C16—H16C···S2<sup>ii</sup> | 0.98 | 3.01  | 3.9663 (16) | 166 |
| C21—H21···S1<sup>iii</sup> | 0.95 | 2.92  | 3.7888 (15) | 153 |
| C22—H22···N1<sup>iv</sup> | 0.95 | 2.64  | 3.5448 (19) | 159 |
| C26—H26A···N2<sup>iv</sup> | 0.98 | 2.70  | 3.531 (2)   | 143 |
| C27—H27B···S2<sup>iv</sup> | 0.98 | 2.98  | 3.7568 (17) | 137 |

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