research communications

Crystal structure of bisbis(4-benzoylpyridine-*κN*)-(methanol-*κO*)bis(thiocyanato-*κN*)cobalt(II)

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The crystal structure of the title compound, $[Co(NCS)_2(C_{12}H_9NO)_2(CH_3OH)_2]$, consists of cobalt(II) cations that are octahedrally coordinated by two N-terminal bonding thiocyanato anions, two methanol molecules and two 4-benzoylpyridine ligands into discrete complexes that are located on centres of inversion. These complexes are further linked by O—H···O hydrogen bonding between the hydroxy H atom of the methanol ligand and the carbonyl O atom of the 4-benzoylpyridine ligand of a neighboring complex into layers parallel to (101). No pronounced intermolecular interactions are observed between these layers.

1. Chemical context

The synthesis of magnetic coordination compounds is still a major topic in coordination chemistry. For example, compounds in which the metal cations are linked by small-sized anionic ligands are of special interest because cooperative magnetic properties can be expected (Palion-Gazda *et al.*, 2015; Massoud *et al.*, 2013). In this context, we and others have reported on a number of one- or two-dimensional thiocyanate coordination compounds that, dependent on the nature of the metal cation and the neutral co-ligand, show different magnetic properties (Palion-Gazda *et al.*, 2015; Massoud *et al.*, 2013; Suckert *et al.*, 2016; Werner *et al.*, 2015a,b,c,d). In the majority of compounds having a chain structure, the metal cations are linked by pairs of anionic ligands, whereby the co-ligands as well as the N and the S atoms of the thiocyanate anions are always *trans*-coordinating. Surprisingly, with 4-benzoylpyridine and cobalt thiocyanate we obtained a compound in which the N-donor co-ligands are still *trans* to each other, whereas the N and the S atoms of the anionic ligands show a *cis*-arrangement (Rams *et al.*, 2017). Like many other Co chain polymers, this compound represent an antiferromagnetic phase of single chain magnets with magnetic properties similar to that of related cobalt compounds with an all *trans*-coordination. Later on, we accidentally obtained a further crystalline phase with 4-benzoylpyridine as a co-ligand by reaction in methanol. Here we report on these results.

2. Structural commentary

The asymmetric unit of the title compound, $[Co(NCS)_2(C_{12}H_9NO)_2(CH_3OH)_2]$, consists of one cobalt(II) cation that is located on a center of inversion as well as of one thiocyanate anion, one methanol molecule and one neutral 4-benzoylpyridine ligand in general positions. The Co^{II} cation
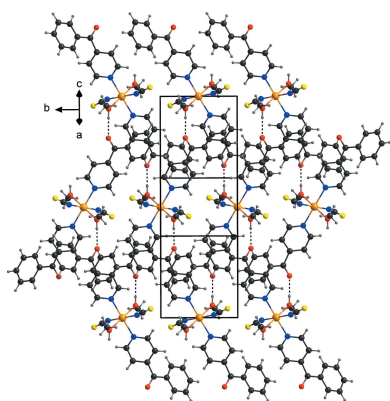
is octahedrally coordinated by two terminal N-bonded anionic ligands, the O atoms of two methanol molecules and the N atoms of two 4-benzoylpyridine ligands (Fig. 1). The Co—N bond lengths to the thiocyanate anions are significantly shorter [2.062 (2) Å] than those to the pyridine N atom of the neutral 4-benzoylpyridine ligand [2.1875 (18) Å]. This is expected and in agreement with bond lengths reported in the closely related structure of [Co(NCS)$_2$(C$_{12}$H$_9$NO)$_2$(CH$_3$CN)$_2$] (Suckert *et al.*, 2017) where methanol is replaced by aceto-nitrile, and also for related compounds reported in the literature (Soliman *et al.*, 2014). The 4-benzoylpyridine ligand is not planar, with the phenyl rings inclined by 61.34 (9)°. This value is in agreement with those retrieved from literature which vary between 40.4 and 74.8° (Escuer *et al.*, 2004).
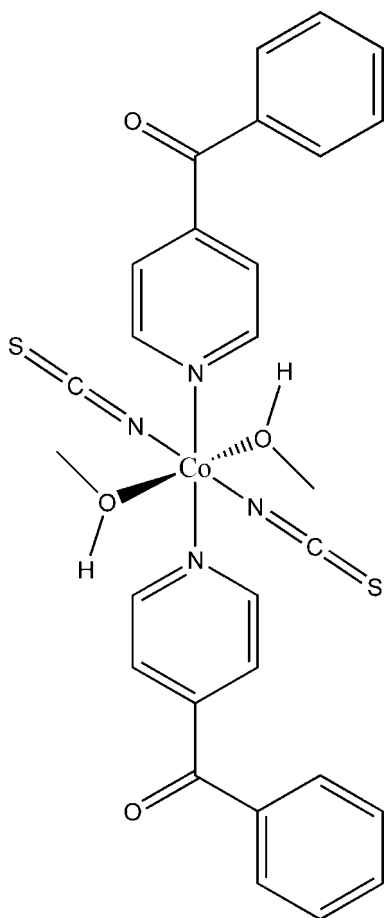
3. Supramolecular features

In the crystal structure of the title compound, the discrete complexes are linked by intermolecular O—H···O hydrogen bonds between the hydroxyl H atom of the methanol molecule and the carbonyl oxygen atom of a 4-benzoylpyridine ligand of a neighboring complex. Each of the complexes is linked to four symmetry-related complexes into layers parallel to (101) (Fig. 2 and Table 1). Between these layers no pronounced intermolecular interactions are observed (Fig. 3).

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O1···O11^i	0.84	1.92	2.752 (3)	173

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

4. Database survey

Altogether, there are 22 coordination compounds with 4-benzoylpyridine ligands compiled in the Cambridge Structure Database (Version 5.38, last update 2016, Groom *et al.*, 2016) of which three contain also thiocyanate anions. In two of these structures Co(II) or Ni(II) cations are octahedrally
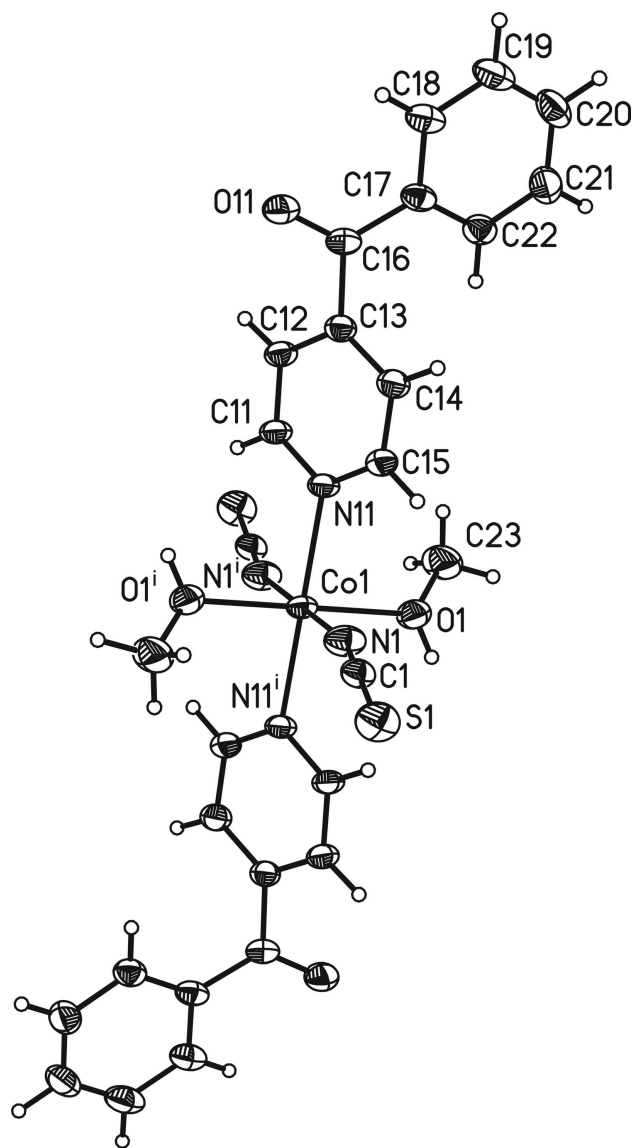

Figure 1
View of one discrete complex with labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) −x + 1, −y, −z + 1.]
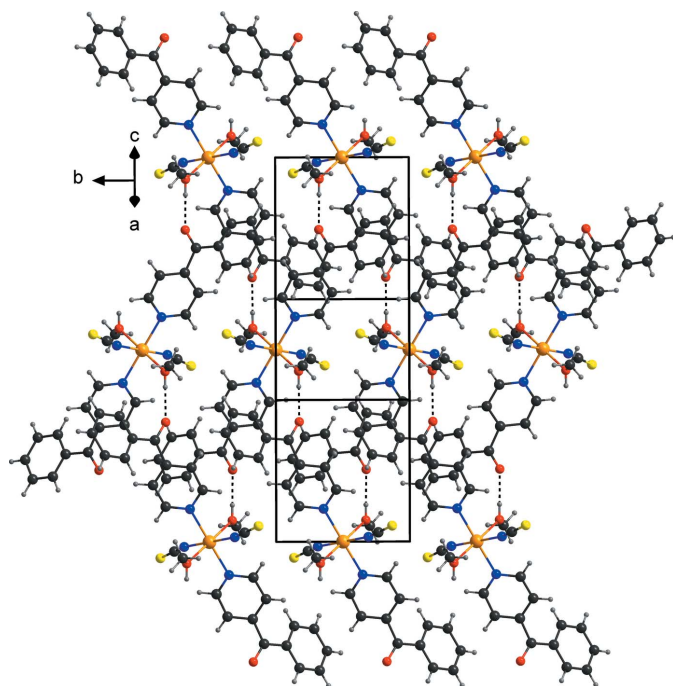
Figure 2
Crystal structure of the title compound in a view onto the O—H⋯O hydrogen-bonded layers (shown as dashed lines).

coordinated by the N atoms of four 4-benzoylpyridine ligands and the N atoms of two thiocyanate anions (Drew *et al.*, 1985; Soliman *et al.*, 2014). In the third compound, Cu(II) cations have a square-planar coordination sphere defined by two 4-benzoylpyridine ligands and two thiocyanate anions (Bai *et al.*, 2011). Finally, we have reported on a compound with a one-dimensional structure, in which the Co(II) cations are linked by μ-1,3-bridging thiocyanate anions (Rams *et al.*, 2017), as well as a compound very similar to the title structure in which Co^{II} cations are coordinated into discrete complexes by two thiocyanate anions, two 4-benzoylpyridine ligands and two acetonitrile molecules (Suckert *et al.*, 2017).
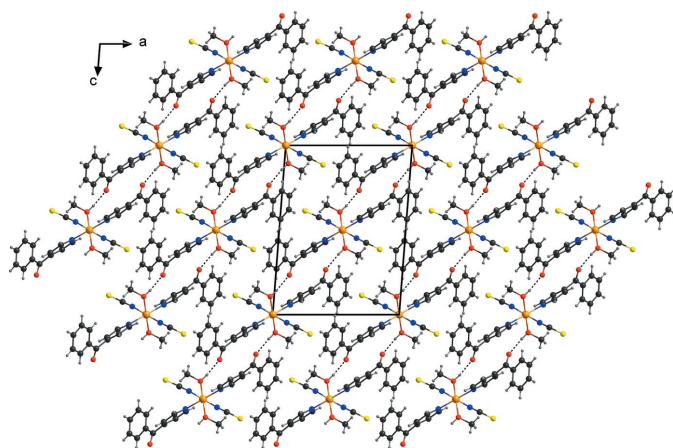

Figure 3
Crystal structure of the title compound in a view perpendicular to the hydrogen-bonded layers along the crystallographic *b* axis. Intermolecular O—H⋯O hydrogen bonds are shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Co(NCS)$_2$(C$_{12}$H$_9$NO)$_2$(CH$_4$O)$_2$]
M_r	605.58
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	200
a, b, c (Å)	12.0367 (10), 7.2497 (4), 16.1396 (13)
β (°)	94.404 (10)
V (Å^3)	1404.22 (18)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.80
Crystal size (mm)	0.26 × 0.20 × 0.09
Data collection	
Diffractometer	Stoe IPDS1
Absorption correction	Numerical (*X-SHAPE* and *X-RED32*; Stoe, 2008)
T_{min}, T_{max}	0.597, 0.901
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13065, 3054, 2571
R_{int}	0.094
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.149, 1.08
No. of reflections	3054
No. of parameters	179
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.98, −0.94

Computer programs: *X-AREA* (Stoe, 2008), *XP* in *SHELXTL* and *SHELXS97* (Sheldrick, 2008), *SHELXL2014*/7 (Sheldrick, 2015) and *DIAMOND* (Brandenburg, 1999), *publCIF* (Westrip, 2010).

5. Synthesis and crystallization

Co(NCS)$_2$ and 4-benzoylpyridine were purchased from Alfa Aesar. Crystals of the title compound suitable for single crystal X-ray diffraction were obtained by reaction of 26.3 mg Co(NCS)$_2$ (0.15 mmol) with 27.5 mg 4-benzoylpyridine (0.15 mmol) in methanol (1.5 ml) after a few days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters U_{iso}(H) = 1.2 U_{eq}(C) for aromatic and U_{iso}(H) = 1.5 U_{eq}(C) for methyl H atoms using a riding model. The methyl hydrogen atoms were allowed to rotate but not to tip. The O—H hydrogen atom was located in a difference map. Its bond length was set to the ideal value of 0.84 Å and finally, it was refined with U_{iso}(H) = 1.5 U_{eq}(O) using a riding model.

Acknowledgements

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supporting information

Crystal structure of bis(4-benzoylpyridine-*κN*)bis(methanol-*κO*)bis(thiocyanato-*κN*)cobalt(II)

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Computing details

Data collection: *X-AREA* (Stoe, 2008); cell refinement: *X-AREA* (Stoe, 2008); data reduction: *X-AREA* (Stoe, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(4-benzoylpyridine-*κN*)bis(methanol-*κO*)bis(thiocyanato-*κN*)cobalt(II)

Crystal data

[Co(NCS)$_2$(C$_{12}$H$_9$NO)$_2$(CH$_4$O)$_2$]	$F(000) = 626$
$M_r = 605.58$	$D_x = 1.432$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.0367$ (10) Å	Cell parameters from 13065 reflections
$b = 7.2497$ (4) Å	$\theta = 2.5–27.0°$
$c = 16.1396$ (13) Å	$\mu = 0.80$ mm^{-1}
$\beta = 94.404$ (10)°	$T = 200$ K
$V = 1404.22$ (18) Å^3	Block, blue
$Z = 2$	$0.26 \times 0.20 \times 0.09$ mm

Data collection

Stoe IPDS-1 diffractometer	3054 independent reflections
phi scans	2571 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (X-SHAPE and X-RED32; Stoe, 2008)	$R_{int} = 0.094$
	$\theta_{max} = 27.0°$, $\theta_{min} = 2.5°$
$T_{min} = 0.597$, $T_{max} = 0.901$	$h = -15 \rightarrow 15$
13065 measured reflections	$k = -9 \rightarrow 9$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1003P)^2 + 0.142P]$ where $P = (F_o^2 + 2F_c^2)/3$
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.052$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.149$	$\Delta\rho_{max} = 0.98$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{min} = -0.94$ e Å^{-3}
3054 reflections	Extinction correction: SHELXL-2014/7 (Sheldrick 2015, Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
179 parameters	
0 restraints	Extinction coefficient: 0.026 (4)
Hydrogen site location: mixed	
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_{iso}*/U_{eq}
Co1	0.5000	0.0000	0.5000	0.02401 (19)
N1	0.38448 (17)	0.1893 (3)	0.45202 (14)	0.0369 (5)
C1	0.30488 (19)	0.2635 (3)	0.42427 (14)	0.0290 (5)
S1	0.19267 (6)	0.36720 (11)	0.38595 (5)	0.0433 (2)
N11	0.63301 (15)	0.1453 (3)	0.44184 (12)	0.0262 (4)
C11	0.71706 (18)	0.0512 (4)	0.41204 (15)	0.0276 (5)
H11	0.7229	−0.0773	0.4232	0.033*
C12	0.79607 (18)	0.1334 (3)	0.36556 (14)	0.0281 (5)
H12	0.8528	0.0614	0.3435	0.034*
C13	0.79087 (18)	0.3217 (3)	0.35185 (14)	0.0269 (5)
C14	0.70540 (19)	0.4217 (4)	0.38427 (16)	0.0309 (5)
H14	0.7002	0.5514	0.3767	0.037*
C15	0.62774 (19)	0.3276 (3)	0.42802 (15)	0.0309 (5)
H15	0.5685	0.3954	0.4490	0.037*
C16	0.87501 (18)	0.4060 (3)	0.29893 (14)	0.0281 (5)
C17	0.93531 (18)	0.5746 (4)	0.32667 (15)	0.0283 (5)
C18	0.9973 (2)	0.6709 (4)	0.27036 (17)	0.0350 (6)
H18	0.9958	0.6320	0.2141	0.042*
C19	1.0602 (2)	0.8220 (4)	0.2966 (2)	0.0425 (6)
H19	1.1008	0.8884	0.2582	0.051*
C20	1.0640 (2)	0.8770 (4)	0.3792 (2)	0.0444 (7)
H20	1.1081	0.9802	0.3973	0.053*
C21	1.0038 (2)	0.7819 (4)	0.43553 (19)	0.0397 (6)
H21	1.0072	0.8196	0.4920	0.048*
C22	0.93860 (19)	0.6321 (4)	0.40941 (15)	0.0311 (5)
H22	0.8962	0.5687	0.4477	0.037*
O11	0.89175 (16)	0.3254 (3)	0.23427 (11)	0.0384 (4)
C23	0.6398 (3)	0.2012 (6)	0.6476 (2)	0.0553 (9)
H23A	0.6339	0.2842	0.6950	0.083*
H23B	0.6714	0.0831	0.6673	0.083*
H23C	0.6882	0.2568	0.6084	0.083*
O1	0.53106 (15)	0.1711 (3)	0.60682 (11)	0.0375 (4)
H1O1	0.4842	0.1720	0.6428	0.056*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0156 (3)	0.0275 (3)	0.0295 (3)	0.00038 (14)	0.00505 (17)	0.00275 (15)
N1	0.0249 (10)	0.0380 (12)	0.0483 (12)	0.0054 (9)	0.0049 (9)	0.0121 (9)

C1	0.0262 (11)	0.0274 (12)	0.0337 (11)	−0.0023 (9)	0.0045 (9)	0.0050 (9)
S1	0.0303 (4)	0.0428 (4)	0.0555 (4)	0.0090 (3)	−0.0038 (3)	0.0089 (3)
N11	0.0190 (8)	0.0278 (10)	0.0324 (9)	−0.0027 (7)	0.0068 (7)	0.0027 (7)
C11	0.0207 (10)	0.0283 (12)	0.0350 (11)	−0.0007 (9)	0.0095 (9)	0.0030 (9)
C12	0.0206 (10)	0.0307 (12)	0.0339 (11)	0.0006 (9)	0.0079 (9)	0.0020 (9)
C13	0.0216 (10)	0.0301 (12)	0.0291 (10)	−0.0025 (9)	0.0038 (8)	0.0002 (8)
C14	0.0253 (11)	0.0259 (12)	0.0421 (13)	−0.0007 (9)	0.0077 (10)	0.0021 (9)
C15	0.0229 (10)	0.0291 (12)	0.0418 (13)	−0.0006 (9)	0.0100 (9)	−0.0024 (9)
C16	0.0193 (10)	0.0342 (13)	0.0311 (11)	−0.0006 (9)	0.0039 (8)	0.0043 (9)
C17	0.0181 (10)	0.0301 (13)	0.0368 (12)	−0.0003 (9)	0.0019 (9)	0.0060 (9)
C18	0.0258 (11)	0.0365 (14)	0.0432 (13)	−0.0037 (10)	0.0060 (10)	0.0087 (10)
C19	0.0287 (12)	0.0343 (15)	0.0655 (18)	−0.0051 (11)	0.0093 (12)	0.0109 (12)
C20	0.0266 (12)	0.0288 (14)	0.077 (2)	−0.0044 (10)	0.0012 (13)	−0.0053 (12)
C21	0.0304 (12)	0.0338 (14)	0.0545 (16)	0.0007 (10)	0.0008 (11)	−0.0081 (11)
C22	0.0224 (10)	0.0323 (13)	0.0385 (12)	0.0003 (9)	0.0023 (9)	0.0014 (9)
O11	0.0376 (10)	0.0444 (11)	0.0348 (9)	−0.0099 (8)	0.0130 (8)	−0.0012 (7)
C23	0.0412 (16)	0.079 (2)	0.0455 (16)	−0.0228 (16)	0.0037 (13)	−0.0180 (15)
O1	0.0316 (9)	0.0504 (12)	0.0313 (9)	−0.0073 (8)	0.0081 (7)	−0.0076 (7)

Geometric parameters (Å, º)

Co1—N1	2.062 (2)	C16—O11	1.226 (3)
Co1—N1i	2.062 (2)	C16—C17	1.474 (3)
Co1—O1	2.1336 (18)	C17—C22	1.397 (3)
Co1—O1i	2.1336 (18)	C17—C18	1.405 (3)
Co1—N11	2.1875 (18)	C18—C19	1.379 (4)
Co1—N11i	2.1875 (18)	C18—H18	0.9500
N1—C1	1.159 (3)	C19—C20	1.389 (5)
C1—S1	1.626 (2)	C19—H19	0.9500
N11—C11	1.340 (3)	C20—C21	1.388 (4)
N11—C15	1.341 (3)	C20—H20	0.9500
C11—C12	1.390 (3)	C21—C22	1.386 (4)
C11—H11	0.9500	C21—H21	0.9500
C12—C13	1.383 (3)	C22—H22	0.9500
C12—H12	0.9500	C23—O1	1.435 (3)
C13—C14	1.393 (3)	C23—H23A	0.9800
C13—C16	1.504 (3)	C23—H23B	0.9800
C14—C15	1.393 (3)	C23—H23C	0.9800
C14—H14	0.9500	O1—H1O1	0.8400
C15—H15	0.9500		
N1—Co1—N1i	180.00 (10)	N11—C15—H15	118.6
N1—Co1—O1	89.30 (9)	C14—C15—H15	118.6
N1i—Co1—O1	90.70 (9)	O11—C16—C17	123.0 (2)
N1—Co1—O1i	90.70 (9)	O11—C16—C13	116.8 (2)
N1i—Co1—O1i	89.30 (9)	C17—C16—C13	120.1 (2)
O1—Co1—O1i	180.0	C22—C17—C18	119.5 (2)
N1—Co1—N11	90.75 (8)	C22—C17—C16	121.0 (2)

N1^i—Co1—N11	89.25 (8)	C18—C17—C16	119.3 (2)
O1—Co1—N11	88.74 (7)	C19—C18—C17	120.1 (3)
O1^i—Co1—N11	91.26 (7)	C19—C18—H18	119.9
N1—Co1—N11^i	89.25 (8)	C17—C18—H18	119.9
N1^i—Co1—N11^i	90.75 (8)	C18—C19—C20	120.0 (3)
O1—Co1—N11^i	91.26 (7)	C18—C19—H19	120.0
O1^i—Co1—N11^i	88.74 (7)	C20—C19—H19	120.0
N11—Co1—N11^i	180.0	C21—C20—C19	120.4 (3)
C1—N1—Co1	165.5 (2)	C21—C20—H20	119.8
N1—C1—S1	179.5 (2)	C19—C20—H20	119.8
C11—N11—C15	118.02 (19)	C22—C21—C20	120.1 (3)
C11—N11—Co1	120.42 (16)	C22—C21—H21	120.0
C15—N11—Co1	121.28 (15)	C20—C21—H21	120.0
N11—C11—C12	122.8 (2)	C21—C22—C17	119.9 (2)
N11—C11—H11	118.6	C21—C22—H22	120.0
C12—C11—H11	118.6	C17—C22—H22	120.0
C13—C12—C11	119.0 (2)	O1—C23—H23A	109.5
C13—C12—H12	120.5	O1—C23—H23B	109.5
C11—C12—H12	120.5	H23A—C23—H23B	109.5
C12—C13—C14	118.6 (2)	O1—C23—H23C	109.5
C12—C13—C16	117.9 (2)	H23A—C23—H23C	109.5
C14—C13—C16	123.4 (2)	H23B—C23—H23C	109.5
C15—C14—C13	118.6 (2)	C23—O1—Co1	123.76 (18)
C15—C14—H14	120.7	C23—O1—H1O1	108.6
C13—C14—H14	120.7	Co1—O1—H1O1	118.5
N11—C15—C14	122.8 (2)		

Symmetry code: (i) −x+1, −y, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O1···O11^{ii}	0.84	1.92	2.752 (3)	173

Symmetry code: (ii) x−1/2, −y+1/2, z+1/2.