

catena-Poly[[diaquabis(thiocyanato- κ N)-cobalt(II)]- μ -4,4'-bipyridine- κ^2 N:N'] 4,4'-bipyridine solvate]

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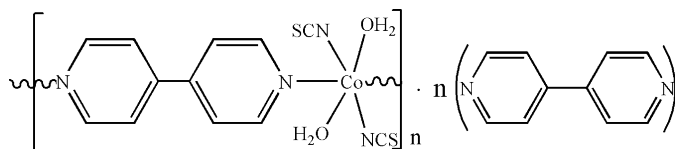
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.042; wR factor = 0.118; data-to-parameter ratio = 15.0.

In the title complex, $[\text{Co}(\text{NCS})_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2] \cdot n \text{C}_{10}\text{H}_8\text{N}_2$, the Co^{II} ion is located on an inversion centre and is coordinated by two N atoms from the two 4,4'-bipyridine ligands, two O atoms from the water molecule, and two N atoms from two isothiocyanate ions in a distorted octahedral environment. In the crystal, the coordinated water molecules, isothiocyanate ions and solvent 4,4'-bipyridine molecules are linked by $\text{O}-\text{H} \cdots \text{S}$ and $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds into layers parallel to the ab plane.

Related literature

For two-dimensional Mn^{II} and one-dimensional Cu^{II} complexes constructed from 4,4'-bipy, see: Yang *et al.* (2008); Zhou & He (2008). For related structures, see: Lu *et al.* (1997); He *et al.* (2006).



Experimental

Crystal data

| | |
|--|-------------------------|
| $[\text{Co}(\text{NCS})_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2] \cdot n \text{C}_{10}\text{H}_8\text{N}_2$ | $b = 9.0147$ (11) Å |
| $M_r = 523.51$ | $c = 10.1114$ (13) Å |
| Triclinic, $P\bar{1}$ | $\alpha = 107.770$ (2)° |
| $a = 7.4433$ (11) Å | $\beta = 103.978$ (2)° |
| | $\gamma = 97.038$ (2)° |

$V = 612.66$ (14) Å³
 $Z = 1$
Mo $K\alpha$ radiation

$\mu = 0.90$ mm⁻¹
 $T = 293$ K
 $0.20 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; (Bruker, 2001))
 $T_{\text{min}} = 0.835$, $T_{\text{max}} = 0.835$

3522 measured reflections
2359 independent reflections
2191 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.118$
 $S = 1.04$
2359 reflections
157 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.77$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.74$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|--------|-------------|--------|-------------|
| Co1—N2 | 2.089 (2) | Co1—N5 | 2.1625 (18) |
| Co1—O1 | 2.0964 (19) | | |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------------|----------|--------------|--------------|----------------|
| O1—H1C \cdots N7 | 0.82 (3) | 1.92 (3) | 2.732 (3) | 171 (3) |
| O1—H1B \cdots S1 ⁱⁱ | 0.82 (3) | 2.52 (3) | 3.279 (2) | 154 (3) |

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2215).

References

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supporting information

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***catena*-Poly[[diaquabis(thiocyanato- κ N)cobalt(II)]- μ -4,4'-bipyridine- κ^2 N:N']
4,4'-bipyridine solvate]**

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S1. Comment

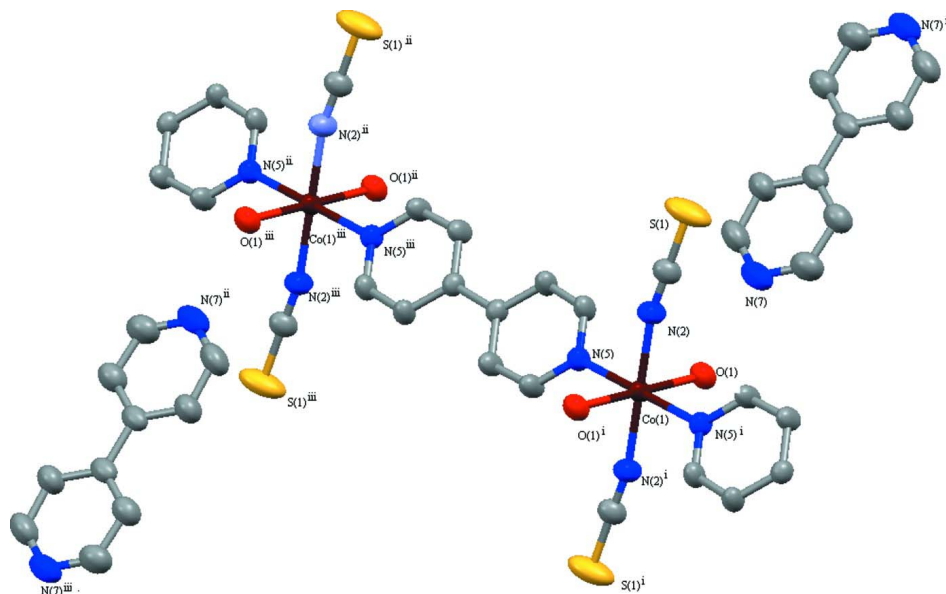
For 2-D Mn^{II} and 1-D Cu^{II} complexes constructed from 4,4'-bipy see: Yang *et al.* (2008) and Zhou, *et al.* (2008). The compound of [Co(4,4'-bipy)(NCS)₂(OH₂)₂].(4,4'-bipy) were reported (Lu, *et al.* 1997) but the polymeric compound has not been synthesized, so far. Herein, we report the crystal structure of a novel polymeric compound, {[Co(4,4'-bipy)(NCS)₂(OH₂)₂].(4,4'-bipy)}_n. The Co^{II} ion is coordinated by two N atoms from 4,4'-bipy ligand, two N atoms from isothiocyanate ions, and two O atoms from two water molecule in a distorted octahedral geometry (Fig. 1, Table 1). O(1), N(2), O(1)ⁱ and N(2)ⁱ [symmetry code: -1 + x, y, z] lie in the equatorial plane, with the O(1)—N(2)—O(1)ⁱ—N(2)ⁱ torsional angle of 0.02 (11)°, while the Co atom deviates from the equatorial plane by 0.051 Å. N(5), N(5)ⁱ atoms occupy the axial sites, which are strictly linear due to a symmetry operation. The bond lengths and angles of the title complex are similar to the compound {[Co(4,4'-bipy)(ambdc)(OH₂)₂](4,4'-bipy)(DMF)}_n (He *et al.*, 2006). In the crystal packing of (I) are linked by O—H...S and O—H...N hydrogen bonds (Table 2, Fig. 2).

S2. Experimental

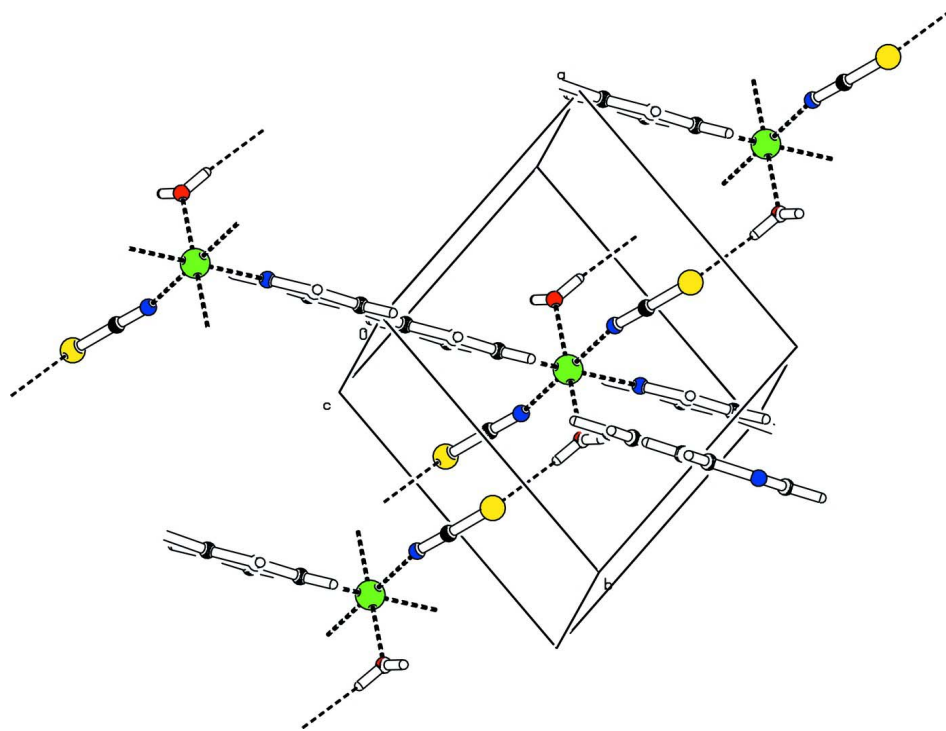
A mixture of Co(CH₃COO)₂ (0.5 mmol), 4,4'-bipy (0.5 mmol and H₂O (10.00 ml), was placed in a Parr Teflon-lined stainless steel vessel (10 ml), and then the vessel was sealed and heated at 393 K for 3 d. After the mixture was slowly cooled to room temperature, a few red crystals of [Co(4,4'-bipy)(NCS)₂(OH₂)₂].(4,4'-bipy) were obtained.

S3. Refinement

H atoms of water molecule were located in a difference map and refined with O—H distance restraints of 0.82 (3) Å, and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Other H atoms bonded to C atoms were introduced at calculated positions and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and C—H distances of 0.93 Å.

**Figure 1**

A part of polymeric chain of Co^{II} octahedra with 4,4-bpy bridging ligand is shown with ellipsoids at the 30% probability level. Symmetry codes used: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - 1, y, z$. (iii) $-x, -y, -z$.

**Figure 2**

The crystal packing of (I) with hydrogen bonds (dashed lines).

catena-Poly[[diaquabis(thiocyanato- κ N)cobalt(II)]- μ -4,4'-bipyridine- κ^2 N:N'] 4,4'-bipyridine solvate]*Crystal data*

[Co(NCS)₂(C₁₀H₈N₂)(H₂O)₂] \cdot C₁₀H₈N₂
 $M_r = 523.51$
 Triclinic, $P\bar{1}$
 Hall symbol: -P 1
 $a = 7.4433$ (11) Å
 $b = 9.0147$ (11) Å
 $c = 10.1114$ (13) Å
 $\alpha = 107.770$ (2)°
 $\beta = 103.978$ (2)°
 $\gamma = 97.038$ (2)°

$V = 612.66$ (14) Å³
 $Z = 1$
 $F(000) = 269$
 $D_x = 1.419$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 $\theta = 1.0$ – 26.0 °
 $\mu = 0.90$ mm⁻¹
 $T = 293$ K
 Block, red
 $0.20 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1997)
 $T_{\min} = 0.835$, $T_{\max} = 0.835$

3522 measured reflections
 2359 independent reflections
 2191 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
 $\theta_{\max} = 26.0$ °, $\theta_{\min} = 2.2$ °
 $h = -9 \rightarrow 4$
 $k = -11 \rightarrow 11$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.118$
 $S = 1.04$
 2359 reflections
 157 parameters
 3 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0744P)^2 + 0.3257P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.77$ e Å⁻³
 $\Delta\rho_{\min} = -0.74$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Co1 | 0.5000 | 0.5000 | 0.5000 | 0.03359 (17) |
| S1 | 0.93240 (12) | 0.61882 (16) | 0.23801 (12) | 0.0837 (4) |
| O1 | 0.3666 (3) | 0.6731 (2) | 0.4436 (2) | 0.0453 (4) |

| | | | | |
|-----|------------|------------|------------|------------|
| H1B | 0.251 (3) | 0.659 (4) | 0.418 (4) | 0.068* |
| H1C | 0.403 (4) | 0.719 (4) | 0.394 (3) | 0.068* |
| N2 | 0.6824 (3) | 0.5256 (3) | 0.3768 (2) | 0.0467 (5) |
| N5 | 0.2992 (3) | 0.3143 (2) | 0.3142 (2) | 0.0365 (4) |
| C1 | 0.2050 (4) | 0.1832 (3) | 0.3238 (3) | 0.0439 (6) |
| H1A | 0.2201 | 0.1757 | 0.4154 | 0.053* |
| C2 | 0.0868 (4) | 0.0590 (3) | 0.2048 (3) | 0.0433 (6) |
| H2A | 0.0247 | -0.0295 | 0.2172 | 0.052* |
| C3 | 0.0605 (3) | 0.0664 (3) | 0.0661 (2) | 0.0326 (5) |
| C4 | 0.1567 (4) | 0.2036 (3) | 0.0576 (2) | 0.0390 (5) |
| H4 | 0.1423 | 0.2157 | -0.0322 | 0.047* |
| C5 | 0.2730 (4) | 0.3217 (3) | 0.1814 (2) | 0.0398 (5) |
| H5 | 0.3369 | 0.4115 | 0.1721 | 0.048* |
| C21 | 0.7868 (4) | 0.5654 (3) | 0.3206 (3) | 0.0439 (6) |
| N7 | 0.4547 (4) | 0.8112 (3) | 0.2551 (3) | 0.0652 (7) |
| C11 | 0.5596 (5) | 0.9552 (4) | 0.2955 (4) | 0.0664 (8) |
| H11 | 0.6222 | 1.0072 | 0.3939 | 0.080* |
| C12 | 0.5829 (5) | 1.0347 (4) | 0.2006 (3) | 0.0579 (7) |
| H12 | 0.6588 | 1.1365 | 0.2356 | 0.070* |
| C13 | 0.4917 (4) | 0.9604 (3) | 0.0537 (3) | 0.0458 (6) |
| C14 | 0.3805 (5) | 0.8079 (4) | 0.0096 (4) | 0.0590 (7) |
| H14 | 0.3170 | 0.7522 | -0.0881 | 0.071* |
| C15 | 0.3664 (6) | 0.7408 (4) | 0.1137 (4) | 0.0695 (9) |
| H15 | 0.2901 | 0.6397 | 0.0828 | 0.083* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|---------------|--------------|--------------|
| Co1 | 0.0348 (3) | 0.0325 (3) | 0.0224 (2) | -0.00978 (17) | 0.00294 (17) | 0.00493 (17) |
| S1 | 0.0513 (5) | 0.1408 (10) | 0.0912 (7) | 0.0135 (5) | 0.0309 (5) | 0.0798 (7) |
| O1 | 0.0453 (10) | 0.0441 (10) | 0.0408 (10) | -0.0031 (8) | 0.0058 (8) | 0.0172 (8) |
| N2 | 0.0450 (12) | 0.0515 (12) | 0.0351 (11) | -0.0079 (10) | 0.0114 (10) | 0.0105 (9) |
| N5 | 0.0366 (10) | 0.0335 (10) | 0.0271 (9) | -0.0071 (8) | 0.0014 (8) | 0.0052 (8) |
| C1 | 0.0494 (14) | 0.0412 (13) | 0.0265 (11) | -0.0144 (11) | 0.0032 (10) | 0.0067 (10) |
| C2 | 0.0469 (14) | 0.0385 (12) | 0.0303 (11) | -0.0154 (10) | 0.0048 (10) | 0.0067 (10) |
| C3 | 0.0293 (10) | 0.0321 (11) | 0.0271 (10) | -0.0005 (9) | 0.0022 (9) | 0.0048 (9) |
| C4 | 0.0471 (13) | 0.0326 (11) | 0.0266 (10) | -0.0036 (10) | -0.0002 (10) | 0.0087 (9) |
| C5 | 0.0451 (13) | 0.0311 (11) | 0.0318 (11) | -0.0072 (10) | 0.0011 (10) | 0.0087 (9) |
| C21 | 0.0379 (13) | 0.0521 (15) | 0.0370 (12) | -0.0010 (11) | 0.0043 (10) | 0.0180 (11) |
| N7 | 0.0780 (18) | 0.0692 (17) | 0.0740 (18) | 0.0243 (15) | 0.0358 (15) | 0.0466 (15) |
| C11 | 0.078 (2) | 0.072 (2) | 0.0585 (19) | 0.0154 (18) | 0.0229 (17) | 0.0335 (17) |
| C12 | 0.0635 (18) | 0.0549 (17) | 0.0609 (18) | 0.0066 (14) | 0.0204 (15) | 0.0285 (14) |
| C13 | 0.0490 (14) | 0.0465 (14) | 0.0560 (15) | 0.0158 (11) | 0.0268 (12) | 0.0266 (13) |
| C14 | 0.073 (2) | 0.0491 (16) | 0.0597 (18) | 0.0059 (14) | 0.0237 (16) | 0.0255 (14) |
| C15 | 0.085 (2) | 0.0537 (18) | 0.082 (2) | 0.0077 (17) | 0.033 (2) | 0.0361 (17) |

Geometric parameters (Å, °)

| | | | |
|--------------------------------------|-------------|----------------------------|-----------|
| Co1—N2 ⁱ | 2.089 (2) | C3—C4 | 1.388 (3) |
| Co1—N2 | 2.089 (2) | C3—C3 ⁱⁱ | 1.486 (4) |
| Co1—O1 | 2.0964 (19) | C4—C5 | 1.374 (3) |
| Co1—O1 ⁱ | 2.0964 (19) | C4—H4 | 0.9300 |
| Co1—N5 | 2.1625 (18) | C5—H5 | 0.9300 |
| Co1—N5 ⁱ | 2.1625 (18) | N7—C11 | 1.318 (5) |
| S1—C21 | 1.630 (3) | N7—C15 | 1.330 (5) |
| O1—H1B | 0.817 (18) | C11—C12 | 1.390 (4) |
| O1—H1C | 0.813 (17) | C11—H11 | 0.9300 |
| N2—C21 | 1.151 (3) | C12—C13 | 1.382 (4) |
| N5—C5 | 1.333 (3) | C12—H12 | 0.9300 |
| N5—C1 | 1.341 (3) | C13—C14 | 1.394 (4) |
| C1—C2 | 1.378 (3) | C13—C13 ⁱⁱⁱ | 1.490 (5) |
| C1—H1A | 0.9300 | C14—C15 | 1.382 (4) |
| C2—C3 | 1.393 (3) | C14—H14 | 0.9300 |
| C2—H2A | 0.9300 | C15—H15 | 0.9300 |
| | | | |
| N2 ⁱ —Co1—N2 | 180.0 | C3—C2—H2A | 120.1 |
| N2 ⁱ —Co1—O1 | 90.16 (9) | C4—C3—C2 | 116.3 (2) |
| N2—Co1—O1 | 89.84 (9) | C4—C3—C3 ⁱⁱ | 121.7 (2) |
| N2 ⁱ —Co1—O1 ⁱ | 89.84 (9) | C2—C3—C3 ⁱⁱ | 122.0 (3) |
| N2—Co1—O1 ⁱ | 90.16 (9) | C5—C4—C3 | 120.3 (2) |
| O1—Co1—O1 ⁱ | 180.0 | C5—C4—H4 | 119.9 |
| N2 ⁱ —Co1—N5 | 88.84 (8) | C3—C4—H4 | 119.9 |
| N2—Co1—N5 | 91.16 (8) | N5—C5—C4 | 123.5 (2) |
| O1—Co1—N5 | 90.36 (7) | N5—C5—H5 | 118.3 |
| O1 ⁱ —Co1—N5 | 89.64 (7) | C4—C5—H5 | 118.3 |
| N2 ⁱ —Co1—N5 ⁱ | 91.16 (8) | N2—C21—S1 | 178.8 (3) |
| N2—Co1—N5 ⁱ | 88.84 (8) | C11—N7—C15 | 116.2 (3) |
| O1—Co1—N5 ⁱ | 89.64 (7) | N7—C11—C12 | 124.3 (3) |
| O1 ⁱ —Co1—N5 ⁱ | 90.36 (7) | N7—C11—H11 | 117.8 |
| N5—Co1—N5 ⁱ | 180.0 | C12—C11—H11 | 117.8 |
| Co1—O1—H1B | 121 (2) | C13—C12—C11 | 119.1 (3) |
| Co1—O1—H1C | 121 (2) | C13—C12—H12 | 120.4 |
| H1B—O1—H1C | 106 (3) | C11—C12—H12 | 120.4 |
| C21—N2—Co1 | 169.0 (2) | C12—C13—C14 | 117.1 (3) |
| C5—N5—C1 | 116.7 (2) | C12—C13—C13 ⁱⁱⁱ | 121.9 (3) |
| C5—N5—Co1 | 120.28 (15) | C14—C13—C13 ⁱⁱⁱ | 121.0 (3) |
| C1—N5—Co1 | 122.85 (15) | C15—C14—C13 | 118.8 (3) |
| N5—C1—C2 | 123.3 (2) | C15—C14—H14 | 120.6 |
| N5—C1—H1A | 118.3 | C13—C14—H14 | 120.6 |
| C2—C1—H1A | 118.3 | N7—C15—C14 | 124.4 (3) |
| C1—C2—C3 | 119.9 (2) | N7—C15—H15 | 117.8 |
| C1—C2—H2A | 120.1 | C14—C15—H15 | 117.8 |

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

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1—H1C \cdots N7 | 0.82 (3) | 1.92 (3) | 2.732 (3) | 171 (3) |
| O1—H1B \cdots S1 ^{iv} | 0.82 (3) | 2.52 (3) | 3.279 (2) | 154 (3) |

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