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Bis(2,2'-bipyridine- κ^2N,N')chlorido-cobalt(II) perchlorate

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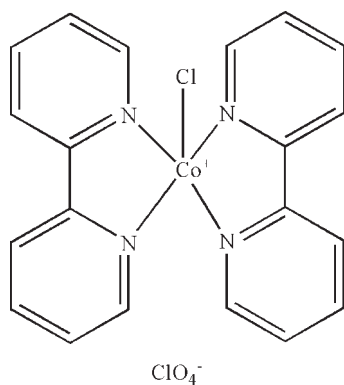
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.043; wR factor = 0.124; data-to-parameter ratio = 13.1.

In the cation of the title compound, $[\text{CoCl}(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{ClO}_4$, the Co^{II} atom displays a distorted trigonal-bipyramidal coordination geometry. The two pyridine rings in each 2,2'-bipyridine ligand form dihedral angles of 10.75 (12) and 4.28 (13)°. The crystal packing is stabilized by interionic $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, $\text{C}-\text{H}\cdots\pi$ interactions and aromatic $\pi-\pi$ stacking interactions, with centroid-centroid distances of 3.616 (7) Å.

Related literature

For the use of 2,2'-bipyridine in coordination chemistry, see: Ruiz-Perez *et al.* (2002). For the structure of the corresponding copper(II) compound, see: Harrison *et al.* (1981).



Experimental

Crystal data

$[\text{CoCl}(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{ClO}_4$
 $M_r = 506.20$
 Monoclinic, $P2_1/n$
 $a = 10.7725$ (12) Å

$b = 12.2696$ (14) Å
 $c = 16.333$ (2) Å
 $\beta = 105.361$ (2)°
 $V = 2081.7$ (4) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.12$ mm⁻¹

$T = 298$ K
 $0.40 \times 0.21 \times 0.19$ mm

Data collection

Bruker SMART CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.664$, $T_{\text{max}} = 0.816$

10284 measured reflections
 3661 independent reflections
 2458 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.124$
 $S = 1.06$
 3661 reflections
 280 parameters

1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³

Table 1
Selected bond lengths (Å).

Co1—N3	1.992 (3)	Co1—N2	2.138 (3)
Co1—N1	1.992 (3)	Co1—Cl1	2.2645 (13)
Co1—N4	2.075 (4)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots O1 ⁱ	0.93	2.41	3.170 (6)	139
C4—H4 \cdots O2 ⁱⁱ	0.93	2.50	3.365 (6)	155
C10—H10 \cdots O3 ⁱⁱⁱ	0.93	2.53	3.116 (6)	122
C11—H11 \cdots Cg1 ^{iv}	0.93	2.85	3.709 (6)	155

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x + 1, y, z$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $-x + 2, -y + 2, -z + 2$. Cg1 is the centroid of the N2/C6–C10 pyridine ring.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); 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: SHELXL97 and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2393).

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supporting information

Acta Cryst. (2009). E65, m1664 [doi:10.1107/S1600536809049034]

Bis(2,2'-bipyridine- κ^2N,N')chloridocobalt(II) perchlorate**Zhongjun Gao and Fahui Li****S1. Comment**

Hydrogen bonding has been intensively investigated in organic crystalline solids, but is relatively unexplored in coordination complexes. In order to search the new functional hydrogen-bonded metal coordination network structures, chelating ligands such as 2,2'-bipyridine (Ruiz-Perez *et al.*, 2002) were selected for study because they can simultaneously coordinate with the metal ions and provide potential intermolecular interaction sites.

In title compound (Fig. 1), the cobalt(II) atom has a distorted trigonal bipyramidal coordination geometry provided by one chloride anion and four nitrogen atoms from the two chelating 2, 2'-bipyridine molecules. The equatorial plane is defined by the N2, N4 and Cl1 atoms, and the sum of the N—Co—N and N—Co—Cl angles is 360.0 (3)°. The apical positions are occupied by the N1 and N3 atoms [N1—Co1—N3 = 174.58 (14)°]. The Co—N bond lengths (Table 1) lie in the range 1.992 (3)-2.138 (3) Å. The N1/C1—C5, N2/C6—C10 and N3/C11—C15, N4/C16—C20 pyridine rings form dihedral angles of 10.75 (12) and 4.28 (13)°, respectively. The structure is similar to that reported previously for the corresponding copper(II) compound (Harrison *et al.*, 1981). In the crystal structure, cations and anions interact through C—H \cdots O hydrogen bonds (Table 2) to form a three-dimensional network. The structure is further stabilized by a C—H \cdots π interaction (C11—H11 \cdots Cg1, 2.85 Å; C11—H11—Cg1, 155°; Cg1 is the centroid of the N2/C6—C10 pyridine ring) and by aromatic π - π stacking interactions involving centrosymmetrically related N3/C11—C15 pyridine rings, with a centroid-to-centroid distance of 3.616 (7) Å.

S2. Experimental

To a solution of Co(ClO₄)₂·6H₂O and CoCl₂·6H₂O (1:1 molar ratio) in ethanol (10 mL) was added a solution of 2,2'-bipyridine (0.1562 g, 1 mmol) in ethanol (20 mL) and the resulting green solution was stirred for 8h at 333 K. The mixture was then filtered and the filtrate was allowed to stand at room temperature for one week to give well shaped green crystals suitable for X-ray analysis (yield 61%). Analysis calculated for C₂₀H₁₆Cl₂N₄O₄Co: C 47.45, H, 3.19; N 11.07%; found: C 47.49, H 3.26, N, 11.12%.

S3. Refinement

All H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

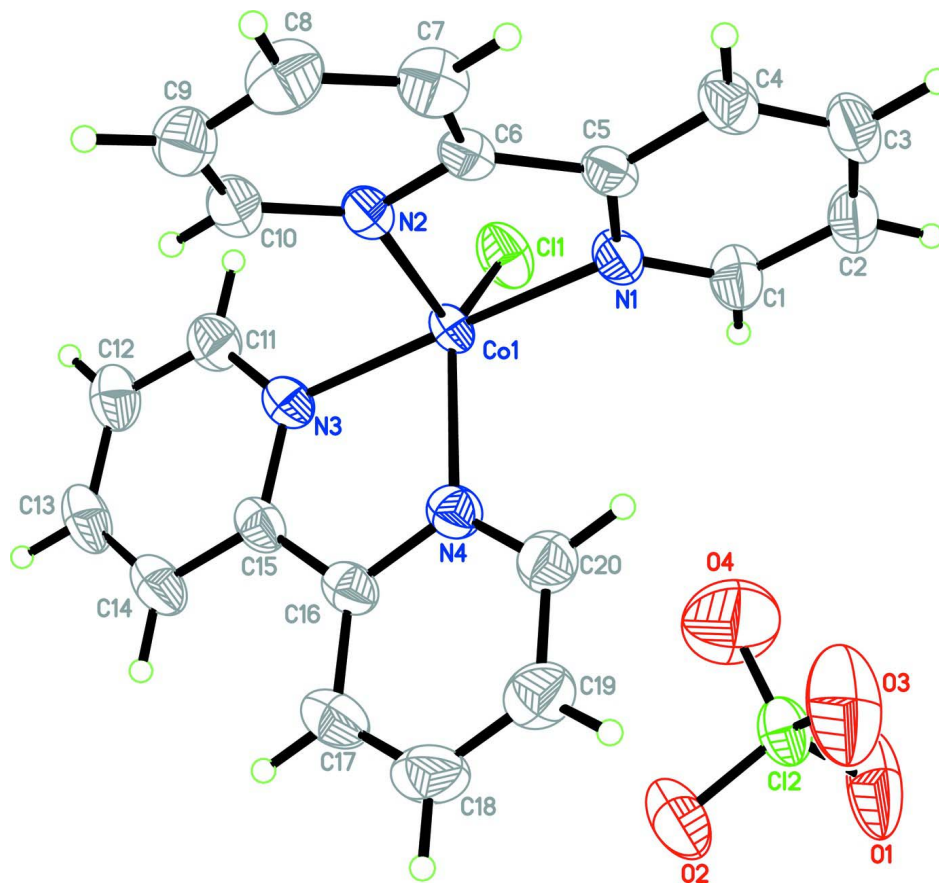


Figure 1

The molecular structure of the title compound with 30% displacement ellipsoids.

Bis(2,2'-bipyridine- κ^2N,N')chloridocobalt(II) perchlorate

Crystal data

[CoCl(C₁₀H₈N₂)₂]ClO₄

$M_r = 506.20$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 10.7725$ (12) Å

$b = 12.2696$ (14) Å

$c = 16.333$ (2) Å

$\beta = 105.361$ (2)°

$V = 2081.7$ (4) Å³

$Z = 4$

$F(000) = 1028$

$D_x = 1.615$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2895 reflections

$\theta = 2.6$ – 25.8°

$\mu = 1.12$ mm⁻¹

$T = 298$ K

Block, green

$0.40 \times 0.21 \times 0.19$ mm

Data collection

Bruker SMART CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.664$, $T_{\max} = 0.816$

10284 measured reflections

3661 independent reflections

2458 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -12 \rightarrow 12$

$k = -14 \rightarrow 14$

$l = -12 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.124$

$S = 1.06$

3661 reflections

280 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 2.7771P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.50 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.39 \text{ e } \text{Å}^{-3}$

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. 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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.73259 (5)	0.95539 (4)	0.86267 (3)	0.04181 (18)
N1	0.7739 (3)	0.9517 (3)	0.7508 (2)	0.0531 (9)
Cl1	0.72296 (14)	1.13977 (10)	0.86111 (8)	0.0720 (4)
Cl2	0.27386 (13)	0.89418 (10)	0.63357 (7)	0.0653 (3)
N2	0.9032 (3)	0.8579 (3)	0.8932 (2)	0.0504 (9)
N3	0.6929 (3)	0.9438 (3)	0.9747 (2)	0.0514 (9)
N4	0.6035 (3)	0.8263 (3)	0.8383 (2)	0.0527 (9)
O1	0.1665 (5)	0.9455 (4)	0.5784 (3)	0.140 (2)
O2	0.2326 (4)	0.8325 (4)	0.6957 (2)	0.1056 (14)
O3	0.3357 (5)	0.8273 (4)	0.5887 (3)	0.143 (2)
O4	0.3567 (6)	0.9733 (4)	0.6800 (4)	0.163 (2)
C1	0.7066 (5)	1.0065 (4)	0.6821 (3)	0.0656 (13)
H1	0.6329	1.0440	0.6851	0.079*
C2	0.7427 (5)	1.0089 (4)	0.6077 (3)	0.0682 (14)
H2	0.6939	1.0468	0.5609	0.082*
C3	0.8520 (5)	0.9544 (4)	0.6034 (3)	0.0691 (14)
H3	0.8790	0.9562	0.5538	0.083*
C4	0.9217 (5)	0.8970 (4)	0.6730 (3)	0.0617 (12)
H4	0.9955	0.8593	0.6708	0.074*
C5	0.8802 (4)	0.8963 (3)	0.7466 (3)	0.0485 (10)
C6	0.9463 (4)	0.8365 (3)	0.8244 (3)	0.0472 (10)
C7	1.0428 (5)	0.7611 (4)	0.8278 (3)	0.0658 (13)
H7	1.0727	0.7473	0.7804	0.079*
C8	1.0942 (5)	0.7065 (4)	0.9037 (4)	0.0742 (14)
H8	1.1589	0.6552	0.9072	0.089*

C9	1.0505 (5)	0.7275 (4)	0.9728 (3)	0.0674 (13)
H9	1.0840	0.6909	1.0237	0.081*
C10	0.9553 (4)	0.8044 (4)	0.9653 (3)	0.0624 (12)
H10	0.9259	0.8198	1.0127	0.075*
C11	0.7445 (5)	1.0087 (4)	1.0417 (3)	0.0623 (12)
H11	0.8073	1.0588	1.0376	0.075*
C12	0.7073 (5)	1.0034 (5)	1.1160 (3)	0.0689 (13)
H12	0.7447	1.0487	1.1615	0.083*
C13	0.6132 (5)	0.9294 (4)	1.1214 (3)	0.0711 (15)
H13	0.5858	0.9245	1.1707	0.085*
C14	0.5602 (5)	0.8629 (4)	1.0530 (3)	0.0679 (14)
H14	0.4959	0.8135	1.0557	0.082*
C15	0.6028 (4)	0.8700 (4)	0.9804 (3)	0.0526 (11)
C16	0.5549 (4)	0.8017 (3)	0.9042 (3)	0.0526 (11)
C17	0.4680 (5)	0.7166 (4)	0.8981 (4)	0.0720 (14)
H17	0.4344	0.6999	0.9435	0.086*
C18	0.4323 (5)	0.6573 (4)	0.8242 (4)	0.0835 (17)
H18	0.3734	0.6006	0.8193	0.100*
C19	0.4824 (5)	0.6808 (4)	0.7588 (4)	0.0751 (15)
H19	0.4596	0.6404	0.7089	0.090*
C20	0.5678 (5)	0.7659 (4)	0.7675 (3)	0.0632 (12)
H20	0.6022	0.7823	0.7224	0.076*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0476 (3)	0.0455 (3)	0.0378 (3)	−0.0002 (3)	0.0210 (2)	0.0038 (2)
N1	0.056 (2)	0.058 (2)	0.049 (2)	0.0005 (19)	0.0199 (17)	0.0079 (18)
Cl1	0.1044 (10)	0.0515 (6)	0.0683 (8)	−0.0031 (7)	0.0372 (7)	0.0040 (6)
Cl2	0.0797 (8)	0.0674 (8)	0.0556 (7)	0.0164 (7)	0.0302 (6)	0.0039 (6)
N2	0.050 (2)	0.057 (2)	0.048 (2)	−0.0015 (17)	0.0184 (17)	0.0080 (17)
N3	0.054 (2)	0.053 (2)	0.052 (2)	0.0006 (18)	0.0244 (17)	0.0030 (17)
N4	0.050 (2)	0.055 (2)	0.056 (2)	0.0011 (17)	0.0181 (17)	0.0032 (18)
O1	0.138 (4)	0.217 (6)	0.072 (3)	0.099 (4)	0.039 (3)	0.055 (3)
O2	0.107 (3)	0.131 (4)	0.093 (3)	0.021 (3)	0.051 (2)	0.047 (3)
O3	0.178 (5)	0.176 (5)	0.095 (3)	0.094 (4)	0.071 (3)	−0.006 (3)
O4	0.191 (6)	0.107 (4)	0.184 (6)	−0.048 (4)	0.034 (5)	−0.021 (4)
C1	0.073 (3)	0.072 (3)	0.052 (3)	0.011 (3)	0.018 (2)	0.010 (2)
C2	0.086 (4)	0.071 (3)	0.045 (3)	−0.004 (3)	0.013 (3)	0.007 (2)
C3	0.094 (4)	0.073 (3)	0.047 (3)	−0.013 (3)	0.031 (3)	−0.001 (3)
C4	0.073 (3)	0.066 (3)	0.055 (3)	−0.006 (3)	0.032 (2)	−0.009 (2)
C5	0.053 (3)	0.046 (2)	0.051 (2)	−0.012 (2)	0.022 (2)	−0.005 (2)
C6	0.049 (2)	0.045 (2)	0.051 (2)	−0.007 (2)	0.020 (2)	−0.0030 (19)
C7	0.070 (3)	0.061 (3)	0.071 (3)	0.006 (3)	0.026 (3)	−0.008 (3)
C8	0.068 (3)	0.061 (3)	0.090 (4)	0.015 (3)	0.014 (3)	−0.001 (3)
C9	0.067 (3)	0.064 (3)	0.070 (3)	0.007 (3)	0.016 (3)	0.011 (3)
C10	0.063 (3)	0.071 (3)	0.055 (3)	0.001 (3)	0.020 (2)	0.012 (2)
C11	0.069 (3)	0.065 (3)	0.057 (3)	0.000 (2)	0.023 (2)	−0.001 (2)

C12	0.085 (4)	0.075 (3)	0.051 (3)	0.014 (3)	0.026 (3)	0.004 (2)
C13	0.091 (4)	0.080 (4)	0.055 (3)	0.019 (3)	0.042 (3)	0.016 (3)
C14	0.072 (3)	0.073 (3)	0.071 (3)	0.008 (3)	0.040 (3)	0.020 (3)
C15	0.053 (3)	0.053 (3)	0.058 (3)	0.012 (2)	0.025 (2)	0.016 (2)
C16	0.048 (3)	0.047 (2)	0.067 (3)	0.008 (2)	0.022 (2)	0.015 (2)
C17	0.073 (3)	0.060 (3)	0.090 (4)	-0.004 (3)	0.034 (3)	0.016 (3)
C18	0.077 (4)	0.059 (3)	0.109 (5)	-0.019 (3)	0.016 (3)	0.007 (3)
C19	0.079 (4)	0.055 (3)	0.084 (4)	-0.006 (3)	0.007 (3)	-0.001 (3)
C20	0.065 (3)	0.063 (3)	0.060 (3)	-0.002 (2)	0.015 (2)	-0.001 (2)

Geometric parameters (Å, °)

Co1—N3	1.992 (3)	C6—C7	1.381 (6)
Co1—N1	1.992 (3)	C7—C8	1.388 (7)
Co1—N4	2.075 (4)	C7—H7	0.9300
Co1—N2	2.138 (3)	C8—C9	1.358 (7)
Co1—Cl1	2.2645 (13)	C8—H8	0.9300
N1—C1	1.344 (6)	C9—C10	1.375 (6)
N1—C5	1.349 (5)	C9—H9	0.9300
Cl2—O3	1.383 (4)	C10—H10	0.9300
Cl2—O4	1.399 (5)	C11—C12	1.375 (6)
Cl2—O1	1.412 (4)	C11—H11	0.9300
Cl2—O2	1.428 (4)	C12—C13	1.381 (7)
N2—C10	1.335 (5)	C12—H12	0.9300
N2—C6	1.351 (5)	C13—C14	1.379 (7)
N3—C15	1.348 (5)	C13—H13	0.9300
N3—C11	1.349 (6)	C14—C15	1.382 (6)
N4—C20	1.342 (5)	C14—H14	0.9300
N4—C16	1.350 (5)	C15—C16	1.475 (6)
C1—C2	1.370 (6)	C16—C17	1.388 (6)
C1—H1	0.9300	C17—C18	1.374 (7)
C2—C3	1.372 (7)	C17—H17	0.9300
C2—H2	0.9300	C18—C19	1.351 (7)
C3—C4	1.379 (7)	C18—H18	0.9300
C3—H3	0.9300	C19—C20	1.373 (6)
C4—C5	1.388 (6)	C19—H19	0.9300
C4—H4	0.9300	C20—H20	0.9300
C5—C6	1.476 (6)		
N3—Co1—N1	174.58 (14)	N2—C6—C5	115.2 (4)
N3—Co1—N4	79.94 (14)	C7—C6—C5	123.6 (4)
N1—Co1—N4	96.21 (14)	C6—C7—C8	118.5 (5)
N3—Co1—N2	97.25 (13)	C6—C7—H7	120.8
N1—Co1—N2	79.29 (13)	C8—C7—H7	120.8
N4—Co1—N2	96.25 (14)	C9—C8—C7	120.5 (5)
N3—Co1—Cl1	93.53 (10)	C9—C8—H8	119.8
N1—Co1—Cl1	91.89 (11)	C7—C8—H8	119.8
N4—Co1—Cl1	137.20 (10)	C8—C9—C10	118.0 (5)

N2—Co1—C11	126.54 (10)	C8—C9—H9	121.0
C1—N1—C5	119.2 (4)	C10—C9—H9	121.0
C1—N1—Co1	123.5 (3)	N2—C10—C9	123.1 (4)
C5—N1—Co1	117.2 (3)	N2—C10—H10	118.5
O3—C12—O4	111.8 (4)	C9—C10—H10	118.5
O3—C12—O1	110.8 (3)	N3—C11—C12	122.2 (5)
O4—C12—O1	109.5 (4)	N3—C11—H11	118.9
O3—C12—O2	110.3 (3)	C12—C11—H11	118.9
O4—C12—O2	104.9 (3)	C11—C12—C13	118.6 (5)
O1—C12—O2	109.4 (3)	C11—C12—H12	120.7
C10—N2—C6	118.8 (4)	C13—C12—H12	120.7
C10—N2—Co1	128.0 (3)	C14—C13—C12	119.4 (4)
C6—N2—Co1	112.2 (3)	C14—C13—H13	120.3
C15—N3—C11	119.4 (4)	C12—C13—H13	120.3
C15—N3—Co1	116.4 (3)	C13—C14—C15	119.8 (5)
C11—N3—Co1	124.1 (3)	C13—C14—H14	120.1
C20—N4—C16	118.7 (4)	C15—C14—H14	120.1
C20—N4—Co1	127.7 (3)	N3—C15—C14	120.6 (4)
C16—N4—Co1	113.5 (3)	N3—C15—C16	114.8 (4)
N1—C1—C2	122.2 (5)	C14—C15—C16	124.5 (4)
N1—C1—H1	118.9	N4—C16—C17	120.5 (5)
C2—C1—H1	118.9	N4—C16—C15	115.0 (4)
C1—C2—C3	119.0 (5)	C17—C16—C15	124.5 (4)
C1—C2—H2	120.5	C18—C17—C16	119.3 (5)
C3—C2—H2	120.5	C18—C17—H17	120.4
C2—C3—C4	119.5 (4)	C16—C17—H17	120.4
C2—C3—H3	120.3	C19—C18—C17	120.2 (5)
C4—C3—H3	120.3	C19—C18—H18	119.9
C3—C4—C5	119.2 (5)	C17—C18—H18	119.9
C3—C4—H4	120.4	C18—C19—C20	118.5 (5)
C5—C4—H4	120.4	C18—C19—H19	120.7
N1—C5—C4	120.8 (4)	C20—C19—H19	120.7
N1—C5—C6	115.4 (3)	N4—C20—C19	122.7 (5)
C4—C5—C6	123.8 (4)	N4—C20—H20	118.6
N2—C6—C7	121.2 (4)	C19—C20—H20	118.6

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots O1 ⁱ	0.93	2.41	3.170 (6)	139
C4—H4 \cdots O2 ⁱⁱ	0.93	2.50	3.365 (6)	155
C10—H10 \cdots O3 ⁱⁱⁱ	0.93	2.53	3.116 (6)	122
C11—H11 \cdots Cg1 ^{iv}	0.93	2.85	3.709 (6)	155

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