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Poly[(μ_2-4,4′-bipyridine-κ^2N:N')bis(μ_2-2-phenoxypropionato-κ^2O:O')cobalt(II)]

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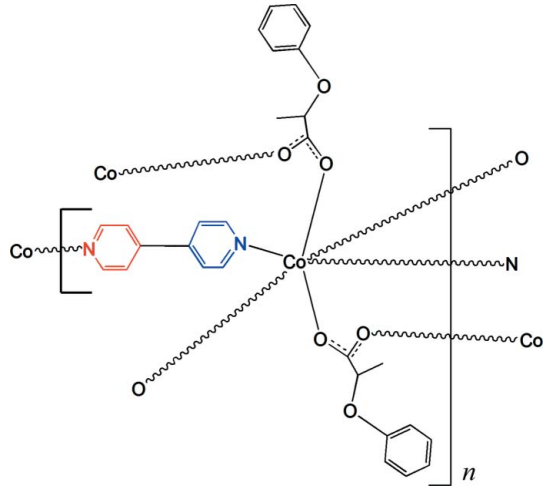
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.027; wR factor = 0.068; data-to-parameter ratio = 13.6.

In the polymeric title compound, $[Co(C_9H_9O_3)_2(C_{10}H_8N_2)]_n$, the Co^{II} ion is located on a twofold rotation axis and is six-coordinated by two N atoms from two 4,4′-bipyridine (4,4′-bipy) ligands in axial positions and by four O atoms from four 2-phenoxypropionate (POPA) anions in equatorial positions, defining a slightly distorted octahedral geometry. The carboxylate group of the POPA anion displays a bis-monodentate mode, linking pairs of Co^{II} ions into a chain parallel to [001]. Adjacent chains are connected in a perpendicular manner through 4,4′-bipy ligands into layers parallel to (100). The 4,4′-bipy ligand is likewise located on a twofold rotation axis, with a dihedral angle between the two pyridine rings of 57.05 (7)°. C—H···O hydrogen-bonding interactions are present within the layers. π–π stacking interactions between the POPA benzene rings of neighbouring layers [centroid-to-centroid distance = 3.976 (3) Å and plane-to-plane distance = 3.618 (3) Å] stabilize the packing of the structure.

Related literature

For background to phenoxyalkanoic acids, see: Müller & Buser (1997). For other metal complexes derived from phenoxypropionic acid, see: Shen *et al.* (2011*a*,*b*,*c*,*d*). For a related cobalt complex, see: Zhuang *et al.* (2007).



Experimental

Crystal data

$[Co(C_9H_9O_3)_2(C_{10}H_8N_2)]$
M_r = 545.44
Monoclinic, $C2/c$
a = 23.6748 (14) Å
b = 11.6289 (7) Å
c = 9.6440 (6) Å
β = 96.353 (4)°
V = 2638.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.70 mm^{-1}
T = 296 K
0.41 × 0.20 × 0.19 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.847, T_{max} = 0.879
8421 measured reflections
2319 independent reflections
2053 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.068
S = 1.06
2319 reflections
170 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—O3	2.0357 (12)	Co1—N1	2.1989 (19)
Co1—O2^{i}	2.1275 (11)	Co1—N2	2.2051 (19)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10···O2^{i}	0.93	2.51	3.079 (2)	120
C15—H15A···O3^{i}	0.93	2.38	3.272 (2)	159

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in

SHELXTL (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2537).

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supporting information

Acta Cryst. (2011). E**67**, m1587–m1588 [doi:10.1107/S1600536811042875]

Poly[(μ_2-4,4′-bipyridine-κ^2N:N')bis(μ_2-2-phenoxypropionato-κ^2O:O')cobalt(II)]

Jin-Bei Shen, Jia-Lu Liu and Guo-Liang Zhao

S1. Comment

The group of phenoxyalkanoic acids include important herbicides. The desired biological activity is largely dependent on the length of the carbon chain of the alkanoic acid, the nature of the phenoxy group, and the position of its attachment to the carbon chain (Müller & Buser, 1997). Therefore the structures of metal complexes of 2-phenoxypropionic acid became interesting for us. Recently, we have reported some results in this regard (Shen *et al.*, 2011*a*,*b*,*c*,*d*). Here, we describe a new Co^{II} complex with 4,4′-bipyridine (4,4′-bipy) as a co-ligand.

The structure of the polymeric title complex is shown in Fig. 1. The Co^{II} ion is located on a twofold rotation axis and is six-coordinated by four carboxylate O atoms from four POPA ligands and two N atoms of two 4,4′-bipy ligands in an octahedral geometry. The Co—O distances are 2.0357 (12) and 2.1275 (11) Å, and the Co—N distances are 2.1989 (19) and 2.2051 (19) Å, all of which are similar to related structures (Zhuang *et al.*, 2007). The 4,4′-bipy ligand exhibits symmetry 2, with a dihedral angle between the two pyridine rings of 57.05 (7)°. The carboxylate groups of the POPA anions display a bis-monodentate mode, bridging pairs of Co^{II} ions into chains parallel to [001]. The 4,4′-bipy molecules connect these chains perpendicularly, resulting in a layered arrangement parallel to (100) (Fig. 2).

As also shown in Fig. 2, intra-layer C—H···O hydrogen bonds between the C atoms of 4,4′-bipy ligands and carboxylate O atoms are present. Adjacent layers are stacked along [100] through π—π interactions between benzene rings of the POPA anions, with centroid–centroid and plane to plane distance of 3.976 (3) Å and 3.618 (3) Å, respectively.

S2. Experimental

Reagents and solvents used were of commercially available quality and were not further purified before using. 2-Phenoxyproionic acid (0.332 g, 2 mmol), 4,4′-bipy (0.156 g, 1 mmol) were mixed in distilled water (30 ml), NaOH (1 *M*) was added dropwise to the solution to adjust a pH of 5–6, then $CoCl_2.6H_2O$ (0.238 g, 1 mmol) was added and the mixture sealed in a 50 ml stainless steel reactor and kept at 433 K for 3 d. The reactor was then cooled to room temperature at a speed of 5 K h^{-1}. Red single crystals were obtained in high yield and filtered off from the solution.

S3. Refinement

The H atoms bonded to C and N atoms were positioned geometrically and refined using a riding model [aliphatic C—H = 0.96 Å (U_{iso}(H) = 1.5U_{eq}(C)), aromatic C—H = 0.93 Å (U_{iso}(H) = 1.2U_{eq}(C))].

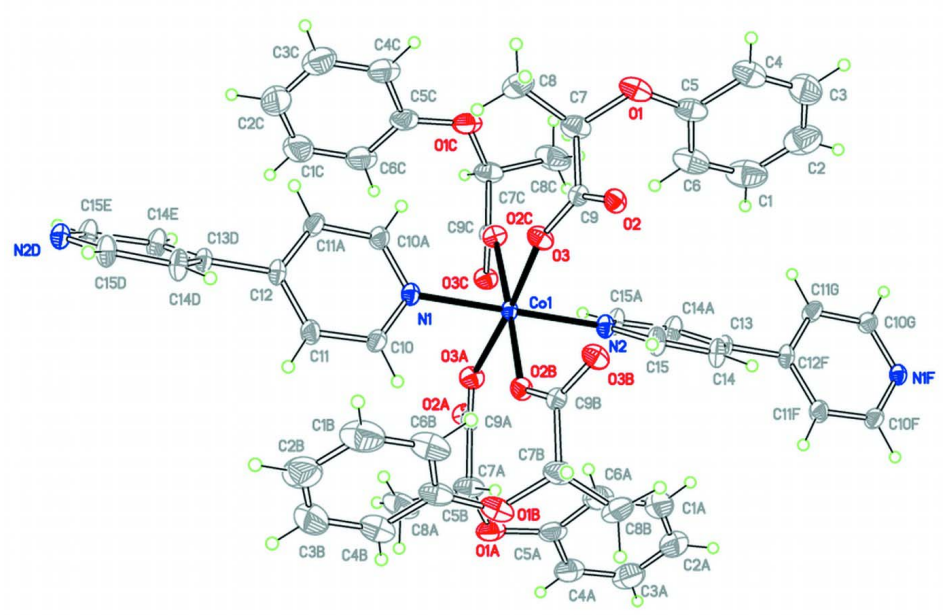

Figure 1

The molecular structure of the title complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms labelled with the suffix A, B, C, D, E, F, G are related by the symmetry operations (-*x* + 1, *y*, -*z* + 1.5), (-*x* + 1, -*y* + 1, -*z* + 2), (*x*, -*y* + 1, *z* - 1/2), (*x*, *y* + 1, *z*), (-*x* + 1, 1 + *y*, -*z* + 1.5), (*x*, *y* - 1, *z*), (-*x* + 1, *y* - 1, -*z* + 1.5), respectively.

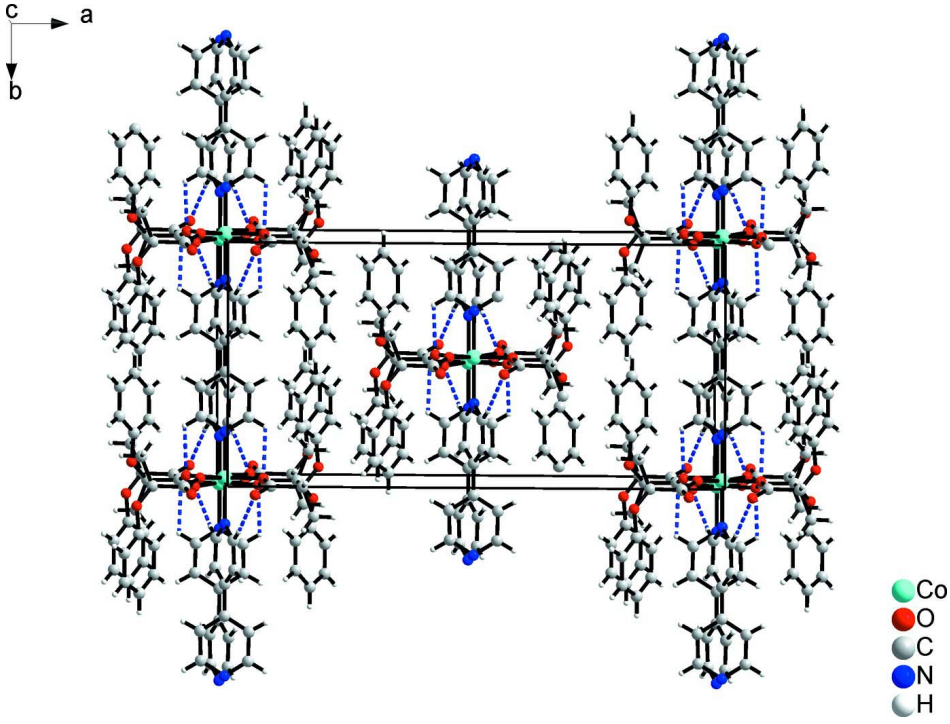

Figure 2

The layered arrangement of title compound, showing intralayer C—H···O interactions.

Poly[(μ_2-4,4′-bipyridine-κ^2N:N')bis(μ_2-2- phenoxypropionato-κ^2O:O')cobalt(II)]

Crystal data

$[Co(C_9H_9O_3)_2(C_{10}H_8N_2)]$
M_r = 545.44
Monoclinic, $C2/c$
Hall symbol: -C 2yc
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b = 11.6289 (7) Å
c = 9.6440 (6) Å
β = 96.353 (4)°
V = 2638.8 (3) Å^3
Z = 4
$F(000)$ = 1132
D_x = 1.373 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3897 reflections
θ = 1.7–25.0°
μ = 0.70 mm^{-1}
T = 296 K
Block, red
0.41 × 0.20 × 0.19 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.847, T_{max} = 0.879
8421 measured reflections
2319 independent reflections
2053 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 25.0°, θ_{min} = 1.7°
h = −28→26
k = −13→11
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.068
S = 1.06
2319 reflections
170 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 1.1007P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Co1	0.5000	0.52263 (3)	0.7500	0.02374 (11)
O3	0.55380 (5)	0.53098 (11)	0.92961 (11)	0.0393 (3)
C9	0.58754 (7)	0.49847 (13)	1.02991 (16)	0.0281 (4)
N1	0.5000	0.71171 (16)	0.7500	0.0290 (4)

C8	0.67426 (10)	0.6225 (2)	1.0358 (3)	0.0794 (8)
H8A	0.7136	0.6252	1.0199	0.119*
H8B	0.6708	0.6423	1.1312	0.119*
H8C	0.6530	0.6762	0.9751	0.119*
C7	0.65102 (8)	0.50059 (19)	1.0060 (2)	0.0493 (5)
H7	0.6548	0.4805	0.9088	0.059*
C11	0.45124 (8)	0.89365 (15)	0.76775 (19)	0.0384 (4)
H11	0.4177	0.9315	0.7812	0.046*
O1	0.68453 (5)	0.42260 (14)	1.09706 (14)	0.0555 (4)
C10	0.45282 (7)	0.77274 (15)	0.76537 (19)	0.0367 (4)
H10	0.4194	0.7328	0.7749	0.044*
C6	0.64660 (10)	0.2551 (2)	0.9605 (3)	0.0699 (7)
H6	0.6246	0.3010	0.8965	0.084*
C1	0.64664 (11)	0.1349 (3)	0.9439 (3)	0.0883 (9)
H1	0.6251	0.1027	0.8671	0.106*
C5	0.67937 (8)	0.3048 (2)	1.0721 (2)	0.0536 (6)
C4	0.71055 (10)	0.2322 (2)	1.1675 (2)	0.0651 (7)
H4	0.7324	0.2641	1.2440	0.078*
C3	0.70968 (11)	0.1124 (3)	1.1507 (3)	0.0810 (8)
H3	0.7308	0.0661	1.2158	0.097*
C2	0.67765 (12)	0.0629 (3)	1.0379 (4)	0.0906 (9)
H2	0.6770	−0.0164	1.0256	0.109*
C12	0.5000	0.95685 (19)	0.7500	0.0307 (5)
O2	0.57552 (5)	0.47394 (10)	1.14927 (11)	0.0339 (3)
C13	0.5000	0.08758 (19)	0.7500	0.0294 (5)
N2	0.5000	0.33300 (16)	0.7500	0.0311 (4)
C14	0.48321 (8)	0.15074 (14)	0.86106 (17)	0.0390 (4)
H14A	0.4708	0.1130	0.9371	0.047*
C15	0.48508 (8)	0.27175 (15)	0.85836 (17)	0.0380 (4)
H15A	0.4754	0.3115	0.9360	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.03125 (19)	0.01885 (18)	0.02070 (16)	0.000	0.00108 (12)	0.000
O3	0.0410 (7)	0.0518 (8)	0.0235 (6)	0.0044 (6)	−0.0037 (5)	−0.0006 (5)
C9	0.0328 (9)	0.0268 (10)	0.0250 (8)	−0.0021 (7)	0.0040 (7)	−0.0023 (6)
N1	0.0354 (11)	0.0228 (11)	0.0283 (10)	0.000	0.0020 (8)	0.000
C8	0.0486 (14)	0.088 (2)	0.1002 (19)	−0.0260 (13)	0.0020 (13)	0.0290 (16)
C7	0.0350 (11)	0.0761 (16)	0.0378 (10)	0.0012 (10)	0.0077 (8)	0.0059 (10)
C11	0.0383 (10)	0.0266 (10)	0.0519 (10)	0.0060 (8)	0.0123 (8)	0.0033 (8)
O1	0.0366 (8)	0.0757 (11)	0.0525 (8)	0.0119 (7)	−0.0024 (6)	−0.0041 (8)
C10	0.0350 (10)	0.0263 (10)	0.0497 (10)	−0.0025 (8)	0.0088 (8)	0.0017 (8)
C6	0.0475 (14)	0.096 (2)	0.0644 (15)	0.0133 (13)	0.0001 (11)	−0.0174 (14)
C1	0.0584 (17)	0.102 (2)	0.103 (2)	0.0051 (16)	0.0024 (15)	−0.0423 (19)
C5	0.0315 (10)	0.0771 (17)	0.0535 (12)	0.0076 (10)	0.0104 (9)	−0.0093 (11)
C4	0.0461 (13)	0.086 (2)	0.0623 (14)	0.0115 (12)	0.0026 (11)	−0.0031 (13)
C3	0.0592 (16)	0.084 (2)	0.101 (2)	0.0153 (15)	0.0129 (15)	0.0090 (17)

C2	0.0567 (17)	0.079 (2)	0.139 (3)	0.0018 (16)	0.0263 (18)	−0.024 (2)
C12	0.0462 (15)	0.0207 (14)	0.0255 (11)	0.000	0.0046 (10)	0.000
O2	0.0351 (7)	0.0398 (7)	0.0276 (6)	0.0029 (5)	0.0070 (5)	0.0071 (5)
C13	0.0388 (14)	0.0197 (13)	0.0294 (11)	0.000	0.0022 (10)	0.000
N2	0.0419 (12)	0.0229 (11)	0.0282 (10)	0.000	0.0019 (9)	0.000
C14	0.0627 (12)	0.0250 (10)	0.0312 (9)	0.0026 (9)	0.0133 (8)	0.0049 (7)
C15	0.0605 (12)	0.0258 (10)	0.0292 (8)	0.0051 (9)	0.0119 (8)	−0.0018 (7)

Geometric parameters (Å, º)

Co1—O3^{i}	2.0357 (12)	C6—C5	1.382 (3)
Co1—O3	2.0357 (12)	C6—C1	1.407 (4)
Co1—O2^{ii}	2.1275 (11)	C6—H6	0.9300
Co1—O2^{iii}	2.1275 (11)	C1—C2	1.384 (4)
Co1—N1	2.1989 (19)	C1—H1	0.9300
Co1—N2	2.2051 (19)	C5—C4	1.398 (3)
O3—C9	1.243 (2)	C4—C3	1.402 (4)
C9—O2	1.2489 (18)	C4—H4	0.9300
C9—C7	1.546 (2)	C3—C2	1.381 (4)
N1—C10	1.3453 (19)	C3—H3	0.9300
N1—C10^{i}	1.3453 (19)	C2—H2	0.9300
C8—C7	1.537 (3)	C12—C11^{i}	1.395 (2)
C8—H8A	0.9600	C12—C13^{iv}	1.520 (3)
C8—H8B	0.9600	O2—Co1^{iii}	2.1275 (11)
C8—H8C	0.9600	C13—C14	1.3924 (19)
C7—O1	1.438 (2)	C13—C14^{i}	1.392 (2)
C7—H7	0.9800	C13—C12^{v}	1.520 (3)
C11—C12	1.395 (2)	N2—C15^{i}	1.3439 (19)
C11—C10	1.407 (2)	N2—C15	1.3439 (19)
C11—H11	0.9300	C14—C15	1.408 (2)
O1—C5	1.394 (3)	C14—H14A	0.9300
C10—H10	0.9300	C15—H15A	0.9300
O3^{i}—Co1—O3	174.53 (7)	N1—C10—C11	123.57 (16)
O3^{i}—Co1—O2^{ii}	95.10 (5)	N1—C10—H10	118.2
O3—Co1—O2^{ii}	84.80 (5)	C11—C10—H10	118.2
O3^{i}—Co1—O2^{iii}	84.80 (5)	C5—C6—C1	119.8 (3)
O3—Co1—O2^{iii}	95.10 (5)	C5—C6—H6	120.1
O2^{ii}—Co1—O2^{iii}	177.85 (6)	C1—C6—H6	120.1
O3^{i}—Co1—N1	87.26 (4)	C2—C1—C6	122.3 (3)
O3—Co1—N1	87.26 (4)	C2—C1—H1	118.9
O2^{ii}—Co1—N1	88.93 (3)	C6—C1—H1	118.9
O2^{iii}—Co1—N1	88.93 (3)	C6—C5—O1	125.2 (2)
O3^{i}—Co1—N2	92.74 (4)	C6—C5—C4	118.1 (2)
O3—Co1—N2	92.74 (4)	O1—C5—C4	116.7 (2)
O2^{ii}—Co1—N2	91.07 (3)	C5—C4—C3	121.6 (2)
O2^{iii}—Co1—N2	91.07 (3)	C5—C4—H4	119.2
N1—Co1—N2	180.0	C3—C4—H4	119.2

C9—O3—Co1	159.26 (12)	C2—C3—C4	120.4 (3)
O3—C9—O2	126.46 (16)	C2—C3—H3	119.8
O3—C9—C7	115.51 (14)	C4—C3—H3	119.8
O2—C9—C7	117.75 (15)	C3—C2—C1	118.0 (3)
C10—N1—C10^{i}	116.3 (2)	C3—C2—H2	121.0
C10—N1—Co1	121.84 (10)	C1—C2—H2	121.0
C10^{i}—N1—Co1	121.84 (10)	C11—C12—C11^{i}	116.4 (2)
C7—C8—H8A	109.5	C11—C12—C13^{iv}	121.80 (10)
C7—C8—H8B	109.5	C11^{i}—C12—C13^{iv}	121.80 (10)
H8A—C8—H8B	109.5	C9—O2—Co1^{iii}	134.85 (11)
C7—C8—H8C	109.5	C14—C13—C14^{i}	116.3 (2)
H8A—C8—H8C	109.5	C14—C13—C12^{v}	121.84 (10)
H8B—C8—H8C	109.5	C14^{i}—C13—C12^{v}	121.84 (10)
O1—C7—C8	107.80 (18)	C15^{i}—N2—C15	116.0 (2)
O1—C7—C9	112.24 (15)	C15^{i}—N2—Co1	122.01 (10)
C8—C7—C9	108.70 (17)	C15—N2—Co1	122.01 (10)
O1—C7—H7	109.4	C13—C14—C15	120.04 (15)
C8—C7—H7	109.4	C13—C14—H14A	120.0
C9—C7—H7	109.4	C15—C14—H14A	120.0
C12—C11—C10	120.05 (16)	N2—C15—C14	123.75 (15)
C12—C11—H11	120.0	N2—C15—H15A	118.1
C10—C11—H11	120.0	C14—C15—H15A	118.1
C5—O1—C7	118.84 (16)		

O2^{ii}—Co1—O3—C9	−81.2 (3)	C1—C6—C5—C4	−1.7 (3)
O2^{iii}—Co1—O3—C9	101.0 (3)	C7—O1—C5—C6	4.0 (3)
N1—Co1—O3—C9	−170.3 (3)	C7—O1—C5—C4	−176.79 (16)
N2—Co1—O3—C9	9.7 (3)	C6—C5—C4—C3	0.9 (3)
Co1—O3—C9—O2	−96.6 (3)	O1—C5—C4—C3	−178.37 (19)
Co1—O3—C9—C7	89.7 (3)	C5—C4—C3—C2	0.1 (4)
O3^{i}—Co1—N1—C10	65.25 (10)	C4—C3—C2—C1	−0.3 (4)
O3—Co1—N1—C10	−114.75 (10)	C6—C1—C2—C3	−0.4 (4)
O2^{ii}—Co1—N1—C10	160.41 (10)	C10—C11—C12—C11^{i}	−0.79 (12)
O2^{iii}—Co1—N1—C10	−19.59 (10)	C10—C11—C12—C13^{iv}	179.21 (12)
O3^{i}—Co1—N1—C10^{i}	−114.75 (10)	O3—C9—O2—Co1^{iii}	−2.7 (3)
O3—Co1—N1—C10^{i}	65.25 (10)	C7—C9—O2—Co1^{iii}	170.92 (12)
O2^{ii}—Co1—N1—C10^{i}	−19.59 (10)	O3^{i}—Co1—N2—C15^{i}	56.44 (11)
O2^{iii}—Co1—N1—C10^{i}	160.41 (10)	O3—Co1—N2—C15^{i}	−123.56 (11)
O3—C9—C7—O1	−156.70 (16)	O2^{ii}—Co1—N2—C15^{i}	−38.72 (10)
O2—C9—C7—O1	29.0 (2)	O2^{iii}—Co1—N2—C15^{i}	141.28 (10)
O3—C9—C7—C8	84.2 (2)	O3^{i}—Co1—N2—C15	−123.56 (11)
O2—C9—C7—C8	−90.2 (2)	O3—Co1—N2—C15	56.44 (11)
C8—C7—O1—C5	−167.58 (16)	O2^{ii}—Co1—N2—C15	141.28 (11)
C9—C7—O1—C5	72.7 (2)	O2^{iii}—Co1—N2—C15	−38.72 (11)
C10^{i}—N1—C10—C11	−0.85 (13)	C14^{i}—C13—C14—C15	−1.47 (13)
Co1—N1—C10—C11	179.15 (13)	C12^{v}—C13—C14—C15	178.53 (13)
C12—C11—C10—N1	1.7 (3)	C15^{i}—N2—C15—C14	−1.59 (14)

C5—C6—C1—C2	1.5 (4)	Co1—N2—C15—C14	178.41 (14)
C1—C6—C5—O1	177.6 (2)	C13—C14—C15—N2	3.2 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···O2^{iii}	0.93	2.51	3.079 (2)	120
C15—H15*A*···O3^{iii}	0.93	2.38	3.272 (2)	159

Symmetry code: (iii) −*x*+1, −*y*+1, −*z*+2.