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Piperazine-1,4-diium bis(pyridine-2,6-dicarboxylato-κ^3O^2,N,O^6)cobaltate(II) tetrahydrate

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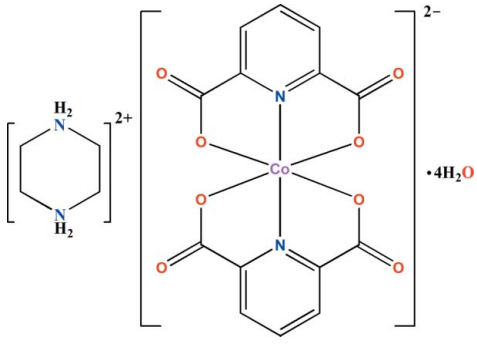
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.077; data-to-parameter ratio = 16.5.

The asymmetric unit of the title complex, $(C_4H_{12}N_2)[Co(C_7H_3NO_4)_2]\cdot 4H_2O$, consists of one piperazinediium dication, one $[Co(py\text{-}2,6\text{-}dc)_2]^{2-}$ dianion (where py-2,6-dc is pyridine-2,6-dicarboxylate) and four water molecules. The piperazinediium cation adopts a chair conformation and the Co^{II} ion is six-coordinated in an N_2O_4 environment, having a distorted octahedral geometry. In the crystal, intermolecular O—H···O, N—H···O and weak C—H···O hydrogen bonds link the components, forming a three-dimensional network.

Related literature

The structure determination of title compound was performed as a part of our project on the synthesis of new proton-transfer compounds, see: Raissi Shabari *et al.* (2010). For bond lengths in a related cobaltate(II) complex, see: Pasdar *et al.* (2011). For bond lengths and angles in the piperazinediium dication, see: Sutherland & Harrison (2009); Allen *et al.* (1995). For positive-charge-assisted hydrogen bonds, see: Gilli *et al.* (1994).



Experimental

Crystal data

$(C_4H_{12}N_2)[Co(C_7H_3NO_4)_2]\cdot 4H_2O$
M_r = 549.36
Monoclinic, $P2_1/n$
a = 7.9537 (16) Å
b = 13.420 (3) Å
c = 21.004 (4) Å
β = 90.55 (3)°
V = 2241.8 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.84 mm^{-1}
T = 150 K
0.5 × 0.40 × 0.15 mm

Data collection

Stoe IPDS 2T diffractometer
Absorption correction: numerical [shape of crystal determined optically (*X-RED* and *X-SHAPE*; Stoe & Cie, 2005)]
T_{min} = 0.670, T_{max} = 0.878
15339 measured reflections
6018 independent reflections
5226 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.077
S = 1.07
6018 reflections
364 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12B···O3^{i}	0.79 (3)	2.06 (3)	2.8428 (18)	174 (3)
O11—H11B···O5	0.83 (3)	2.00 (3)	2.8290 (18)	177 (3)
O11—H11A···O1^{ii}	0.81 (3)	2.02 (3)	2.8173 (19)	170 (3)
O10—H10B···O7	0.79 (3)	2.15 (3)	2.9213 (19)	165 (3)
O10—H10A···O11^{iii}	0.87 (3)	1.99 (3)	2.854 (2)	172 (3)
O9—H9B···O8	0.79 (3)	1.96 (3)	2.7521 (18)	175 (2)
O9—H9A···O12^{iv}	0.83 (3)	2.01 (3)	2.840 (2)	173 (3)
N4—H4B···O3^{v}	0.89 (2)	1.92 (2)	2.7973 (18)	165 (2)
N4—H4A···O6^{iii}	0.91 (2)	1.89 (2)	2.7592 (17)	161 (2)
N3—H3B···O9^{vi}	0.91 (2)	1.86 (2)	2.6958 (18)	152 (2)
N3—H3A···O2	0.91 (2)	2.50 (2)	3.1126 (19)	124.5 (18)
N3—H3A···O1	0.91 (2)	1.88 (2)	2.7957 (18)	176 (2)
C18—H18B···O10^{vii}	0.97	2.58	3.457 (2)	151
C17—H17B···O7^{vii}	0.97	2.36	3.127 (2)	135
C16—H16B···O12^{iv}	0.97	2.52	3.293 (2)	137
C15—H15B···O10^{vi}	0.97	2.60	3.261 (2)	126
C15—H15A···O2	0.97	2.54	3.140 (2)	120

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+2, -y+2, -z+1$; (iii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iv) $-x+1, -y+1, -z+1$; (v) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (vi) $x+1, y, z$; (vii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5266).

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1995). *International Tables for Crystallography*, Vol. C, Section 9.5, pp. 685–706. Dordrecht: Kluwer Academic Publishers.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gilli, P., Ferretti, V., Bertolasi, V. & Gilli, G. (1994). *J. Am. Chem. Soc.* **116**, 909–915.
Pasdar, H., Sadat Kashani, S., Ghiasi, R., Aghabozorg, H. & Notash, B. (2011). *Acta Cryst.* E**67**, m507–m508.
Raissi Shabari, A., Kharaghani, S. & Pourayoubi, M. (2010). *Acta Cryst.* E**66**, m1000.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (2005). *X-AREA*, *X-RED* and *X-AREA*. Stoe & Cie, Darmstadt, Germany.
Sutherland, P. A. & Harrison, W. T. A. (2009). *Acta Cryst.* E**65**, m565.

supporting information

Acta Cryst. (2011). E**67**, m985–m986 [doi:10.1107/S1600536811023518]

Piperazine-1,4-diium bis(pyridine-2,6-dicarboxylato-κ^3O^2,N,O^6)cobaltate(II) tetrahydrate

Akbar Raissi Shabari, Nazanin Ghoddoosi, Mehrdad Pourayoubi and Shahram Moradi

S1. Comment

The structure determination of title compound was performed as a part of a project on the synthesis of new proton-transfer compounds (Raissi Shabari *et al.*, 2010).

The Co atom in title compound adopts a distorted octahedral coordination arising from four oxygen and two nitrogen atoms of two pyridine-2,6-dicarboxylato ligands, Fig. 1. The Co—O and Co—N bond lengths are similar to those in a recently published bis(pyridine-2,6-dicarboxylato)cobaltate(II) complex, $(C_6H_{10}N_2)[Co(C_7H_3NO_4)_2].5H_2O$ (Pasdar *et al.*, 2011). The organic dication adopts a typical chair geometry with normal bond lengths and angles (Sutherland & Harrison, 2009; Allen *et al.*, 1995).

The protonated piperazine nitrogen atoms are involved in positive charge assisted (Gilli *et al.*, 1994) N—H···O hydrogen bonds, atom N3 is involved with the O atoms of an adjacent carbonyl of one pyridine-2,6-dicarboxylato ligand and a neighbouring H_2O molecule and atom N4 with two pyridine-2,6-dicarboxylato ligands in two neighbouring complexes.

Cations, anions and four crystallographically independent H_2O molecules are hydrogen bonded in a three-dimensional network through N—H···O, O—H···O and weak C—H···O hydrogen bonds (Table 1).

S2. Experimental

A solution of $Co(NO_3)_2.6H_2O$ (2 mmol) in H_2O was added to a solution of pyridine-2,6-dicarboxylic acid (4 mmol) in H_2O and stirred (45 minutes) at room temperature. To the resulting solution, a solution of piperazine (4 mmol) in H_2O was added and stirred (4 h) at 323 K. Suitable single crystals for X-ray analysis were obtained after slow evaporation at room temperature. IR (KBr, ν, cm^{-1}): 3425, 3240, 3013, 3001, 2725, 2467, 1608, 1568, 1425, 1371, 1279, 1182, 1074, 1036, 914, 824, 760, 733, 692, 677, 592, 534.

S3. Refinement

H atoms of water molecules and N—H groups of cation were found in a difference Fourier map and refined isotropically. Carbon-bound H-atoms were placed in calculated positions, C—H = 0.93 Å (aromatic) and 0.97 Å (CH_2), and were included in the refinement using a riding-model approximation, with $U_{iso} = 1.2U_{eq}$ (C).

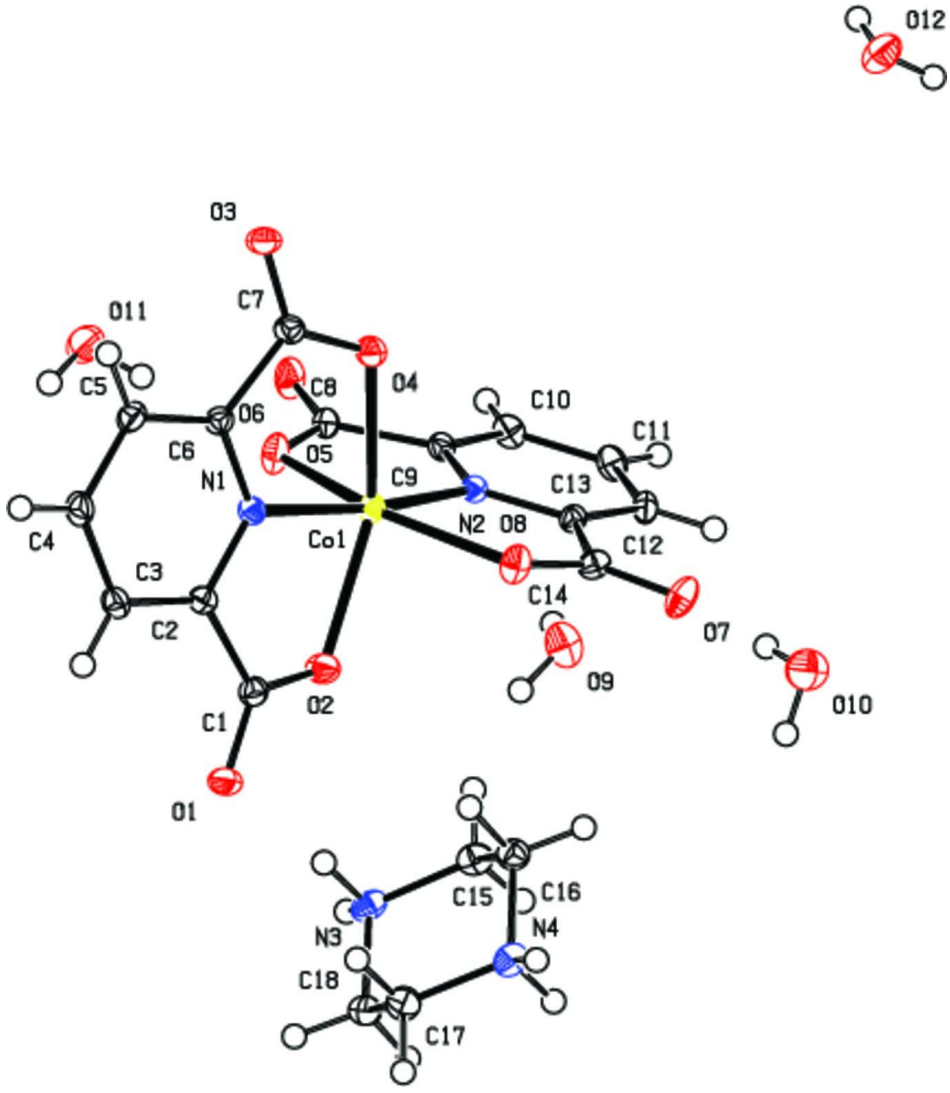

Figure 1

Molecular structure and atom labeling scheme for title complex with displacement ellipsoids drawn at the 50% probability level.

Piperazine-1,4-diium bis(pyridine-2,6-dicarboxylato- κ^3O^2,N,O^6)cobaltate(II) tetrahydrate

Crystal data

$(C_4H_{12}N_2)[Co(C_7H_3NO_4)_2]\cdot 4H_2O$
$M_r = 549.36$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 7.9537\ (16)$ Å
$b = 13.420\ (3)$ Å
$c = 21.004\ (4)$ Å
$\beta = 90.55\ (3)°$
$V = 2241.8\ (8)$ Å^3
$Z = 4$

$F(000) = 1140$
$D_x = 1.628$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6018 reflections
$\theta = 2.5–29.1°$
$\mu = 0.84$ mm^{-1}
$T = 150$ K
Plate, pink
0.5 × 0.4 × 0.15 mm

Data collection

Stoe IPDS 2T diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0.15 mm pixels mm^{-1}
rotation method scans
Absorption correction: numerical shape of crystal determined optically
T_{min} = 0.670, T_{max} = 0.878

15339 measured reflections
6018 independent reflections
5226 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 29.1°, θ_{min} = 2.5°
h = −10→10
k = −16→18
l = −24→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.077
S = 1.07
6018 reflections
364 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 1.2111P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.48 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.33 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_{iso}*/U_{eq}
O10	0.26226 (16)	0.55638 (11)	0.28084 (7)	0.0288 (3)
Co1	0.73056 (2)	0.745668 (14)	0.504511 (9)	0.01278 (6)
C18	1.08242 (19)	0.81672 (13)	0.23202 (8)	0.0195 (3)
H18A	1.1280	0.7659	0.2043	0.023*
H18B	1.1624	0.8712	0.2344	0.023*
C16	0.76380 (18)	0.73170 (12)	0.26866 (7)	0.0173 (3)
H16A	0.6828	0.6777	0.2667	0.021*
H16B	0.7185	0.7836	0.2957	0.021*
C15	0.92728 (19)	0.69397 (11)	0.29675 (7)	0.0176 (3)
H15A	0.9091	0.6714	0.3400	0.021*
H15B	0.9670	0.6378	0.2720	0.021*
C17	0.9172 (2)	0.85410 (12)	0.20509 (8)	0.0197 (3)
H17A	0.8759	0.9083	0.2311	0.024*
H17B	0.9339	0.8793	0.1623	0.024*
N4	0.79141 (16)	0.77200 (10)	0.20359 (6)	0.0165 (2)

N3	1.05640 (16)	0.77441 (11)	0.29680 (6)	0.0175 (3)
O5	0.91680 (15)	0.73565 (8)	0.58111 (5)	0.0206 (2)
N1	0.71594 (14)	0.89536 (9)	0.51050 (6)	0.0128 (2)
O4	0.53764 (14)	0.77007 (8)	0.57578 (5)	0.0188 (2)
O2	0.89349 (14)	0.79723 (8)	0.43015 (5)	0.0191 (2)
O8	0.57909 (14)	0.68290 (8)	0.42961 (5)	0.0187 (2)
C7	0.53098 (18)	0.85856 (11)	0.59591 (7)	0.0145 (3)
C6	0.62806 (17)	0.93522 (11)	0.55788 (7)	0.0132 (3)
C9	0.86203 (17)	0.56523 (11)	0.56247 (7)	0.0128 (3)
C13	0.69018 (17)	0.53516 (11)	0.47424 (7)	0.0124 (3)
O3	0.44917 (14)	0.88780 (9)	0.64298 (5)	0.0190 (2)
O1	0.95932 (14)	0.93309 (8)	0.37446 (5)	0.0188 (2)
O7	0.51331 (14)	0.53761 (9)	0.38257 (6)	0.0218 (2)
N2	0.76472 (14)	0.59801 (9)	0.51494 (6)	0.0116 (2)
C14	0.58397 (18)	0.58788 (11)	0.42379 (7)	0.0148 (3)
C8	0.94256 (18)	0.64790 (11)	0.60154 (7)	0.0149 (3)
C2	0.80213 (17)	0.95197 (11)	0.46993 (7)	0.0128 (3)
C5	0.62615 (19)	1.03742 (11)	0.56736 (7)	0.0159 (3)
H5	0.5664	1.0652	0.6008	0.019*
C12	0.71303 (17)	0.43292 (11)	0.47966 (7)	0.0147 (3)
H12	0.6622	0.3892	0.4510	0.018*
C10	0.88885 (18)	0.46439 (11)	0.57169 (7)	0.0163 (3)
H10	0.9551	0.4417	0.6054	0.020*
C1	0.89276 (17)	0.89032 (11)	0.42059 (7)	0.0147 (3)
C3	0.80328 (18)	1.05509 (11)	0.47560 (7)	0.0151 (3)
H3	0.8610	1.0946	0.4468	0.018*
C11	0.81438 (18)	0.39770 (11)	0.52927 (7)	0.0169 (3)
H11	0.8322	0.3296	0.5340	0.020*
C4	0.71541 (19)	1.09736 (11)	0.52577 (8)	0.0172 (3)
H4	0.7165	1.1661	0.5315	0.021*
O9	0.37881 (15)	0.76948 (10)	0.33746 (7)	0.0244 (3)
O6	1.02757 (14)	0.62407 (9)	0.64909 (6)	0.0223 (2)
O11	0.9680 (2)	0.87887 (11)	0.67821 (7)	0.0312 (3)
O12	0.46115 (18)	0.06341 (10)	0.71858 (6)	0.0260 (3)
H3B	1.157 (3)	0.7514 (16)	0.3122 (11)	0.029 (6)*
H4B	0.828 (3)	0.7228 (18)	0.1787 (11)	0.029 (6)*
H3A	1.022 (3)	0.8243 (18)	0.3232 (11)	0.031 (6)*
H4A	0.694 (3)	0.7923 (19)	0.1846 (11)	0.034 (6)*
H9B	0.437 (3)	0.7419 (18)	0.3625 (12)	0.031 (6)*
H10B	0.324 (4)	0.561 (2)	0.3103 (15)	0.050 (8)*
H10A	0.321 (3)	0.582 (2)	0.2501 (14)	0.051 (8)*
H9A	0.432 (4)	0.815 (2)	0.3200 (14)	0.052 (8)*
H12A	0.508 (3)	0.050 (2)	0.7517 (14)	0.051 (8)*
H12B	0.464 (3)	0.013 (2)	0.6991 (14)	0.045 (8)*
H11B	0.950 (3)	0.838 (2)	0.6492 (14)	0.046 (7)*
H11A	0.989 (3)	0.929 (2)	0.6591 (13)	0.046 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O10	0.0222 (6)	0.0391 (8)	0.0252 (7)	−0.0005 (5)	−0.0045 (5)	0.0017 (6)
Co1	0.01592 (9)	0.00943 (9)	0.01298 (10)	0.00047 (7)	−0.00079 (6)	0.00003 (7)
C18	0.0185 (7)	0.0244 (8)	0.0158 (7)	−0.0038 (6)	0.0021 (5)	−0.0007 (6)
C16	0.0154 (6)	0.0188 (7)	0.0177 (7)	0.0008 (5)	0.0014 (5)	−0.0008 (5)
C15	0.0211 (7)	0.0161 (7)	0.0156 (7)	0.0040 (5)	−0.0001 (5)	0.0027 (5)
C17	0.0262 (8)	0.0165 (7)	0.0165 (7)	−0.0008 (6)	−0.0016 (6)	0.0040 (6)
N4	0.0158 (6)	0.0190 (6)	0.0147 (6)	0.0039 (5)	−0.0044 (5)	0.0003 (5)
N3	0.0149 (6)	0.0247 (7)	0.0128 (6)	0.0044 (5)	−0.0024 (5)	−0.0024 (5)
O5	0.0275 (6)	0.0138 (5)	0.0202 (5)	−0.0027 (4)	−0.0086 (4)	−0.0010 (4)
N1	0.0126 (5)	0.0118 (5)	0.0140 (6)	0.0001 (4)	0.0003 (4)	0.0004 (4)
O4	0.0240 (5)	0.0130 (5)	0.0194 (5)	−0.0025 (4)	0.0056 (4)	−0.0011 (4)
O2	0.0243 (5)	0.0142 (5)	0.0188 (5)	0.0013 (4)	0.0063 (4)	−0.0001 (4)
O8	0.0235 (5)	0.0147 (5)	0.0177 (5)	0.0013 (4)	−0.0082 (4)	0.0011 (4)
C7	0.0156 (6)	0.0153 (7)	0.0126 (6)	−0.0003 (5)	−0.0003 (5)	0.0021 (5)
C6	0.0149 (6)	0.0127 (6)	0.0120 (6)	0.0004 (5)	0.0000 (5)	0.0002 (5)
C9	0.0113 (6)	0.0143 (6)	0.0129 (6)	−0.0016 (5)	−0.0012 (5)	0.0005 (5)
C13	0.0113 (6)	0.0139 (6)	0.0120 (6)	0.0000 (5)	−0.0007 (5)	−0.0011 (5)
O3	0.0236 (5)	0.0180 (5)	0.0154 (5)	−0.0002 (4)	0.0067 (4)	0.0003 (4)
O1	0.0230 (5)	0.0181 (5)	0.0154 (5)	−0.0018 (4)	0.0053 (4)	0.0013 (4)
O7	0.0243 (6)	0.0231 (6)	0.0179 (5)	0.0034 (4)	−0.0092 (4)	−0.0060 (4)
N2	0.0111 (5)	0.0121 (5)	0.0117 (5)	−0.0002 (4)	−0.0005 (4)	0.0004 (4)
C14	0.0140 (6)	0.0180 (7)	0.0123 (6)	0.0026 (5)	−0.0014 (5)	0.0002 (5)
C8	0.0137 (6)	0.0170 (7)	0.0139 (6)	−0.0036 (5)	−0.0013 (5)	−0.0015 (5)
C2	0.0120 (6)	0.0138 (6)	0.0124 (6)	0.0002 (5)	−0.0004 (5)	0.0012 (5)
C5	0.0191 (6)	0.0145 (7)	0.0141 (6)	0.0000 (5)	0.0005 (5)	−0.0031 (5)
C12	0.0143 (6)	0.0124 (6)	0.0173 (7)	−0.0019 (5)	−0.0009 (5)	−0.0031 (5)
C10	0.0152 (6)	0.0163 (7)	0.0174 (7)	0.0002 (5)	−0.0033 (5)	0.0045 (5)
C1	0.0133 (6)	0.0168 (7)	0.0142 (6)	−0.0007 (5)	−0.0003 (5)	−0.0014 (5)
C3	0.0160 (6)	0.0126 (6)	0.0168 (7)	−0.0020 (5)	−0.0004 (5)	0.0018 (5)
C11	0.0178 (6)	0.0109 (6)	0.0221 (7)	0.0002 (5)	−0.0009 (6)	0.0024 (5)
C4	0.0204 (7)	0.0109 (6)	0.0202 (7)	−0.0016 (5)	−0.0003 (6)	−0.0007 (5)
O9	0.0182 (5)	0.0233 (6)	0.0315 (7)	0.0007 (5)	−0.0089 (5)	0.0059 (5)
O6	0.0243 (5)	0.0227 (6)	0.0196 (6)	−0.0062 (4)	−0.0116 (4)	0.0031 (5)
O11	0.0541 (9)	0.0202 (6)	0.0195 (6)	−0.0074 (6)	0.0038 (6)	−0.0005 (5)
O12	0.0400 (7)	0.0204 (6)	0.0175 (6)	0.0034 (5)	−0.0031 (5)	−0.0012 (5)

Geometric parameters (Å, º)

O10—H10B	0.79 (3)	O8—C14	1.2817 (19)
O10—H10A	0.87 (3)	C7—O3	1.2518 (19)
Co1—N2	2.0117 (13)	C7—C6	1.518 (2)
Co1—N1	2.0162 (13)	C6—C5	1.386 (2)
Co1—O8	2.1446 (12)	C9—N2	1.3321 (18)
Co1—O2	2.1532 (13)	C9—C10	1.383 (2)
Co1—O4	2.1787 (13)	C9—C8	1.518 (2)

Co1—O5	2.1807 (13)	C13—N2	1.3357 (18)
C18—N3	1.491 (2)	C13—C12	1.389 (2)
C18—C17	1.511 (2)	C13—C14	1.5229 (19)
C18—H18A	0.9700	O1—C1	1.2485 (19)
C18—H18B	0.9700	O7—C14	1.2293 (18)
C16—N4	1.488 (2)	C8—O6	1.2426 (18)
C16—C15	1.510 (2)	C2—C3	1.389 (2)
C16—H16A	0.9700	C2—C1	1.514 (2)
C16—H16B	0.9700	C5—C4	1.388 (2)
C15—N3	1.490 (2)	C5—H5	0.9300
C15—H15A	0.9700	C12—C11	1.394 (2)
C15—H15B	0.9700	C12—H12	0.9300
C17—N4	1.488 (2)	C10—C11	1.391 (2)
C17—H17A	0.9700	C10—H10	0.9300
C17—H17B	0.9700	C3—C4	1.391 (2)
N4—H4B	0.89 (2)	C3—H3	0.9300
N4—H4A	0.91 (2)	C11—H11	0.9300
N3—H3B	0.91 (2)	C4—H4	0.9300
N3—H3A	0.91 (2)	O9—H9B	0.79 (3)
O5—C8	1.2692 (19)	O9—H9A	0.83 (3)
N1—C6	1.3335 (19)	O11—H11B	0.83 (3)
N1—C2	1.3358 (19)	O11—H11A	0.81 (3)
O4—C7	1.2619 (18)	O12—H12A	0.80 (3)
O2—C1	1.2652 (19)	O12—H12B	0.79 (3)

H10B—O10—H10A	103 (3)	C6—N1—Co1	118.50 (10)
N2—Co1—N1	169.23 (5)	C2—N1—Co1	119.77 (10)
N2—Co1—O8	76.55 (5)	C7—O4—Co1	113.82 (10)
N1—Co1—O8	113.87 (5)	C1—O2—Co1	115.50 (10)
N2—Co1—O2	108.30 (5)	C14—O8—Co1	116.32 (9)
N1—Co1—O2	76.15 (5)	O3—C7—O4	125.69 (14)
O8—Co1—O2	86.10 (5)	O3—C7—C6	118.30 (13)
N2—Co1—O4	99.70 (5)	O4—C7—C6	115.99 (13)
N1—Co1—O4	76.46 (5)	N1—C6—C5	120.71 (14)
O8—Co1—O4	99.71 (5)	N1—C6—C7	113.19 (12)
O2—Co1—O4	151.99 (4)	C5—C6—C7	126.06 (13)
N2—Co1—O5	76.63 (4)	N2—C9—C10	121.04 (13)
N1—Co1—O5	93.13 (4)	N2—C9—C8	113.76 (13)
O8—Co1—O5	152.85 (4)	C10—C9—C8	125.15 (13)
O2—Co1—O5	98.38 (5)	N2—C13—C12	120.96 (13)
O4—Co1—O5	88.87 (5)	N2—C13—C14	113.07 (12)
N3—C18—C17	109.89 (13)	C12—C13—C14	125.97 (13)
N3—C18—H18A	109.7	C9—N2—C13	121.49 (13)
C17—C18—H18A	109.7	C9—N2—Co1	118.93 (10)
N3—C18—H18B	109.7	C13—N2—Co1	119.58 (10)
C17—C18—H18B	109.7	O7—C14—O8	126.80 (14)
H18A—C18—H18B	108.2	O7—C14—C13	118.81 (13)
N4—C16—C15	110.28 (12)	O8—C14—C13	114.39 (12)

N4—C16—H16A	109.6	O6—C8—O5	126.53 (14)
C15—C16—H16A	109.6	O6—C8—C9	118.02 (13)
N4—C16—H16B	109.6	O5—C8—C9	115.43 (13)
C15—C16—H16B	109.6	N1—C2—C3	120.99 (14)
H16A—C16—H16B	108.1	N1—C2—C1	112.12 (12)
N3—C15—C16	110.38 (12)	C3—C2—C1	126.89 (13)
N3—C15—H15A	109.6	C6—C5—C4	118.47 (14)
C16—C15—H15A	109.6	C6—C5—H5	120.8
N3—C15—H15B	109.6	C4—C5—H5	120.8
C16—C15—H15B	109.6	C13—C12—C11	118.08 (13)
H15A—C15—H15B	108.1	C13—C12—H12	121.0
N4—C17—C18	110.13 (13)	C11—C12—H12	121.0
N4—C17—H17A	109.6	C9—C10—C11	118.40 (13)
C18—C17—H17A	109.6	C9—C10—H10	120.8
N4—C17—H17B	109.6	C11—C10—H10	120.8
C18—C17—H17B	109.6	O1—C1—O2	125.15 (14)
H17A—C17—H17B	108.1	O1—C1—C2	119.23 (13)
C16—N4—C17	110.77 (12)	O2—C1—C2	115.62 (13)
C16—N4—H4B	108.8 (15)	C2—C3—C4	117.93 (14)
C17—N4—H4B	109.6 (15)	C2—C3—H3	121.0
C16—N4—H4A	112.4 (15)	C4—C3—H3	121.0
C17—N4—H4A	110.8 (16)	C10—C11—C12	120.02 (14)
H4B—N4—H4A	104 (2)	C10—C11—H11	120.0
C15—N3—C18	112.15 (12)	C12—C11—H11	120.0
C15—N3—H3B	110.8 (14)	C5—C4—C3	120.28 (14)
C18—N3—H3B	109.0 (14)	C5—C4—H4	119.9
C15—N3—H3A	108.6 (14)	C3—C4—H4	119.9
C18—N3—H3A	108.7 (15)	H9B—O9—H9A	110 (2)
H3B—N3—H3A	107 (2)	H11B—O11—H11A	103 (3)
C8—O5—Co1	114.39 (9)	H12A—O12—H12B	104 (3)
C6—N1—C2	121.59 (13)		

N4—C16—C15—N3	56.04 (16)	C8—C9—N2—Co1	−2.77 (16)
N3—C18—C17—N4	−57.15 (17)	C12—C13—N2—C9	−0.7 (2)
C15—C16—N4—C17	−58.43 (16)	C14—C13—N2—C9	179.69 (12)
C18—C17—N4—C16	59.08 (16)	C12—C13—N2—Co1	179.15 (11)
C16—C15—N3—C18	−55.72 (17)	C14—C13—N2—Co1	−0.48 (16)
C17—C18—N3—C15	56.17 (17)	N1—Co1—N2—C9	−12.6 (3)
N2—Co1—O5—C8	−8.50 (11)	O8—Co1—N2—C9	−178.50 (11)
N1—Co1—O5—C8	168.13 (11)	O2—Co1—N2—C9	100.29 (11)
O8—Co1—O5—C8	−17.59 (17)	O4—Co1—N2—C9	−80.74 (11)
O2—Co1—O5—C8	−115.43 (11)	O5—Co1—N2—C9	5.75 (10)
O4—Co1—O5—C8	91.75 (11)	N1—Co1—N2—C13	167.6 (2)
N2—Co1—N1—C6	−59.3 (3)	O8—Co1—N2—C13	1.66 (10)
O8—Co1—N1—C6	105.67 (11)	O2—Co1—N2—C13	−79.55 (11)
O2—Co1—N1—C6	−175.04 (11)	O4—Co1—N2—C13	99.42 (11)
O4—Co1—N1—C6	10.90 (10)	O5—Co1—N2—C13	−174.09 (11)
O5—Co1—N1—C6	−77.18 (11)	Co1—O8—C14—O7	−176.49 (13)

N2—Co1—N1—C2	116.5 (3)	Co1—O8—C14—C13	3.39 (16)
O8—Co1—N1—C2	−78.56 (11)	N2—C13—C14—O7	177.88 (14)
O2—Co1—N1—C2	0.73 (10)	C12—C13—C14—O7	−1.7 (2)
O4—Co1—N1—C2	−173.33 (11)	N2—C13—C14—O8	−2.00 (18)
O5—Co1—N1—C2	98.59 (11)	C12—C13—C14—O8	178.38 (14)
N2—Co1—O4—C7	156.74 (10)	Co1—O5—C8—O6	−171.44 (13)
N1—Co1—O4—C7	−12.98 (10)	Co1—O5—C8—C9	9.52 (16)
O8—Co1—O4—C7	−125.39 (10)	N2—C9—C8—O6	175.91 (13)
O2—Co1—O4—C7	−25.34 (16)	C10—C9—C8—O6	−6.8 (2)
O5—Co1—O4—C7	80.51 (11)	N2—C9—C8—O5	−4.96 (19)
N2—Co1—O2—C1	−176.16 (10)	C10—C9—C8—O5	172.35 (14)
N1—Co1—O2—C1	−6.37 (10)	C6—N1—C2—C3	−0.1 (2)
O8—Co1—O2—C1	109.39 (11)	Co1—N1—C2—C3	−175.70 (10)
O4—Co1—O2—C1	6.00 (17)	C6—N1—C2—C1	179.60 (12)
O5—Co1—O2—C1	−97.55 (11)	Co1—N1—C2—C1	3.96 (15)
N2—Co1—O8—C14	−2.85 (11)	N1—C6—C5—C4	1.1 (2)
N1—Co1—O8—C14	180.00 (10)	C7—C6—C5—C4	−176.42 (13)
O2—Co1—O8—C14	107.02 (11)	N2—C13—C12—C11	0.8 (2)
O4—Co1—O8—C14	−100.60 (11)	C14—C13—C12—C11	−179.66 (13)
O5—Co1—O8—C14	6.25 (17)	N2—C9—C10—C11	1.3 (2)
Co1—O4—C7—O3	−168.85 (12)	C8—C9—C10—C11	−175.84 (14)
Co1—O4—C7—C6	12.83 (16)	Co1—O2—C1—O1	−169.47 (12)
C2—N1—C6—C5	−1.3 (2)	Co1—O2—C1—C2	10.27 (16)
Co1—N1—C6—C5	174.37 (11)	N1—C2—C1—O1	170.25 (13)
C2—N1—C6—C7	176.50 (12)	C3—C2—C1—O1	−10.1 (2)
Co1—N1—C6—C7	−7.81 (15)	N1—C2—C1—O2	−9.50 (18)
O3—C7—C6—N1	177.41 (13)	C3—C2—C1—O2	170.14 (14)
O4—C7—C6—N1	−4.14 (18)	N1—C2—C3—C4	1.6 (2)
O3—C7—C6—C5	−4.9 (2)	C1—C2—C3—C4	−178.01 (13)
O4—C7—C6—C5	173.53 (14)	C9—C10—C11—C12	−1.2 (2)
C10—C9—N2—C13	−0.4 (2)	C13—C12—C11—C10	0.2 (2)
C8—C9—N2—C13	177.06 (12)	C6—C5—C4—C3	0.5 (2)
C10—C9—N2—Co1	179.80 (11)	C2—C3—C4—C5	−1.8 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H12*B*···O3^{i}	0.79 (3)	2.06 (3)	2.8428 (18)	174 (3)
O11—H11*B*···O5	0.83 (3)	2.00 (3)	2.8290 (18)	177 (3)
O11—H11*A*···O1^{ii}	0.81 (3)	2.02 (3)	2.8173 (19)	170 (3)
O10—H10*B*···O7	0.79 (3)	2.15 (3)	2.9213 (19)	165 (3)
O10—H10*A*···O11^{iii}	0.87 (3)	1.99 (3)	2.854 (2)	172 (3)
O9—H9*B*···O8	0.79 (3)	1.96 (3)	2.7521 (18)	175 (2)
O9—H9*A*···O12^{iv}	0.83 (3)	2.01 (3)	2.840 (2)	173 (3)
N4—H4*B*···O3^{v}	0.89 (2)	1.92 (2)	2.7973 (18)	165 (2)
N4—H4*A*···O6^{iii}	0.91 (2)	1.89 (2)	2.7592 (17)	161 (2)
N3—H3*B*···O9^{vi}	0.91 (2)	1.86 (2)	2.6958 (18)	152 (2)
N3—H3*A*···O2	0.91 (2)	2.50 (2)	3.1126 (19)	124.5 (18)

N3—H3*A*···O1	0.91 (2)	1.88 (2)	2.7957 (18)	176 (2)
C18—H18*B*···O10^{vii}	0.97	2.58	3.457 (2)	151
C17—H17*B*···O7^{vii}	0.97	2.36	3.127 (2)	135
C16—H16*B*···O12^{iv}	0.97	2.52	3.293 (2)	137
C15—H15*B*···O10^{vi}	0.97	2.60	3.261 (2)	126
C15—H15*A*···O2	0.97	2.54	3.140 (2)	120

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