Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Piperazinium hexaaquacobalt(II) bis[bis(pyridine-2,6-dicarboxylato)-cobaltate(II)] octahydrate

Hossein Aghabozorg,[a]* Jafar Attar Gharamaleki,[a] Mohammad Ghadermazi,[b] Pouya Ghasemikhah[a] and Janet Soleimannejad[c]

[a]Department of Chemistry, Teacher Training University, 49 Mofateh Avenue, 15614 Tehran, Iran, [b]Department of Chemistry, Faculty of Science, Kurdistan University, Sanandaj, Iran, and [c]Department of Chemistry, Ilam University, Ilam, Iran
Correspondence e-mail: haghabozorg@yahoo.com, aghabozorg@saba.tmu.ac.ir

Received 15 May 2007; accepted 25 May 2007

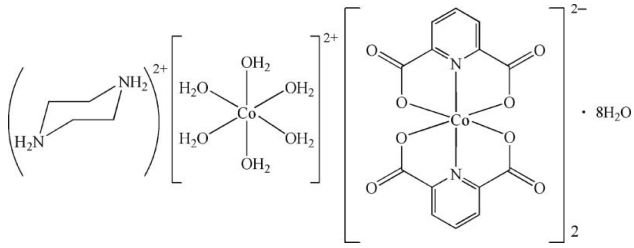
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.003 Å; R factor = 0.036; wR factor = 0.097; data-to-parameter ratio = 15.7.

The title compound, $(C_4H_{12}N_2)[Co(H_2O)_6][Co(C_7H_3O_4)_2]_2\cdot 8H_2O$, was obtained by the reaction of cobalt(II) nitrate hexahydrate with the proton-transfer compound piperazinediium pyridine-2,6-dicarboxylate or $(pipzH_2)(pydc)$ (where pipz is piperazine and $pydcH_2$ is pyridine-2,6-dicarboxylic acid) in aqueous solution. The anionic complex, $[Co(pydc)_2]^{2-}$, features six-coordinate Co^{II} with a distorted octahedral geometry. The structure also contains hexaaquacobalt(II) cations (site symmetry $\overline{1}$), and piperazinium (site symmetry $\overline{1}$) as counter-ions and eight uncoordinated water molecules. The torsion angles indicate that the $(pydc)^{2-}$ units are almost perpendicular to each other. In the crystal structure, extensive O—H···O, N—H···O and C—H···O hydrogen bonds, as well as ion pairing and distances for π–π interactions between anion fragments, play an important role in stabilizing the structure.

Related literature

The reaction between $Co(NO_3)_2\cdot 6H_2O$ and the proton-transfer compound $(GH)_2(pydc)$ (G is guanidine) in a 1:2 molar ratio leads to the formation of red crystals of $(GH)_2[Co(H_2O)_6][Co(pydc)_2]_2$ (Aghabozorg *et al.*, 2006*a*).

For related literature, see: Aghabozorg *et al.* (2006*b*, 2006*c*, 2006*d*, 2006*e*, 2006*f*, 2007); Manteghi *et al.* (2007).



Experimental

Crystal data

$(C_4H_{12}N_2)[Co(H_2O)_6]$-$[Co(C_7H_3O_4)_2]_2\cdot 8H_2O$
M_r = 1177.59
Triclinic, $P\overline{1}$
a = 8.4682 (10) Å
b = 11.9287 (14) Å
c = 12.9091 (15) Å
α = 63.478 (2)°
β = 78.683 (2)°
γ = 83.063 (2)°
V = 1143.3 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.18 mm^{-1}
T = 150 (2) K
0.50 × 0.48 × 0.20 mm

Data collection

Bruker SMART 1000 diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.589, T_{max} = 0.798
9953 measured reflections
5061 independent reflections
4261 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.097
S = 1.06
5061 reflections
322 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···O1	0.90	1.92	2.808 (2)	167
N3—H3A···O8^{i}	0.90	1.91	2.772 (2)	159
O9—H9B···O3^{ii}	0.95	1.92	2.855 (2)	168
O9—H9A···O15^{iii}	0.95	1.82	2.767 (2)	171
O10—H10B···O13	0.95	1.76	2.683 (3)	162
O10—H10A···O6^{ii}	0.95	1.79	2.719 (2)	166
O11—H11B···O14	0.95	1.77	2.692 (3)	163
O11—H11A···O1^{iv}	0.95	1.98	2.906 (2)	163
O12—H12B···O7	0.95	1.87	2.808 (2)	171
O12—H12A···O4^{v}	0.95	1.86	2.795 (2)	166
O13—H13B···O13^{vi}	0.95	1.92	2.868 (5)	179
O13—H13A···O4^{vi}	0.95	1.83	2.770 (3)	171
O14—H14B···O5^{ii}	0.95	1.79	2.732 (3)	170
O14—H14A···O13	0.95	2.20	3.123 (4)	164
O15—H15D···O12^{vii}	0.95	1.86	2.772 (3)	161
O15—H15C···O8	0.95	1.86	2.770 (2)	161

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, -y+1, -z+1$; (iii) $x-1, y, z+1$; (iv) $-x, -y, -z+1$; (v) $-x+1, -y, -z+1$; (vi) $-x+1, -y+1, -z+1$; (vii) $-x+1, -y, -z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2005); software used to prepare material for publication: *SHELXTL*.

 doi:10.1107/S1600536807025640

Financial support by Ilam University and the Teacher Training University is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2127).

References

Aghabozorg, H., Aghajani, Z. & Sharif, M. A. (2006*f*). *Acta Cryst.* E**62**, m1930–m1932.
Aghabozorg, H., Attar Gharamaleki, J., Ghasemikhah, P., Ghadermazi, M. & Soleimannejad, J. (2007). *Acta Cryst.* E**63**, m1710–1711.
Aghabozorg, H., Ghadermazi, M. & Attar Gharamaleki, J. (2006*b*). *Acta Cryst.* E**62**, o3174–o3176.
Aghabozorg, H., Ghadermazi, M., Manteghi, F. & Nakhjavan, B. (2006*a*). *Z. Anorg. Allg. Chem.* **632**, 2058–2064.
Aghabozorg, H., Ghasemikhah, P., Ghadermazi, M., Attar Gharamaleki, J. & Sheshmani, S. (2006*c*). *Acta Cryst.* E**62**, m2269–m2271.
Aghabozorg, H., Ghasemikhah, P., Soleimannejad, J., Ghadermazi, M. & Attar Gharamaleki, J. (2006*d*). *Acta Cryst.* E**62**, m2266–m2268.
Aghabozorg, H., Zabihi, F., Ghadermazi, M., Attar Gharamaleki, J. & Sheshmani, S. (2006*e*). *Acta Cryst.* E**62**, m2091–m2093.
Bruker (1998). *SMART* (Version 5.0), *SAINT* (Version 4.0) and *SADABS* (Version 2.0). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2005). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Manteghi, F., Ghadermazi, M. & Aghabozorg, H. (2007). *Acta Cryst.* E**63**, o2809.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supplementary materials

Acta Cryst. (2007). E**63**, m1803-m1804 [**doi:10.1107/S1600536807025640**]

Piperazinium hexaaquacobalt(II) bis[bis(pyridine-2,6-dicarboxylato)cobaltate(II)] octahydrate

H. Aghabozorg, J. Attar Gharamaleki, M. Ghadermazi, P. Ghasemikhah and J. Soleimannejad

Comment

Non-covalent interactions including hydrogen bonds are of great importance in stabilizing the structures of different compounds in solid state. We have so far synthesized several proton transfer compounds (Aghabozorg *et al.*, 2006*b*; Manteghi *et al.*, 2007) and their metal-organic complexes (Aghabozorg *et al.*, 2006*c*; Aghabozorg *et al.*, 2006 d; Aghabozorg *et al.*, 2006 e; Aghabozorg *et al.*, 2007). A wide range of various hydrogen bonds was observed in these compounds and water molecules were involved in hydrogen bonding formation of some of these structures.

Here, we report on the synthesis and X-ray crystal structure of the title compound, (I). The molecular structure of the compound (I) is shown in Fig. 1. The intermolecular hydrogen bond distances are listed in Table 1. This compound crystallizes in the triclinic system, space group $P\,\bar{1}$ with one formula in the unit cell. The most important feature of the title compound is the formation of both anionic $[Co(pydc)_2]^{2-}$ and cationic $[Co(H_2O)_6]^{2+}$ complexes (site symmetry $\bar{1}$), and $(pipzH_2)^{2+}$ ion (site symmetry $\bar{1}$), simultaneously. In the anionic complex, $[Co(pydc)_2]^{2-}$, the metal ion is hexacoordinated by two nitrogen atoms N1, and N2 and four oxygen atoms O2, O3, O6 and O7 of carboxylate groups of two $(pydc)^{2-}$ fragments which act as tridentate ligands. N1 and N2 atoms of the two $(pydc)^{2-}$ fragments occupy the axial positions, while oxygen atoms form the equatorial plane. The N1—Co2—N2 angle revealed with a 14.88° deviation from linearity.

The mean Co—N and Co—O bond lengths for Co2 are 2.0147 (18) and 2.1575 (17) Å, respectively and are consistent with the corresponding data reported in the literature (Aghabozorg *et al.*, 2006*a*). According to bond lengths, bond and torsion angles, arrangement of the six donor atoms around Co2 is distorted octahedral.

The dihedral angel between the two planes of Co2N2O6 and N2Co2O2 [86.81 (9)°] indicate that two dianionic $(pydc)^{2-}$ units are almost perpendicular to each other.

In the cationic complex, $[Co(H_2O)_6]^{2+}$, the metal ion is hexacoordinated by six oxygen atoms of water molecules with a nearly octahedral geometry around the central atom. The extensive O—H···O, N—H···O and C—H···O hydrogen bonds between $[Co(H_2O)_6]^{2+}$, $[Co(pydc)_2]^{2-}$, $(pipzH_2)^{2+}$ and uncoordinated water molecules play an important role in stabilizing and architecture of the crystal (Table 1). The intermolecular forces in this compound consist of hydrogen bonding and ion pairing as well as π-π stacking between anion-anion fragments (3.5277 (15) Å $-x$, $-y+2$, $-z+1$) (Fig. 2) (Aghabozorg, *et al.*, 2006f). These interactions result in the formation of a supramolecular structure based on a hydrogen-bonded network.

Experimental

The proton transfer compound, $(pipzH_2)(pydc)$, was prepared by the reaction of pyridine-2,6-dicarboxylic acid, $pydcH_2$, with piperazine, (pipz). The reaction between $Co(NO_3)_2{\cdot}6H_2O$ (143 mg, 0.5 mmol) in water (25 ml) and the proton transfer

compound, ($pipzH_2$)(pydc) (253 mg, 1.0 mmol) in water (25 ml), in a 1:2 molar ratio was carried out and a purple crystalline compound was obtained by the slow evaporation of the solvent at room temperature.

Refinement

Hydrogen atoms were positioned geometrically and refined with a riding model (including torsional freedom for methyl groups), with C—H = 0.95–0.98 Å, and with U(H) constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Figures

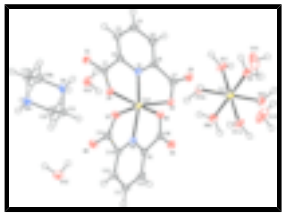


Fig. 1. Molecular structure of compound (I), displacement ellipsoids are at the 50% probability level. The rest of fragments could be generated by symmetry. [symmetry codes: (*a*) −*x*, −*y* + 1, −*z* + 1, (*b*) −*x*, −*y*, −*z*].

Fig. 2. π-π Stacking interactions between two aromatic rings of (I). The average distance between the planes is 3.5277 (15) Å (−*x*, 2 − *y*, 1 − *z*).

Piperazinium hexaaquacobalt(II) bis[bis(pyridine-2,6-dicarboxylato)cobaltate(II)] octahydrate

Crystal data

$(C_4H_{12}N_2)[Co(H_2O)_6][Co(C_7H_3O_4)_2]_2{\cdot}8H_2O$	$Z = 1$
$M_r = 1177.59$	$F_{000} = 607$
Triclinic, $P\overline{1}$	$D_x = 1.710$ Mg m^{-3}
$a = 8.4682$ (10) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 11.9287$ (14) Å	Cell parameters from 7659 reflections
$c = 12.9091$ (15) Å	$\theta = 2.5$–27.5°
$\alpha = 63.478$ (2)°	$\mu = 1.18$ mm^{-1}
$\beta = 78.683$ (2)°	$T = 150$ (2) K
$\gamma = 83.063$ (2)°	Block, purple
$V = 1143.3$ (2) Å^3	0.50 × 0.48 × 0.20 mm

Data collection

Bruker SMART 1000 diffractometer	5061 independent reflections
Radiation source: fine-focus sealed tube	4261 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.025$
Detector resolution: 100 pixels mm^{-1}	$\theta_{max} = 27.6^\circ$
$T = 150(2)$ K	$\theta_{min} = 1.8^\circ$
ω scans	$h = -10 \rightarrow 10$

Absorption correction: multi-scan (SADABS; Bruker, 1998)

T_{min} = 0.589, T_{max} = 0.798

9953 measured reflections

k = −15→15

l = −16→16

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.036

$wR(F^2)$ = 0.097

S = 1.06

5061 reflections

322 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.4524P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max}$ = 0.59 e Å^{-3}

$\Delta\rho_{min}$ = −0.61 e Å^{-3}

Extinction correction: none

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 $F^2 > 2$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	0.0000	0.5000	0.5000	0.01842 (11)
Co2	0.22003 (4)	0.25036 (2)	0.23467 (2)	0.01670 (9)
N1	0.2066 (2)	0.08823 (16)	0.38145 (15)	0.0165 (4)
N2	0.2792 (2)	0.38844 (16)	0.07167 (15)	0.0163 (4)
N3	−0.1311 (2)	0.04921 (17)	0.05881 (16)	0.0210 (4)
H3B	−0.1022	0.0221	0.1301	0.025*
H3A	−0.2268	0.0916	0.0558	0.025*
O1	−0.0037 (2)	−0.05806 (14)	0.26917 (13)	0.0238 (3)
O2	0.0688 (2)	0.13971 (13)	0.20204 (13)	0.0224 (3)
O3	0.32424 (19)	0.29185 (13)	0.35241 (13)	0.0201 (3)
O4	0.4158 (2)	0.19928 (15)	0.52370 (14)	0.0243 (4)
O5	−0.03682 (19)	0.58947 (14)	0.11407 (14)	0.0237 (3)
O6	0.04162 (19)	0.39324 (13)	0.22919 (13)	0.0204 (3)
O7	0.4431 (2)	0.17914 (14)	0.16162 (13)	0.0238 (4)

O8	0.61077 (19)	0.21798 (14)	−0.00623 (13)	0.0242 (4)
O9	−0.2103 (2)	0.48680 (15)	0.61912 (15)	0.0303 (4)
H9B	−0.2614	0.5548	0.6339	0.036*
H9A	−0.2648	0.4103	0.6613	0.036*
O10	0.1082 (2)	0.58551 (14)	0.57348 (14)	0.0229 (3)
H10B	0.2198	0.5651	0.5762	0.028*
H10A	0.0612	0.5788	0.6491	0.028*
O11	0.0824 (2)	0.32105 (14)	0.61321 (15)	0.0293 (4)
H11B	0.1654	0.3186	0.6542	0.035*
H11A	0.0526	0.2378	0.6368	0.035*
O12	0.5233 (2)	−0.07835 (16)	0.24549 (15)	0.0348 (4)
H12B	0.4914	0.0070	0.2255	0.042*
H12A	0.5606	−0.1126	0.3188	0.042*
O13	0.4299 (2)	0.5784 (2)	0.5563 (3)	0.0603 (7)
H13B	0.4766	0.5256	0.5199	0.072*
H13A	0.4914	0.6496	0.5330	0.072*
O14	0.2727 (3)	0.3327 (2)	0.7521 (2)	0.0516 (6)
H14A	0.3261	0.4091	0.7047	0.062*
H14B	0.1995	0.3646	0.7995	0.062*
O15	0.6190 (3)	0.27236 (17)	−0.23945 (16)	0.0410 (5)
H15D	0.5929	0.1973	−0.2399	0.049*
H15C	0.6323	0.2384	−0.1595	0.049*
C1	0.0628 (3)	0.02551 (19)	0.27641 (18)	0.0193 (4)
C2	0.1404 (3)	−0.00853 (18)	0.38368 (18)	0.0175 (4)
C3	0.1429 (3)	−0.12571 (19)	0.47785 (19)	0.0207 (5)
H3	0.0966	−0.1949	0.4788	0.025*
C4	0.2147 (3)	−0.1393 (2)	0.57052 (19)	0.0226 (5)
H4	0.2170	−0.2185	0.6366	0.027*
C5	0.2834 (3)	−0.03764 (19)	0.56740 (19)	0.0196 (4)
H5	0.3331	−0.0459	0.6305	0.024*
C6	0.2773 (3)	0.07649 (19)	0.46932 (18)	0.0169 (4)
C7	0.3451 (3)	0.19821 (19)	0.44923 (18)	0.0182 (4)
C8	0.0529 (3)	0.49527 (19)	0.13425 (19)	0.0184 (4)
C9	0.1906 (3)	0.49543 (18)	0.04015 (18)	0.0168 (4)
C10	0.2280 (3)	0.59417 (19)	−0.07070 (19)	0.0197 (4)
H10	0.1656	0.6706	−0.0934	0.024*
C11	0.3584 (3)	0.5779 (2)	−0.14681 (18)	0.0208 (5)
H11	0.3864	0.6439	−0.2228	0.025*
C12	0.4488 (3)	0.4653 (2)	−0.11257 (19)	0.0204 (4)
H12	0.5380	0.4530	−0.1645	0.024*
C13	0.4050 (3)	0.37179 (19)	−0.00081 (18)	0.0172 (4)
C14	0.4942 (3)	0.24579 (19)	0.05474 (19)	0.0192 (4)
C15	−0.0037 (3)	0.1319 (2)	−0.0319 (2)	0.0249 (5)
H15B	0.0112	0.2018	−0.0137	0.030*
H15A	−0.0383	0.1681	−0.1098	0.030*
C16	0.1531 (3)	0.0588 (2)	−0.0353 (2)	0.0243 (5)
H16B	0.2351	0.1139	−0.0976	0.029*
H16A	0.1920	0.0278	0.0407	0.029*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0220 (2)	0.01281 (19)	0.0190 (2)	−0.00347 (15)	0.00298 (16)	−0.00748 (16)
Co2	0.02253 (17)	0.01160 (14)	0.01341 (15)	−0.00183 (11)	−0.00085 (11)	−0.00368 (11)
N1	0.0185 (9)	0.0144 (8)	0.0159 (8)	−0.0020 (7)	−0.0002 (7)	−0.0067 (7)
N2	0.0190 (9)	0.0137 (8)	0.0152 (8)	−0.0009 (7)	−0.0023 (7)	−0.0055 (7)
N3	0.0226 (10)	0.0197 (9)	0.0189 (9)	0.0052 (7)	−0.0026 (7)	−0.0086 (7)
O1	0.0345 (9)	0.0176 (7)	0.0211 (8)	−0.0064 (7)	−0.0063 (7)	−0.0079 (6)
O2	0.0332 (9)	0.0150 (7)	0.0180 (7)	−0.0048 (6)	−0.0057 (6)	−0.0047 (6)
O3	0.0271 (8)	0.0146 (7)	0.0173 (7)	−0.0036 (6)	−0.0031 (6)	−0.0054 (6)
O4	0.0292 (9)	0.0227 (8)	0.0234 (8)	−0.0021 (7)	−0.0093 (7)	−0.0097 (6)
O5	0.0250 (8)	0.0154 (7)	0.0282 (8)	0.0028 (6)	−0.0015 (7)	−0.0093 (6)
O6	0.0249 (8)	0.0161 (7)	0.0162 (7)	−0.0003 (6)	−0.0001 (6)	−0.0050 (6)
O7	0.0301 (9)	0.0169 (7)	0.0172 (7)	0.0036 (6)	−0.0003 (6)	−0.0035 (6)
O8	0.0243 (9)	0.0231 (8)	0.0205 (8)	0.0070 (6)	0.0002 (6)	−0.0088 (6)
O9	0.0312 (9)	0.0205 (8)	0.0359 (9)	−0.0071 (7)	0.0143 (8)	−0.0159 (7)
O10	0.0258 (8)	0.0220 (8)	0.0232 (8)	−0.0054 (6)	0.0027 (6)	−0.0133 (6)
O11	0.0369 (10)	0.0152 (7)	0.0337 (9)	−0.0031 (7)	−0.0124 (8)	−0.0055 (7)
O12	0.0580 (13)	0.0203 (8)	0.0270 (9)	0.0056 (8)	−0.0138 (8)	−0.0099 (7)
O13	0.0295 (11)	0.0450 (12)	0.122 (2)	−0.0093 (9)	0.0042 (13)	−0.0545 (14)
O14	0.0386 (12)	0.0798 (16)	0.0611 (14)	0.0221 (11)	−0.0193 (10)	−0.0538 (13)
O15	0.0647 (14)	0.0318 (10)	0.0238 (9)	−0.0193 (9)	−0.0017 (9)	−0.0077 (8)
C1	0.0230 (11)	0.0175 (10)	0.0160 (10)	−0.0014 (8)	0.0004 (8)	−0.0073 (8)
C2	0.0189 (10)	0.0147 (9)	0.0168 (10)	−0.0012 (8)	0.0009 (8)	−0.0064 (8)
C3	0.0232 (11)	0.0147 (9)	0.0218 (11)	−0.0036 (8)	−0.0011 (9)	−0.0061 (8)
C4	0.0256 (12)	0.0151 (10)	0.0199 (10)	0.0002 (9)	−0.0021 (9)	−0.0019 (8)
C5	0.0203 (11)	0.0186 (10)	0.0177 (10)	0.0009 (8)	−0.0030 (8)	−0.0063 (8)
C6	0.0160 (10)	0.0175 (10)	0.0155 (9)	0.0000 (8)	0.0009 (8)	−0.0072 (8)
C7	0.0172 (10)	0.0178 (10)	0.0199 (10)	−0.0004 (8)	0.0008 (8)	−0.0100 (8)
C8	0.0206 (11)	0.0154 (9)	0.0212 (10)	−0.0035 (8)	−0.0029 (8)	−0.0093 (8)
C9	0.0204 (10)	0.0133 (9)	0.0182 (10)	−0.0024 (8)	−0.0046 (8)	−0.0071 (8)
C10	0.0235 (11)	0.0142 (9)	0.0203 (10)	−0.0013 (8)	−0.0062 (9)	−0.0053 (8)
C11	0.0259 (12)	0.0166 (10)	0.0156 (10)	−0.0045 (9)	−0.0029 (8)	−0.0027 (8)
C12	0.0212 (11)	0.0203 (10)	0.0178 (10)	−0.0026 (8)	−0.0011 (8)	−0.0070 (8)
C13	0.0197 (10)	0.0145 (9)	0.0168 (10)	−0.0010 (8)	−0.0021 (8)	−0.0066 (8)
C14	0.0209 (11)	0.0166 (10)	0.0201 (10)	0.0010 (8)	−0.0051 (8)	−0.0076 (8)
C15	0.0363 (14)	0.0130 (9)	0.0214 (11)	−0.0015 (9)	0.0004 (10)	−0.0057 (8)
C16	0.0256 (12)	0.0251 (11)	0.0242 (11)	−0.0084 (9)	0.0005 (9)	−0.0123 (9)

Geometric parameters (Å, °)

Co1—O10^{i}	2.0522 (16)	O11—H11A	0.9499
Co1—O10	2.0522 (16)	O12—H12B	0.9500
Co1—O9^{i}	2.0824 (16)	O12—H12A	0.9500
Co1—O9	2.0824 (16)	O13—H13B	0.9499
Co1—O11	2.1056 (16)	O13—H13A	0.9500

Co1—O11^{i}	2.1056 (15)	O14—H14A	0.9501
Co2—N1	2.0098 (17)	O14—H14B	0.9499
Co2—N2	2.0204 (17)	O15—H15D	0.9499
Co2—O6	2.1224 (15)	O15—H15C	0.9501
Co2—O3	2.1534 (16)	C1—C2	1.518 (3)
Co2—O2	2.1623 (16)	C2—C3	1.385 (3)
Co2—O7	2.1927 (16)	C3—C4	1.384 (3)
N1—C2	1.330 (3)	C3—H3	0.9500
N1—C6	1.330 (3)	C4—C5	1.388 (3)
N2—C13	1.332 (3)	C4—H4	0.9500
N2—C9	1.335 (3)	C5—C6	1.389 (3)
N3—C16^{ii}	1.488 (3)	C5—H5	0.9500
N3—C15	1.495 (3)	C6—C7	1.520 (3)
N3—H3B	0.9024	C8—C9	1.510 (3)
N3—H3A	0.9001	C9—C10	1.394 (3)
O1—C1	1.249 (3)	C10—C11	1.384 (3)
O2—C1	1.269 (2)	C10—H10	0.9500
O3—C7	1.278 (3)	C11—C12	1.393 (3)
O4—C7	1.233 (3)	C11—H11	0.9500
O5—C8	1.232 (3)	C12—C13	1.384 (3)
O6—C8	1.282 (2)	C12—H12	0.9500
O7—C14	1.262 (3)	C13—C14	1.523 (3)
O8—C14	1.246 (3)	C15—C16	1.503 (3)
O9—H9B	0.9500	C15—H15B	0.9900
O9—H9A	0.9499	C15—H15A	0.9900
O10—H10B	0.9501	C16—N3^{ii}	1.488 (3)
O10—H10A	0.9501	C16—H16B	0.9900
O11—H11B	0.9501	C16—H16A	0.9900
O10^{i}—Co1—O10	180.000 (1)	H14A—O14—H14B	95.2
O10^{i}—Co1—O9^{i}	89.89 (7)	H15D—O15—H15C	98.0
O10—Co1—O9^{i}	90.11 (7)	O1—C1—O2	125.5 (2)
O10^{i}—Co1—O9	90.11 (7)	O1—C1—C2	118.72 (18)
O10—Co1—O9	89.89 (7)	O2—C1—C2	115.76 (19)
O9^{i}—Co1—O9	180.000 (1)	N1—C2—C3	121.1 (2)
O10^{i}—Co1—O11	88.04 (7)	N1—C2—C1	113.09 (17)
O10—Co1—O11	91.96 (7)	C3—C2—C1	125.8 (2)
O9^{i}—Co1—O11	88.93 (7)	C4—C3—C2	118.2 (2)
O9—Co1—O11	91.07 (7)	C4—C3—H3	120.9
O10^{i}—Co1—O11^{i}	91.96 (7)	C2—C3—H3	120.9
O10—Co1—O11^{i}	88.04 (7)	C3—C4—C5	120.31 (19)
O9^{i}—Co1—O11^{i}	91.07 (7)	C3—C4—H4	119.8
O9—Co1—O11^{i}	88.93 (7)	C5—C4—H4	119.8
O11—Co1—O11^{i}	180.0	C4—C5—C6	118.0 (2)
N1—Co2—N2	165.15 (7)	C4—C5—H5	121.0
N1—Co2—O6	117.76 (6)	C6—C5—H5	121.0
N2—Co2—O6	76.99 (6)	N1—C6—C5	120.9 (2)

N1—Co2—O3	76.50 (6)	N1—C6—C7	113.00 (17)
N2—Co2—O3	107.36 (6)	C5—C6—C7	126.0 (2)
O6—Co2—O3	87.84 (6)	O4—C7—O3	125.7 (2)
N1—Co2—O2	76.73 (6)	O4—C7—C6	119.32 (18)
N2—Co2—O2	101.16 (7)	O3—C7—C6	114.95 (19)
O6—Co2—O2	95.55 (6)	O5—C8—O6	126.4 (2)
O3—Co2—O2	151.30 (6)	O5—C8—C9	118.87 (18)
N1—Co2—O7	89.59 (6)	O6—C8—C9	114.73 (18)
N2—Co2—O7	75.79 (6)	N2—C9—C10	120.6 (2)
O6—Co2—O7	152.52 (6)	N2—C9—C8	113.56 (17)
O3—Co2—O7	96.68 (6)	C10—C9—C8	125.86 (19)
O2—Co2—O7	93.31 (6)	C11—C10—C9	118.23 (19)
C2—N1—C6	121.47 (18)	C11—C10—H10	120.9
C2—N1—Co2	118.78 (14)	C9—C10—H10	120.9
C6—N1—Co2	119.43 (14)	C10—C11—C12	120.36 (19)
C13—N2—C9	121.70 (18)	C10—C11—H11	119.8
C13—N2—Co2	119.90 (14)	C12—C11—H11	119.8
C9—N2—Co2	118.39 (14)	C13—C12—C11	118.1 (2)
C16^{ii}—N3—C15	110.72 (17)	C13—C12—H12	120.9
C16^{ii}—N3—H3B	110.6	C11—C12—H12	120.9
C15—N3—H3B	108.7	N2—C13—C12	121.02 (19)
C16^{ii}—N3—H3A	106.0	N2—C13—C14	113.12 (18)
C15—N3—H3A	110.2	C12—C13—C14	125.8 (2)
H3B—N3—H3A	110.6	O8—C14—O7	125.70 (19)
C1—O2—Co2	114.35 (14)	O8—C14—C13	118.81 (19)
C7—O3—Co2	115.43 (14)	O7—C14—C13	115.48 (19)
C8—O6—Co2	116.30 (13)	N3—C15—C16	110.58 (17)
C14—O7—Co2	115.18 (13)	N3—C15—H15B	109.5
Co1—O9—H9B	124.4	C16—C15—H15B	109.5
Co1—O9—H9A	120.9	N3—C15—H15A	109.5
H9B—O9—H9A	114.8	C16—C15—H15A	109.5
Co1—O10—H10B	115.3	H15B—C15—H15A	108.1
Co1—O10—H10A	118.6	N3^{ii}—C16—C15	110.06 (19)
H10B—O10—H10A	106.0	N3^{ii}—C16—H16B	109.6
Co1—O11—H11B	116.5	C15—C16—H16B	109.6
Co1—O11—H11A	134.4	N3^{ii}—C16—H16A	109.6
H11B—O11—H11A	109.0	C15—C16—H16A	109.6
H12B—O12—H12A	108.2	H16B—C16—H16A	108.2
H13B—O13—H13A	112.9		
N2—Co2—N1—C2	−74.0 (3)	O2—C1—C2—N1	−1.3 (3)
O6—Co2—N1—C2	98.84 (16)	O1—C1—C2—C3	−1.1 (3)
O3—Co2—N1—C2	179.05 (17)	O2—C1—C2—C3	177.4 (2)
O2—Co2—N1—C2	9.51 (15)	N1—C2—C3—C4	0.7 (3)
O7—Co2—N1—C2	−83.98 (16)	C1—C2—C3—C4	−177.9 (2)
N2—Co2—N1—C6	99.7 (3)	C2—C3—C4—C5	−0.7 (3)
O6—Co2—N1—C6	−87.52 (16)	C3—C4—C5—C6	0.1 (3)
O3—Co2—N1—C6	−7.31 (15)	C2—N1—C6—C5	−0.5 (3)

O2—Co2—N1—C6	−176.85 (17)	Co2—N1—C6—C5	−173.96 (16)
O7—Co2—N1—C6	89.66 (16)	C2—N1—C6—C7	180.00 (18)
N1—Co2—N2—C13	−5.8 (4)	Co2—N1—C6—C7	6.5 (2)
O6—Co2—N2—C13	−179.31 (17)	C4—C5—C6—N1	0.5 (3)
O3—Co2—N2—C13	97.16 (17)	C4—C5—C6—C7	180.0 (2)
O2—Co2—N2—C13	−86.12 (17)	Co2—O3—C7—O4	173.03 (17)
O7—Co2—N2—C13	4.49 (16)	Co2—O3—C7—C6	−5.8 (2)
N1—Co2—N2—C9	174.9 (2)	N1—C6—C7—O4	−178.97 (19)
O6—Co2—N2—C9	1.46 (16)	C5—C6—C7—O4	1.6 (3)
O3—Co2—N2—C9	−82.07 (17)	N1—C6—C7—O3	0.0 (3)
O2—Co2—N2—C9	94.65 (16)	C5—C6—C7—O3	−179.5 (2)
O7—Co2—N2—C9	−174.74 (17)	Co2—O6—C8—O5	−179.05 (18)
N1—Co2—O2—C1	−9.99 (15)	Co2—O6—C8—C9	1.4 (2)
N2—Co2—O2—C1	154.97 (15)	C13—N2—C9—C10	−0.2 (3)
O6—Co2—O2—C1	−127.24 (15)	Co2—N2—C9—C10	179.05 (16)
O3—Co2—O2—C1	−31.6 (2)	C13—N2—C9—C8	179.58 (19)
O7—Co2—O2—C1	78.80 (15)	Co2—N2—C9—C8	−1.2 (2)
N1—Co2—O3—C7	7.07 (15)	O5—C8—C9—N2	−179.8 (2)
N2—Co2—O3—C7	−158.05 (15)	O6—C8—C9—N2	−0.2 (3)
O6—Co2—O3—C7	126.30 (15)	O5—C8—C9—C10	−0.1 (3)
O2—Co2—O3—C7	28.7 (2)	O6—C8—C9—C10	179.6 (2)
O7—Co2—O3—C7	−80.89 (15)	N2—C9—C10—C11	0.2 (3)
N1—Co2—O6—C8	−179.67 (15)	C8—C9—C10—C11	−179.5 (2)
N2—Co2—O6—C8	−1.55 (15)	C9—C10—C11—C12	0.1 (3)
O3—Co2—O6—C8	106.82 (15)	C10—C11—C12—C13	−0.5 (3)
O2—Co2—O6—C8	−101.75 (15)	C9—N2—C13—C12	−0.3 (3)
O7—Co2—O6—C8	6.5 (2)	Co2—N2—C13—C12	−179.48 (16)
N1—Co2—O7—C14	170.69 (16)	C9—N2—C13—C14	177.03 (19)
N2—Co2—O7—C14	−6.67 (16)	Co2—N2—C13—C14	−2.2 (2)
O6—Co2—O7—C14	−14.7 (2)	C11—C12—C13—N2	0.6 (3)
O3—Co2—O7—C14	−112.95 (16)	C11—C12—C13—C14	−176.3 (2)
O2—Co2—O7—C14	94.01 (16)	Co2—O7—C14—O8	−173.99 (19)
Co2—O2—C1—O1	−172.74 (18)	Co2—O7—C14—C13	7.5 (2)
Co2—O2—C1—C2	8.9 (2)	N2—C13—C14—O8	177.5 (2)
C6—N1—C2—C3	−0.1 (3)	C12—C13—C14—O8	−5.4 (3)
Co2—N1—C2—C3	173.36 (16)	N2—C13—C14—O7	−3.9 (3)
C6—N1—C2—C1	178.64 (18)	C12—C13—C14—O7	173.3 (2)
Co2—N1—C2—C1	−7.9 (2)	C16^{ii}—N3—C15—C16	−57.7 (3)
O1—C1—C2—N1	−179.8 (2)	N3—C15—C16—N3^{ii}	57.3 (3)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) −*x*, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3B···O1	0.90	1.92	2.808 (2)	167
N3—H3A···O8^{iii}	0.90	1.91	2.772 (2)	159
O9—H9B···O3^{i}	0.95	1.92	2.855 (2)	168
O9—H9A···O15^{iv}	0.95	1.82	2.767 (2)	171

O10—H10B···O13	0.95	1.76	2.683 (3)	162
O10—H10A···O6^{i}	0.95	1.79	2.719 (2)	166
O11—H11B···O14	0.95	1.77	2.692 (3)	163
O11—H11A···O1^{v}	0.95	1.98	2.906 (2)	163
O12—H12B···O7	0.95	1.87	2.808 (2)	171
O12—H12A···O4^{vi}	0.95	1.86	2.795 (2)	166
O13—H13B···O13^{vii}	0.95	1.92	2.868 (5)	179
O13—H13A···O4^{vii}	0.95	1.83	2.770 (3)	171
O14—H14B···O5^{i}	0.95	1.79	2.732 (3)	170
O14—H14A···O13	0.95	2.20	3.123 (4)	164
O15—H15D···O12^{viii}	0.95	1.86	2.772 (3)	161
O15—H15C···O8	0.95	1.86	2.770 (2)	161

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

Fig. 1

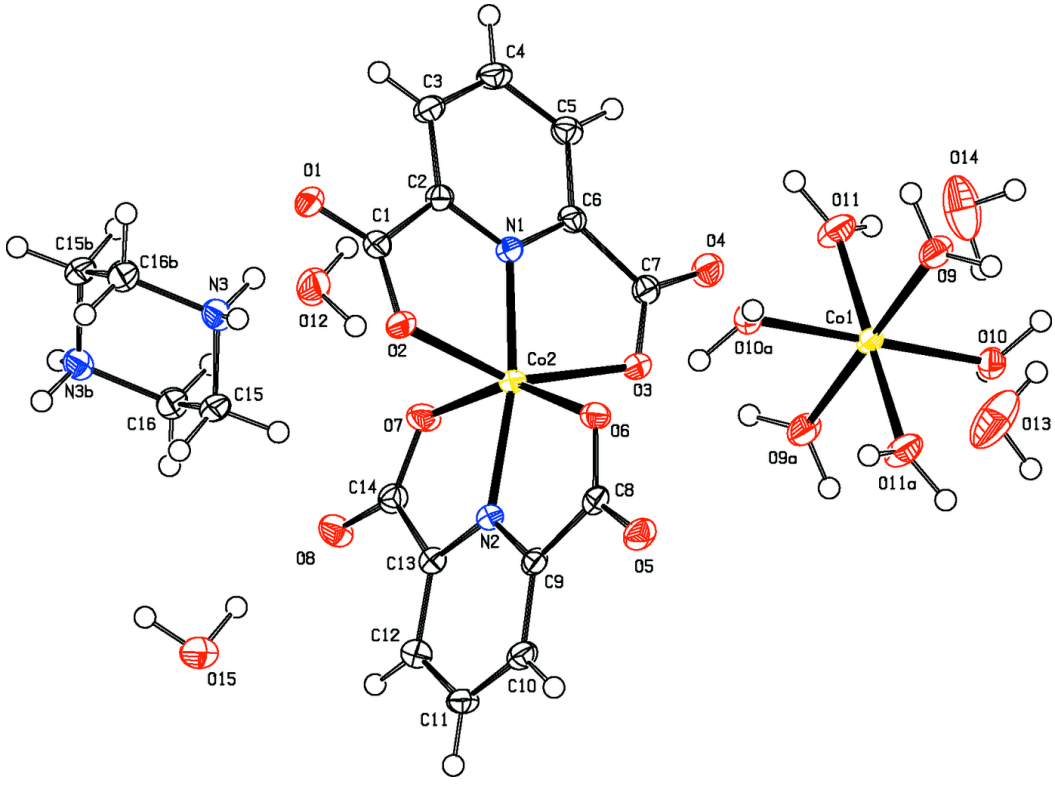

C4
C3
C5
O1
C2
C6
C1
N1
O4
C7
C15b
C16b
N3
O12
O2
Co2
O3
N3b
C15
O7
O6
C16
C14
C8
O8
N2
O5
C13
C9
O15
C12
C10
C11
O14
O11
O9
Co1
O10a
O10
O13
O9a
O11a

Fig. 2