

Diaqua(2,9-dimethyl-1,10-phenanthroline- κ^2N,N')(4-hydroxybenzoato- κ^2O,O')cobalt(II) nitrate dihydrate

 Cuiqing Zhai,^a Fengmei Yan^b and Peizheng Zhao^{c*}

^aCollege of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, People's Republic of China, ^bDepartment of Chemistry and Chemical Engineering, Huanghuai University, Zhumadian 463000, People's Republic of China, and ^cCollege of Chemistry and Environmental Science, Henan Normal University, Xinxiang 453007, People's Republic of China
Correspondence e-mail: pz_zhao@hotmail.com

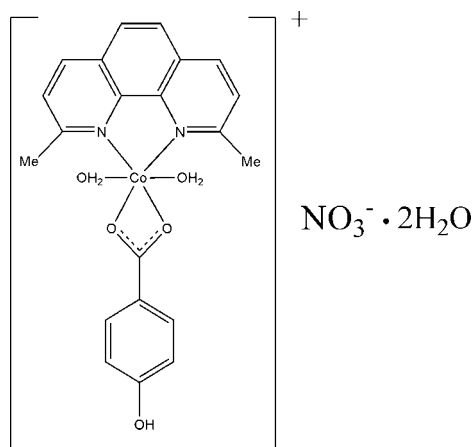
Received 28 October 2008; accepted 16 November 2008

Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.029; wR factor = 0.081; data-to-parameter ratio = 13.7.

In the title compound, $[Co(C_7H_5O_3)(C_{14}H_{12}N_2)(H_2O)_2]NO_3 \cdot 2H_2O$, the Co^{II} ion is six-coordinated by two N atoms of a 2,9-dimethyl-1,10-phenanthroline (dmphen) ligand, two carboxylate O atoms of one 4-hydroxybenzoate anion and two O atoms of two water molecules, in a distorted octahedral environment; the two water molecules occupy the apical positions. In the crystal structure, the ionic units and water molecules are linked through $O-H \cdots O$ hydrogen bonds, leading to the formation of a three-dimensional network. In addition, $\pi-\pi$ interactions between a pyridine ring of the dmphen ligand and the benzene ring of the hydroxybenzoate anion [centroid-centroid separation = $3.6861(3)$ Å] are observed.

Related literature

For related structures, see: Xuan *et al.* (2007); Xuan & Zhao (2007*a,b*).



Experimental

Crystal data

$[Co(C_7H_5O_3)(C_{14}H_{12}N_2)(H_2O)_2]NO_3 \cdot 2H_2O$
 $M_r = 538.37$
 Monoclinic, $P2_1/c$
 $a = 9.8001(8)$ Å
 $b = 22.2638(19)$ Å
 $c = 10.8676(9)$ Å
 $\beta = 94.602(1)^\circ$
 $V = 2363.5(3)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.79$ mm⁻¹
 $T = 291(2)$ K
 $0.35 \times 0.25 \times 0.14$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
 $T_{min} = 0.771$, $T_{max} = 0.899$
 17391 measured reflections
 4385 independent reflections
 3689 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.081$
 $S = 1.01$
 4385 reflections
 319 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.36$ e Å⁻³
 $\Delta\rho_{min} = -0.24$ e Å⁻³

Table 1

Selected bond lengths (Å).

Co1—O5	2.0685 (14)	Co1—N2	2.1357 (15)
Co1—O4	2.1187 (14)	Co1—O1	2.1425 (13)
Co1—N1	2.1213 (15)	Co1—O2	2.2311 (13)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O10—H8W ⁱⁱ ···O6	0.83	2.26	2.960 (3)	142
O9—H5W ⁱⁱ ···O6	0.83	2.09	2.904 (3)	169
O9—H6W ⁱⁱ ···O7 ⁱ	0.83	2.09	2.888 (3)	161
O10—H7W ⁱⁱ ···O8 ⁱⁱ	0.83	2.01	2.829 (3)	169
O5—H4W ⁱⁱ ···O10	0.81	1.93	2.720 (2)	167
O4—H2W ⁱⁱ ···O2 ⁱⁱⁱ	0.83	2.01	2.846 (2)	180
O5—H3W ⁱⁱ ···O1 ^{iv}	0.82	2.05	2.826 (2)	157
O4—H1W ⁱⁱ ···O9 ^v	0.82	1.96	2.758 (2)	164
O3—H3 ⁱⁱ ···O8 ^{vi}	0.82	2.57	3.133 (3)	127
O3—H3 ⁱⁱ ···O7 ^{vi}	0.82	2.07	2.861 (3)	164

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; 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: *publCIF* (Westrip, 2008).

Financial support from the Science Fund of Henan Province for Distinguished Young Scholars (grant No. 07410051005) is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2703).

References

- Bruker (1997). *SMART*, *SAINTE* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Westrip, S. P. (2008). *pubCIF*. In preparation.
- Xuan, X. & Zhao, P. (2007a). *Acta Cryst.* **E63**, m2856.
- Xuan, X. & Zhao, P. (2007b). *Acta Cryst.* **E63**, m3009.
- Xuan, X.-P., Zhao, P.-Z. & Tang, Q.-H. (2007). *Acta Cryst.* **E63**, m2405.

supplementary materials

Acta Cryst. (2008). E64, m1591-m1592 [doi:10.1107/S1600536808038117]

Diaqua(2,9-dimethyl-1,10-phenanthroline- κ^2N,N')(4-hydroxybenzoato- κ^2O,O')cobalt(II) nitrate dihydrate

C. Zhai, F. Yan and P. Zhao

Comment

We have recently reported the syntheses and crystal structures of [Ni(dmphen)(3-OH-benzoate)(H₂O)NO₃] (Xuan & Zhao, 2007*a*), [Ni(dmphen)(benzoate)(H₂O)NO₃] (Xuan *et al.*, 2007) and [Co(dmphen)(3-OH-benzoate)(H₂O)NO₃](Xuan & Zhao, 2007*b*) complexes. Now, we report here the crystal structure of the title compound.

Each Co^{II} ion is six-coordinated by two N atoms from a dmphen ligand, and two O atoms from two water molecules and two O atoms from carboxylate group of one 4-hydroxy-benzoate anion (Fig.1). The CoO₄N₂ unit forms a distorted octahedral geometry, with two O atoms of two water molecules occupying the axial positions at 2.0685 (14) or 2.1187 (14) Å (Table 1). The equatorial plane is defined by the N atoms of dmphen and carboxy O atoms of the 3-hydroxybenzoate anion.

In the crystal structure, an extensive series of O—H···O hydrogen bonds, involving the coordinated and solvent water molecules, 4-hydroxybenzoate and nitrate anions, lead to a supramolecular network structure (Table 2 and Fig. 2). In addition, inversion related molecules are linked via π - π interactions involving the pyridine ring of the dmphen (N1/C1-C4/C12; centroid Cg1) ligand and the benzene ring of the hydroxybenzoate (C15—C20; centroid Cg2) anion (Fig.3); the Cg1—Cg2ⁱⁱⁱ distance is 3.6861 (11) Å (symmetry code is given in Table 2). This combination of hydrogen bonds and stacking interactions build a three-dimensional network.

Experimental

To a solution of 2,9-dimethyl-1,10-phenanthroline (0.1095 g, 0.5 mmol), 4-hydroxy-benzoate (0.1382 g, 1 mmol) and sodium hydroxide (0.03740 g, 1 mmol) in ethanol-water (*v:v* 1:1, 15 ml) was added a solution of Ni(NO₃)₂·6H₂O (0.1457 g, 0.5 mmol) in distilled water (10 ml). The resulting solution was stirred for 5 h at 323 K and then the precipitate obtained was filtered. Pink single crystals of the title compound were obtained by slow evaporation of the filtrate over 80 d.

Refinement

C-bound H atoms were placed in calculated positions and were included in the refinement in the riding-model approximation, with C-H distances of 0.93 or 0.96 Å and $U_{\text{iso}}(\text{H})$ values of 1.2 or 1.5 times $U_{\text{eq}}(\text{C})$. The hydroxyl H atom was also placed in the calculated position (O-H = 0.82 Å) and refined with free torsion angles to fit the electron density. Water H atoms were located in a difference Fourier map and were allowed to ride on the parent atoms. For all O-bound H atoms the $U_{\text{iso}}(\text{H})$ values were set at 1.5 $U_{\text{eq}}(\text{O})$.

Figures

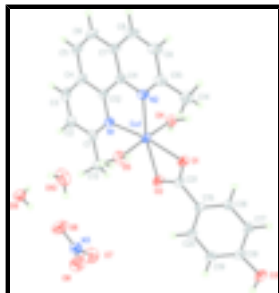


Fig. 1. The molecular structure of the title compound, with atom labels and 30% probability displacement ellipsoids.

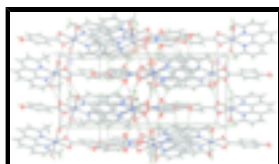


Fig. 2. The crystal structure of the title compound, viewed along the *c* axis. Hydrogen bonds are shown as dashed lines.

Diaqua(2,9-dimethyl-1,10-phenanthroline- κ^2N,N')(4-hydroxybenzoato- κ^2O,O')cobalt(II) nitrate dihydrate

Crystal data

[Co(C₇H₅O₃)(C₁₄H₁₂N₂)(H₂O)₂](NO₃)₂·2H₂O

M_r = 538.37

Monoclinic, *P*2₁/*c*

Hall symbol: -*P* 2ybc

a = 9.8001 (8) Å

b = 22.2638 (19) Å

c = 10.8676 (9) Å

β = 94.602 (1)°

V = 2363.5 (3) Å³

Z = 4

*F*₀₀₀ = 1116

D_x = 1.513 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 6780 reflections

θ = 2.3–27.4°

μ = 0.79 mm⁻¹

T = 291 (2) K

Block, pink

0.35 × 0.25 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer

4385 independent reflections

Radiation source: fine-focus sealed tube

3689 reflections with *I* > 2σ(*I*)

Monochromator: graphite

*R*_{int} = 0.024

T = 291(2) K

θ_{max} = 25.5°

φ and ω scans

θ_{min} = 2.3°

Absorption correction: multi-scan (SADABS; Bruker, 1997)

h = -11→11

*T*_{min} = 0.771, *T*_{max} = 0.899

k = -26→26

17391 measured reflections

l = -12→13

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.9518P]$
$wR(F^2) = 0.081$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{\max} = 0.002$
4385 reflections	$\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
319 parameters	$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0047 (4)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.24510 (2)	0.564923 (11)	0.97828 (2)	0.02979 (10)
O1	0.17733 (13)	0.49074 (6)	1.08320 (12)	0.0366 (3)
O2	0.33021 (13)	0.47337 (6)	0.95100 (12)	0.0374 (3)

supplementary materials

O3	0.2669 (2)	0.21307 (7)	1.18959 (16)	0.0605 (5)
H3	0.2922	0.1902	1.1368	0.091*
O4	0.41725 (13)	0.57880 (6)	1.10585 (13)	0.0393 (3)
H1W	0.3985	0.5685	1.1749	0.059*
H2W	0.4911	0.5635	1.0890	0.059*
O5	0.08164 (14)	0.54783 (7)	0.85063 (13)	0.0463 (4)
H3W	0.0120	0.5431	0.8866	0.070*
H4W	0.0724	0.5513	0.7766	0.070*
O6	0.2587 (2)	0.46630 (9)	0.4839 (2)	0.0894 (7)
O7	0.3605 (2)	0.38408 (10)	0.5460 (2)	0.0809 (6)
O8	0.1450 (2)	0.38603 (9)	0.5079 (2)	0.0793 (6)
N1	0.32511 (15)	0.62761 (7)	0.85585 (14)	0.0318 (3)
N2	0.15796 (15)	0.64623 (7)	1.04080 (15)	0.0335 (4)
N3	0.2548 (2)	0.41299 (10)	0.51267 (18)	0.0539 (5)
C1	0.40177 (19)	0.61783 (9)	0.76179 (18)	0.0365 (4)
C2	0.4510 (2)	0.66576 (10)	0.6932 (2)	0.0453 (5)
H2	0.5028	0.6578	0.6270	0.054*
C3	0.4234 (2)	0.72318 (10)	0.7231 (2)	0.0488 (5)
H3A	0.4580	0.7547	0.6788	0.059*
C4	0.3424 (2)	0.73521 (9)	0.8210 (2)	0.0411 (5)
C5	0.3063 (2)	0.79459 (9)	0.8560 (2)	0.0508 (6)
H5A	0.3428	0.8274	0.8170	0.061*
C6	0.2207 (3)	0.80379 (9)	0.9444 (2)	0.0522 (6)
H6A	0.1975	0.8428	0.9649	0.063*
C7	0.1645 (2)	0.75432 (9)	1.0074 (2)	0.0425 (5)
C8	0.0722 (2)	0.76153 (10)	1.0991 (2)	0.0523 (6)
H8A	0.0427	0.7997	1.1195	0.063*
C9	0.0264 (2)	0.71247 (10)	1.1575 (2)	0.0495 (6)
H9	-0.0353	0.7172	1.2176	0.059*
C10	0.07125 (19)	0.65450 (9)	1.12827 (19)	0.0393 (5)
C11	0.20282 (19)	0.69525 (8)	0.98025 (18)	0.0343 (4)
C12	0.29325 (18)	0.68556 (8)	0.88414 (18)	0.0334 (4)
C13	0.4357 (2)	0.55479 (10)	0.7305 (2)	0.0475 (5)
H13A	0.5202	0.5434	0.7752	0.071*
H13B	0.4450	0.5517	0.6435	0.071*
H13C	0.3638	0.5286	0.7527	0.071*
C14	0.0247 (2)	0.60129 (10)	1.1968 (2)	0.0500 (6)
H14A	-0.0272	0.5751	1.1406	0.075*
H14B	-0.0317	0.6144	1.2599	0.075*
H14C	0.1028	0.5802	1.2340	0.075*
C15	0.25751 (18)	0.38985 (8)	1.06962 (18)	0.0315 (4)
C16	0.21346 (19)	0.37361 (8)	1.18382 (18)	0.0350 (4)
H16	0.1813	0.4030	1.2350	0.042*
C17	0.2169 (2)	0.31459 (9)	1.22188 (19)	0.0398 (5)
H17	0.1887	0.3044	1.2989	0.048*
C18	0.2626 (2)	0.27028 (9)	1.1450 (2)	0.0401 (5)
C19	0.3045 (2)	0.28577 (9)	1.03029 (19)	0.0408 (5)
H19	0.3334	0.2561	0.9781	0.049*
C20	0.3033 (2)	0.34506 (9)	0.99351 (19)	0.0374 (4)

H20	0.3333	0.3552	0.9172	0.045*
C21	0.25521 (18)	0.45407 (9)	1.03250 (17)	0.0326 (4)
O9	0.38611 (19)	0.56246 (7)	0.35357 (16)	0.0590 (4)
H5W	0.3520	0.5320	0.3824	0.089*
H6W	0.4632	0.5696	0.3884	0.089*
O10	0.0934 (2)	0.55782 (10)	0.60222 (17)	0.0801 (6)
H7W	0.0195	0.5697	0.5695	0.120*
H8W	0.1089	0.5228	0.5809	0.120*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02697 (15)	0.02584 (15)	0.03723 (16)	0.00085 (9)	0.00663 (10)	0.00142 (10)
O1	0.0339 (7)	0.0294 (7)	0.0479 (8)	0.0028 (5)	0.0117 (6)	0.0027 (6)
O2	0.0354 (7)	0.0328 (7)	0.0457 (8)	-0.0002 (6)	0.0131 (6)	0.0061 (6)
O3	0.0890 (13)	0.0308 (8)	0.0644 (11)	0.0015 (8)	0.0237 (10)	0.0087 (7)
O4	0.0313 (7)	0.0439 (8)	0.0428 (8)	0.0022 (6)	0.0042 (6)	0.0025 (6)
O5	0.0323 (7)	0.0644 (10)	0.0423 (8)	-0.0086 (7)	0.0028 (6)	0.0030 (7)
O6	0.123 (2)	0.0482 (12)	0.1012 (16)	-0.0095 (11)	0.0364 (15)	0.0098 (10)
O7	0.0641 (12)	0.0851 (14)	0.0940 (16)	0.0112 (11)	0.0088 (11)	-0.0044 (12)
O8	0.0701 (13)	0.0730 (13)	0.0944 (15)	-0.0149 (11)	0.0030 (11)	0.0118 (11)
N1	0.0275 (8)	0.0300 (8)	0.0381 (9)	0.0009 (6)	0.0030 (6)	0.0036 (7)
N2	0.0275 (8)	0.0311 (8)	0.0421 (9)	0.0027 (6)	0.0030 (7)	-0.0035 (7)
N3	0.0643 (14)	0.0494 (12)	0.0491 (12)	-0.0014 (10)	0.0115 (10)	-0.0038 (9)
C1	0.0293 (10)	0.0426 (11)	0.0375 (11)	0.0018 (8)	0.0022 (8)	0.0050 (9)
C2	0.0391 (11)	0.0553 (14)	0.0422 (12)	-0.0014 (10)	0.0080 (9)	0.0113 (10)
C3	0.0433 (12)	0.0488 (13)	0.0542 (14)	-0.0077 (10)	0.0030 (10)	0.0193 (11)
C4	0.0393 (11)	0.0342 (11)	0.0484 (12)	-0.0040 (8)	-0.0049 (9)	0.0097 (9)
C5	0.0586 (14)	0.0299 (11)	0.0622 (15)	-0.0052 (10)	-0.0047 (12)	0.0104 (10)
C6	0.0642 (15)	0.0247 (10)	0.0656 (16)	0.0058 (10)	-0.0087 (12)	0.0015 (10)
C7	0.0411 (12)	0.0333 (11)	0.0516 (13)	0.0077 (9)	-0.0055 (9)	-0.0022 (9)
C8	0.0513 (13)	0.0366 (12)	0.0684 (16)	0.0153 (10)	0.0008 (11)	-0.0092 (11)
C9	0.0425 (12)	0.0484 (13)	0.0589 (14)	0.0131 (10)	0.0111 (10)	-0.0110 (11)
C10	0.0298 (10)	0.0410 (11)	0.0472 (12)	0.0036 (8)	0.0041 (8)	-0.0066 (9)
C11	0.0306 (9)	0.0285 (10)	0.0426 (11)	0.0013 (8)	-0.0044 (8)	0.0010 (8)
C12	0.0277 (9)	0.0306 (10)	0.0411 (11)	0.0005 (7)	-0.0028 (8)	0.0034 (8)
C13	0.0509 (13)	0.0468 (12)	0.0471 (13)	0.0047 (10)	0.0180 (10)	0.0009 (10)
C14	0.0475 (13)	0.0481 (13)	0.0576 (14)	0.0002 (10)	0.0235 (11)	-0.0060 (11)
C15	0.0272 (9)	0.0291 (9)	0.0385 (10)	-0.0024 (7)	0.0041 (8)	0.0015 (8)
C16	0.0323 (10)	0.0337 (10)	0.0396 (11)	0.0005 (8)	0.0071 (8)	-0.0011 (8)
C17	0.0419 (11)	0.0371 (11)	0.0416 (11)	-0.0036 (9)	0.0109 (9)	0.0064 (9)
C18	0.0424 (11)	0.0292 (10)	0.0489 (12)	-0.0045 (8)	0.0041 (9)	0.0052 (9)
C19	0.0455 (11)	0.0324 (10)	0.0453 (12)	-0.0011 (9)	0.0082 (9)	-0.0059 (9)
C20	0.0389 (11)	0.0373 (11)	0.0369 (11)	-0.0017 (9)	0.0090 (8)	0.0007 (9)
C21	0.0283 (9)	0.0324 (10)	0.0373 (11)	-0.0018 (8)	0.0028 (8)	0.0009 (8)
O9	0.0772 (12)	0.0438 (9)	0.0572 (10)	0.0025 (8)	0.0119 (9)	0.0023 (7)
O10	0.0746 (13)	0.1064 (17)	0.0584 (12)	0.0092 (11)	0.0001 (10)	-0.0031 (11)

supplementary materials

Geometric parameters (Å, °)

Co1—O5	2.0685 (14)	C6—C7	1.430 (3)
Co1—O4	2.1187 (14)	C6—H6A	0.93
Co1—N1	2.1213 (15)	C7—C11	1.406 (3)
Co1—N2	2.1357 (15)	C7—C8	1.407 (3)
Co1—O1	2.1425 (13)	C8—C9	1.358 (3)
Co1—O2	2.2311 (13)	C8—H8A	0.93
O1—C21	1.273 (2)	C9—C10	1.408 (3)
O2—C21	1.270 (2)	C9—H9	0.93
O3—C18	1.362 (2)	C10—C14	1.490 (3)
O3—H3	0.82	C11—C12	1.439 (3)
O4—H1W	0.82	C13—H13A	0.96
O4—H2W	0.83	C13—H13B	0.96
O5—H3W	0.82	C13—H13C	0.96
O5—H4W	0.81	C14—H14A	0.96
O6—N3	1.229 (3)	C14—H14B	0.96
O7—N3	1.249 (3)	C14—H14C	0.96
O8—N3	1.229 (3)	C15—C20	1.392 (3)
N1—C1	1.334 (2)	C15—C16	1.394 (3)
N1—C12	1.368 (2)	C15—C21	1.485 (3)
N2—C10	1.338 (2)	C16—C17	1.377 (3)
N2—C11	1.365 (2)	C16—H16	0.93
C1—C2	1.409 (3)	C17—C18	1.390 (3)
C1—C13	1.488 (3)	C17—H17	0.93
C2—C3	1.352 (3)	C18—C19	1.386 (3)
C2—H2	0.93	C19—C20	1.379 (3)
C3—C4	1.403 (3)	C19—H19	0.93
C3—H3A	0.93	C20—H20	0.93
C4—C12	1.407 (3)	O9—H5W	0.83
C4—C5	1.428 (3)	O9—H6W	0.83
C5—C6	1.341 (3)	O10—H7W	0.82
C5—H5A	0.93	O10—H8W	0.83
O5—Co1—O4	177.28 (6)	C11—C7—C6	120.0 (2)
O5—Co1—N1	90.33 (6)	C8—C7—C6	123.0 (2)
O4—Co1—N1	89.97 (6)	C9—C8—C7	119.7 (2)
O5—Co1—N2	93.52 (6)	C9—C8—H8A	120.2
O4—Co1—N2	89.19 (6)	C7—C8—H8A	120.2
N1—Co1—N2	79.59 (6)	C8—C9—C10	120.7 (2)
O5—Co1—O1	87.63 (6)	C8—C9—H9	119.7
O4—Co1—O1	91.65 (5)	C10—C9—H9	119.7
N1—Co1—O1	170.71 (6)	N2—C10—C9	120.96 (19)
N2—Co1—O1	109.58 (6)	N2—C10—C14	118.91 (17)
O5—Co1—O2	91.17 (6)	C9—C10—C14	120.12 (19)
O4—Co1—O2	86.19 (5)	N2—C11—C7	123.02 (19)
N1—Co1—O2	110.90 (5)	N2—C11—C12	118.08 (16)
N2—Co1—O2	168.50 (6)	C7—C11—C12	118.90 (18)
O1—Co1—O2	60.11 (5)	N1—C12—C4	122.56 (18)

C21—O1—Co1	92.40 (11)	N1—C12—C11	118.00 (16)
C21—O2—Co1	88.46 (11)	C4—C12—C11	119.42 (18)
C18—O3—H3	109.5	C1—C13—H13A	109.5
Co1—O4—H1W	109.5	C1—C13—H13B	109.5
Co1—O4—H2W	117.1	H13A—C13—H13B	109.5
H1W—O4—H2W	110.5	C1—C13—H13C	109.5
Co1—O5—H3W	109.5	H13A—C13—H13C	109.5
Co1—O5—H4W	132.1	H13B—C13—H13C	109.5
H3W—O5—H4W	117.1	C10—C14—H14A	109.5
C1—N1—C12	118.60 (16)	C10—C14—H14B	109.5
C1—N1—Co1	129.23 (13)	H14A—C14—H14B	109.5
C12—N1—Co1	112.14 (12)	C10—C14—H14C	109.5
C10—N2—C11	118.69 (16)	H14A—C14—H14C	109.5
C10—N2—Co1	129.48 (13)	H14B—C14—H14C	109.5
C11—N2—Co1	111.83 (12)	C20—C15—C16	118.73 (17)
O6—N3—O8	120.4 (2)	C20—C15—C21	121.77 (17)
O6—N3—O7	122.0 (2)	C16—C15—C21	119.49 (17)
O8—N3—O7	117.6 (2)	C17—C16—C15	120.86 (18)
N1—C1—C2	121.30 (19)	C17—C16—H16	119.6
N1—C1—C13	118.61 (17)	C15—C16—H16	119.6
C2—C1—C13	120.09 (19)	C16—C17—C18	119.85 (18)
C3—C2—C1	120.4 (2)	C16—C17—H17	120.1
C3—C2—H2	119.8	C18—C17—H17	120.1
C1—C2—H2	119.8	O3—C18—C19	123.33 (19)
C2—C3—C4	119.94 (19)	O3—C18—C17	116.85 (18)
C2—C3—H3A	120.0	C19—C18—C17	119.79 (18)
C4—C3—H3A	120.0	C20—C19—C18	120.15 (19)
C3—C4—C12	117.17 (19)	C20—C19—H19	119.9
C3—C4—C5	123.1 (2)	C18—C19—H19	119.9
C12—C4—C5	119.7 (2)	C19—C20—C15	120.59 (19)
C6—C5—C4	121.0 (2)	C19—C20—H20	119.7
C6—C5—H5A	119.5	C15—C20—H20	119.7
C4—C5—H5A	119.5	O2—C21—O1	119.03 (18)
C5—C6—C7	120.8 (2)	O2—C21—C15	121.20 (17)
C5—C6—H6A	119.6	O1—C21—C15	119.77 (16)
C7—C6—H6A	119.6	H5W—O9—H6W	111.3
C11—C7—C8	116.9 (2)	H7W—O10—H8W	110.8
O5—Co1—O1—C21	93.01 (11)	C11—N2—C10—C9	0.2 (3)
O4—Co1—O1—C21	-84.36 (11)	Co1—N2—C10—C9	179.14 (15)
N2—Co1—O1—C21	-174.09 (11)	C11—N2—C10—C14	-178.51 (18)
O2—Co1—O1—C21	0.29 (10)	Co1—N2—C10—C14	0.4 (3)
O5—Co1—O2—C21	-86.88 (11)	C8—C9—C10—N2	-1.2 (3)
O4—Co1—O2—C21	93.81 (11)	C8—C9—C10—C14	177.5 (2)
N1—Co1—O2—C21	-177.68 (10)	C10—N2—C11—C7	1.4 (3)
N2—Co1—O2—C21	27.2 (3)	Co1—N2—C11—C7	-177.69 (15)
O1—Co1—O2—C21	-0.29 (10)	C10—N2—C11—C12	-178.40 (17)
O5—Co1—N1—C1	-83.02 (16)	Co1—N2—C11—C12	2.5 (2)
O4—Co1—N1—C1	94.28 (16)	C8—C7—C11—N2	-2.0 (3)
N2—Co1—N1—C1	-176.54 (17)	C6—C7—C11—N2	176.94 (19)

supplementary materials

O2—Co1—N1—C1	8.36 (18)	C8—C7—C11—C12	177.86 (18)
O5—Co1—N1—C12	98.92 (13)	C6—C7—C11—C12	-3.2 (3)
O4—Co1—N1—C12	-83.79 (12)	C1—N1—C12—C4	-2.5 (3)
N2—Co1—N1—C12	5.40 (12)	Co1—N1—C12—C4	175.82 (14)
O2—Co1—N1—C12	-169.70 (11)	C1—N1—C12—C11	175.81 (17)
O5—Co1—N2—C10	87.09 (17)	Co1—N1—C12—C11	-5.9 (2)
O4—Co1—N2—C10	-93.10 (17)	C3—C4—C12—N1	2.1 (3)
N1—Co1—N2—C10	176.78 (18)	C5—C4—C12—N1	-179.36 (18)
O1—Co1—N2—C10	-1.64 (18)	C3—C4—C12—C11	-176.18 (18)
O2—Co1—N2—C10	-26.8 (4)	C5—C4—C12—C11	2.4 (3)
O5—Co1—N2—C11	-93.90 (13)	N2—C11—C12—N1	2.4 (3)
O4—Co1—N2—C11	85.91 (13)	C7—C11—C12—N1	-177.50 (17)
N1—Co1—N2—C11	-4.21 (12)	N2—C11—C12—C4	-179.31 (17)
O1—Co1—N2—C11	177.37 (12)	C7—C11—C12—C4	0.8 (3)
O2—Co1—N2—C11	152.2 (2)	C20—C15—C16—C17	1.0 (3)
C12—N1—C1—C2	0.8 (3)	C21—C15—C16—C17	-178.71 (17)
Co1—N1—C1—C2	-177.17 (14)	C15—C16—C17—C18	-1.1 (3)
C12—N1—C1—C13	-179.64 (17)	C16—C17—C18—O3	178.27 (19)
Co1—N1—C1—C13	2.4 (3)	C16—C17—C18—C19	0.0 (3)
N1—C1—C2—C3	1.2 (3)	O3—C18—C19—C20	-176.9 (2)
C13—C1—C2—C3	-178.3 (2)	C17—C18—C19—C20	1.2 (3)
C1—C2—C3—C4	-1.6 (3)	C18—C19—C20—C15	-1.4 (3)
C2—C3—C4—C12	0.0 (3)	C16—C15—C20—C19	0.2 (3)
C2—C3—C4—C5	-178.5 (2)	C21—C15—C20—C19	179.93 (18)
C3—C4—C5—C6	175.1 (2)	Co1—O2—C21—O1	0.49 (17)
C12—C4—C5—C6	-3.3 (3)	Co1—O2—C21—C15	-179.24 (16)
C4—C5—C6—C7	0.9 (4)	Co1—O1—C21—O2	-0.51 (17)
C5—C6—C7—C11	2.4 (3)	Co1—O1—C21—C15	179.23 (15)
C5—C6—C7—C8	-178.8 (2)	C20—C15—C21—O2	-21.5 (3)
C11—C7—C8—C9	0.9 (3)	C16—C15—C21—O2	158.19 (18)
C6—C7—C8—C9	-178.0 (2)	C20—C15—C21—O1	158.77 (18)
C7—C8—C9—C10	0.6 (3)	C16—C15—C21—O1	-21.5 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O10—H8W \cdots O6	0.83	2.26	2.960 (3)	142
O9—H5W \cdots O6	0.83	2.09	2.904 (3)	169
O9—H6W \cdots O7 ⁱ	0.83	2.09	2.888 (3)	161
O10—H7W \cdots O8 ⁱⁱ	0.83	2.01	2.829 (3)	169
O5—H4W \cdots O10	0.81	1.93	2.720 (2)	167
O4—H2W \cdots O2 ⁱⁱⁱ	0.83	2.01	2.846 (2)	180
O5—H3W \cdots O1 ^{iv}	0.82	2.05	2.826 (2)	157
O4—H1W \cdots O9 ^v	0.82	1.96	2.758 (2)	164
O3—H3 \cdots O8 ^{vi}	0.82	2.57	3.133 (3)	127
O3—H3 \cdots O7 ^{vi}	0.82	2.07	2.861 (3)	164

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

Fig. 1

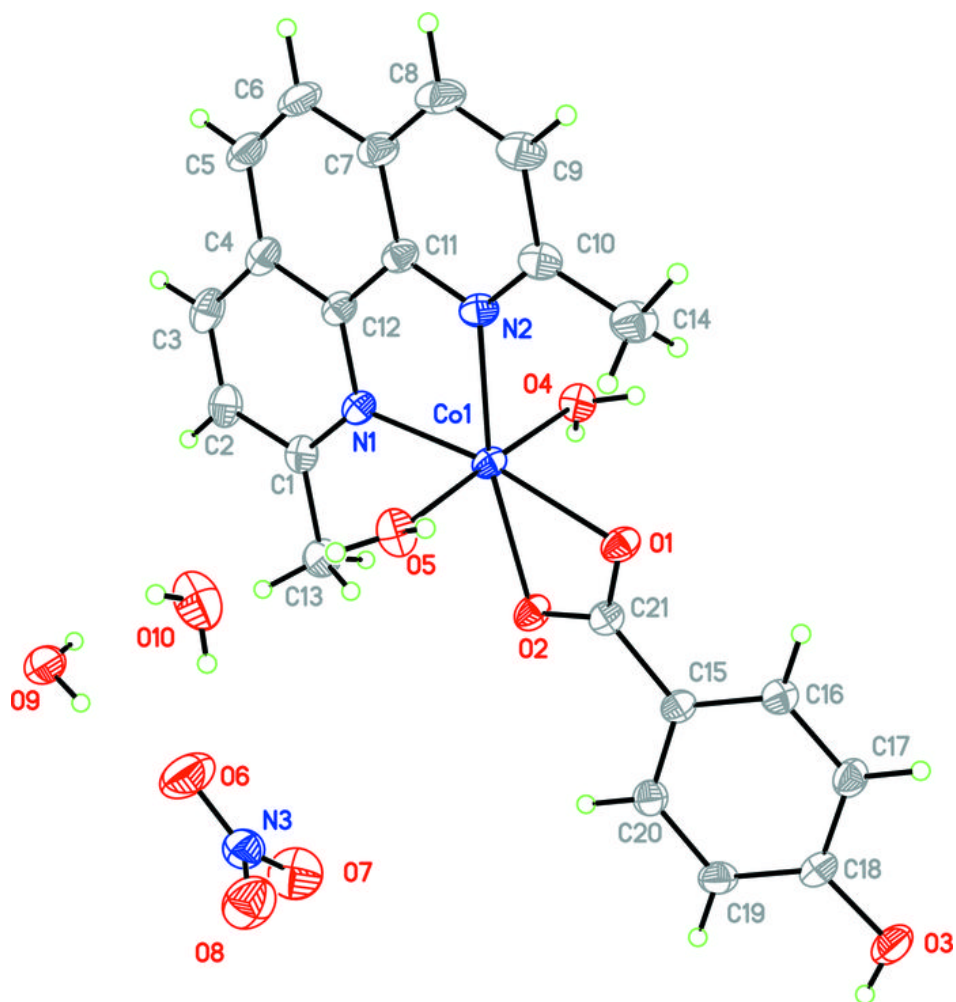


Fig. 2

