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Triaqua(N^2, N^4 -di-2-pyridylpyrimidine-2,4-diamine)cobalt(II) fumarate

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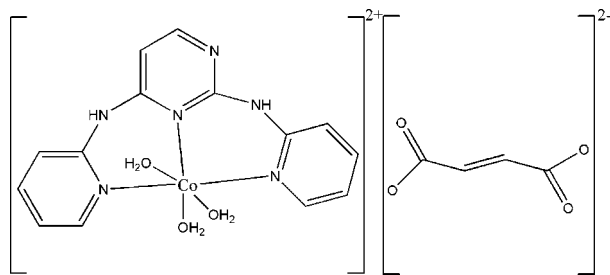
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.026; wR factor = 0.078; data-to-parameter ratio = 12.2.

The Co atom in the title compound, $[\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_6)(\text{H}_2\text{O})_3]\text{C}_4\text{H}_2\text{O}_4$, has a *mer*- CoN_3O_3 octahedral coordination arising from the tridentate N^2, N^4 -di-2-pyridylpyrimidine-2,4-diamine (tpda) ligand and three coordinated water molecules. The asymmetric unit contains two fumarate half-anions, both completed by inversion symmetry. A network of $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds leads to a three-dimensional network in the crystal structure.

Related literature

For a related structure, see: Fang *et al.* (2005). For background, see: Sheu *et al.* (1996); Peng *et al.* (2000).



Experimental

Crystal data

$[\text{Co}(\text{C}_{14}\text{H}_{12}\text{N}_6)(\text{H}_2\text{O})_3]\text{C}_4\text{H}_2\text{O}_4$
 $M_r = 491.33$
 Monoclinic, $P2_1/n$
 $a = 9.3239$ (3) Å
 $b = 17.1115$ (6) Å
 $c = 13.1395$ (5) Å
 $\beta = 96.224$ (1)°

$V = 2084.00$ (13) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.88$ mm⁻¹
 $T = 298$ (2) K
 $0.29 \times 0.25 \times 0.18$ mm

Data collection

Bruker APEX CCD diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.785$, $T_{\max} = 0.858$

10365 measured reflections
 3746 independent reflections
 3363 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.078$
 $S = 0.86$
 3746 reflections
 307 parameters
 9 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Selected bond lengths (Å).

Co1—O1	2.0989 (13)	Co1—N1	2.0790 (15)
Co1—O2	2.0905 (13)	Co1—N3	2.0624 (14)
Co1—O3	2.0396 (13)	Co1—N5	2.0803 (16)

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O2—H2D ⁱ ···O4 ⁱ	0.836 (10)	1.943 (14)	2.7396 (19)	159 (2)
O2—H2C···O6 ⁱⁱ	0.841 (10)	1.898 (10)	2.7374 (18)	176 (3)
O3—H3C···O7 ⁱⁱⁱ	0.840 (9)	1.858 (11)	2.6929 (18)	172 (3)
O3—H3D···O5 ⁱⁱⁱ	0.832 (10)	1.734 (11)	2.559 (2)	171 (2)
O1—H1D···O6 ^{iv}	0.829 (10)	1.930 (13)	2.7374 (19)	165 (3)
O1—H1C···O4 ⁱⁱⁱ	0.832 (10)	2.001 (13)	2.8143 (19)	166 (2)
N4—H4A···O5 ^v	0.86	1.93	2.782 (2)	169
N2—H2···O7 ^{vi}	0.86	2.28	3.002 (2)	141

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

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); 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: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2798).

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supplementary materials

Acta Cryst. (2008). E64, m1406 [doi:10.1107/S1600536808032613]

Triaqua(*N*²,*N*⁴-di-2-pyridylpyrimidine-2,4-diamine)cobalt(II) fumarate

M. Yang

Comment

Transition metal complexes with polypyridylamine ligands, possessing diverse structures and unusual optical and electro-magnetic properties (Sheu *et al.*, 1996), have aroused great interest among researchers. The tri-pyridyldiamine ligand can exhibit donor as well as acceptor properties and can act as a chelating ligand (Peng *et al.*, 2000). In this paper, we report the synthesis and crystal structure of the title compound, (I), (Fig. 1).

The Co atom in (I) has an octahedral coordination formed by the N,N,N-tridentate tpda ligand and three coordinated water molecules. The tpda ligand is tri-coordinated, with the peripheral N1 and N5 atoms in the axial positions [N1—Co1—N5 = 174.48 (6)°] and the central N3 atom in the equatorial plane of the bipyramid. The remaining two equatorial positions are occupied by water molecules (Table 1). The three pyridine rings of the tpda ligand are not coplanar: the dihedral angles between the planes of the central pyridine ring and two peripheral rings are 18.5 (4) and 26.4 (2)° respectively.

The H atoms of both NH groups of the tpda ligand and coordinated water molecules are involved in hydrogen bonds with O atoms of carboxylate groups of fumarate which link the complex molecules to form an infinite three-dimensional network (Table 2, Fig. 2).

The molecular configuration of (I) is similar to that of [2,6-bis(2-pyridylamino)pyridine]dinitrato cadmium monohydrate (Fang *et al.*, 2005).

Experimental

Tpda (0.025 g, 0.07 mmol), Co(NO₃)₂ (0.026 g, 0.1 mmol), fumaric acid (0.023 g, 0.09 mmol) and NaOH (0.041 g, 0.1 mmol) were mixed in acetonitrile, and the mixture was heated for six hours under reflux with stirring. The resultant was then filtered to give a solution which was infiltrated by diethyl ether in a closed vessel, one week later some pink blocks of (I) were obtained.

Refinement

The water H atoms were located in a difference map and refined with the restraint O—H = 0.85 (1)Å and a fixed U_{iso} value of 0.08Å². The other H atoms were positioned geometrically (C—H = 0.93Å, N—H = 0.86Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$.

Figures

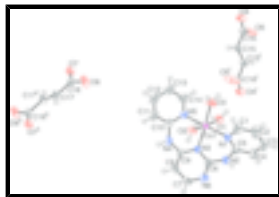


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids for the non-hydrogen atoms. Symmetry codes: (i) 1-x, 1-y, -z; (ii) 1-x, -y, 2-z.

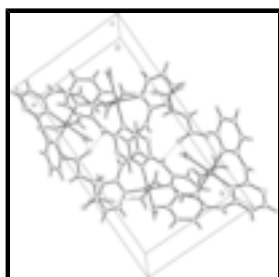


Fig. 2. The packing diagram of (I), viewed along the *a* axis; hydrogen bonds are shown as dashed lines.

Triaqua(*N*²,*N*⁴-di-2-pyridylpyrimidine-2,4-diamine)cobalt(II) fumarate

Crystal data

[Co(C₁₄H₁₂N₆)(H₂O)₃]C₄H₂O₄

M_r = 491.33

Monoclinic, *P*2₁/*n*

Hall symbol: -*P* 2yn

a = 9.3239 (3) Å

b = 17.1115 (6) Å

c = 13.1395 (5) Å

β = 96.224 (1)°

V = 2084.00 (13) Å³

Z = 4

*F*₀₀₀ = 1012

D_x = 1.566 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 3746 reflections

θ = 2.0–25.2°

μ = 0.88 mm⁻¹

T = 298 (2) K

Block, pink

0.29 × 0.25 × 0.18 mm

Data collection

Bruker APEX CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 298(2) K

ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

*T*_{min} = 0.785, *T*_{max} = 0.858

10365 measured reflections

3746 independent reflections

3363 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.014

θ_{max} = 25.2°

θ_{min} = 2.0°

h = -11→8

k = -18→20

l = -15→15

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.026$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.078$	$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.982P]$
$S = 0.86$	where $P = (F_o^2 + 2F_c^2)/3$
3746 reflections	$(\Delta/\sigma)_{\max} = 0.001$
307 parameters	$\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$
9 restraints	$\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	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 $F^2 > \sigma(F^2)$ 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	0.89198 (2)	0.212482 (12)	0.174122 (15)	0.02637 (9)
N1	1.07828 (17)	0.25958 (9)	0.12520 (12)	0.0386 (3)
N2	1.12613 (18)	0.14671 (9)	0.03083 (12)	0.0428 (4)
H2	1.1513	0.1318	-0.0272	0.051*
N3	0.96644 (15)	0.10180 (8)	0.14666 (11)	0.0311 (3)
N4	0.81107 (18)	0.04503 (9)	0.25721 (12)	0.0418 (4)
H4A	0.8147	0.0119	0.3066	0.050*
N5	0.69822 (17)	0.16405 (10)	0.20828 (12)	0.0411 (4)
N6	1.1419 (2)	0.01872 (10)	0.08085 (15)	0.0527 (4)
O1	0.80120 (15)	0.22962 (8)	0.02251 (10)	0.0413 (3)
O2	0.98217 (16)	0.20786 (7)	0.32677 (10)	0.0404 (3)
O3	0.82120 (18)	0.31928 (8)	0.21618 (11)	0.0515 (4)
O4	0.31016 (15)	0.62641 (8)	0.05353 (10)	0.0449 (3)
O5	0.2958 (2)	0.57346 (11)	-0.09942 (12)	0.0843 (7)
O6	0.56949 (16)	0.15459 (8)	0.92018 (12)	0.0521 (4)
O7	0.35145 (14)	0.10201 (8)	0.89469 (10)	0.0432 (3)

supplementary materials

C1	1.1139 (3)	0.33447 (13)	0.14869 (18)	0.0572 (6)
H1A	1.0742	0.3578	0.2031	0.069*
C2	1.2052 (3)	0.37778 (15)	0.0965 (2)	0.0756 (8)
H2A	1.2276	0.4291	0.1152	0.091*
C3	1.2637 (3)	0.34310 (15)	0.0147 (2)	0.0701 (7)
H3A	1.3229	0.3718	-0.0241	0.084*
C4	1.2337 (3)	0.26690 (14)	-0.00838 (18)	0.0548 (5)
H4	1.2728	0.2426	-0.0624	0.066*
C5	1.1431 (2)	0.22600 (11)	0.05069 (14)	0.0389 (4)
C6	1.0754 (2)	0.08795 (10)	0.08910 (14)	0.0356 (4)
C7	1.0969 (2)	-0.04032 (12)	0.13765 (18)	0.0523 (5)
H7	1.1423	-0.0886	0.1355	0.063*
C8	0.9887 (2)	-0.03233 (11)	0.19754 (15)	0.0425 (4)
H8	0.9600	-0.0737	0.2365	0.051*
C9	0.9231 (2)	0.03917 (10)	0.19853 (13)	0.0348 (4)
C10	0.6933 (2)	0.09433 (12)	0.25191 (15)	0.0423 (4)
C11	0.5709 (3)	0.06721 (17)	0.2948 (2)	0.0669 (7)
H11	0.5709	0.0186	0.3263	0.080*
C12	0.4505 (3)	0.1148 (2)	0.2887 (3)	0.0845 (9)
H12	0.3688	0.0992	0.3180	0.101*
C13	0.4526 (3)	0.1857 (2)	0.2388 (2)	0.0773 (8)
H13	0.3714	0.2176	0.2317	0.093*
C14	0.5759 (2)	0.20770 (15)	0.2004 (2)	0.0587 (6)
H14	0.5766	0.2555	0.1667	0.070*
C15	0.4580 (2)	0.51840 (11)	0.02931 (13)	0.0376 (4)
H15	0.4687	0.5068	0.0989	0.045*
C16	0.3459 (2)	0.57780 (10)	-0.00850 (14)	0.0362 (4)
C17	0.5353 (2)	0.03277 (11)	0.99689 (14)	0.0372 (4)
H17	0.6254	0.0371	1.0344	0.045*
C18	0.4805 (2)	0.10121 (10)	0.93323 (13)	0.0353 (4)
H1C	0.782 (3)	0.2754 (7)	0.005 (2)	0.080*
H1D	0.733 (2)	0.2009 (12)	0.001 (2)	0.080*
H3D	0.785 (3)	0.3513 (12)	0.1732 (13)	0.080*
H3C	0.827 (3)	0.3404 (14)	0.2742 (9)	0.080*
H2C	1.007 (3)	0.2514 (8)	0.353 (2)	0.080*
H2D	1.044 (2)	0.1753 (10)	0.350 (2)	0.080*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02877 (14)	0.02434 (14)	0.02585 (14)	0.00162 (8)	0.00225 (9)	-0.00098 (8)
N1	0.0415 (9)	0.0367 (8)	0.0378 (8)	-0.0084 (7)	0.0053 (7)	-0.0034 (6)
N2	0.0500 (10)	0.0384 (9)	0.0432 (9)	-0.0037 (7)	0.0204 (7)	-0.0032 (7)
N3	0.0336 (8)	0.0285 (7)	0.0315 (7)	-0.0020 (6)	0.0049 (6)	-0.0015 (6)
N4	0.0486 (9)	0.0378 (8)	0.0410 (9)	-0.0051 (7)	0.0139 (7)	0.0064 (7)
N5	0.0344 (8)	0.0476 (9)	0.0419 (9)	0.0019 (7)	0.0063 (7)	-0.0009 (7)
N6	0.0538 (11)	0.0425 (10)	0.0641 (11)	0.0088 (8)	0.0162 (9)	-0.0029 (8)
O1	0.0443 (8)	0.0391 (7)	0.0381 (7)	-0.0007 (6)	-0.0059 (6)	0.0020 (6)

O2	0.0501 (8)	0.0356 (7)	0.0338 (7)	0.0059 (6)	-0.0036 (6)	-0.0028 (5)
O3	0.0763 (10)	0.0389 (8)	0.0367 (7)	0.0209 (7)	-0.0056 (7)	-0.0068 (6)
O4	0.0464 (8)	0.0398 (7)	0.0477 (8)	0.0067 (6)	0.0009 (6)	-0.0092 (6)
O5	0.1314 (17)	0.0680 (11)	0.0454 (9)	0.0625 (12)	-0.0268 (10)	-0.0174 (8)
O6	0.0531 (8)	0.0400 (8)	0.0595 (9)	-0.0146 (7)	-0.0111 (7)	0.0168 (6)
O7	0.0394 (7)	0.0431 (7)	0.0461 (7)	0.0006 (6)	0.0008 (6)	0.0109 (6)
C1	0.0691 (15)	0.0468 (12)	0.0583 (13)	-0.0196 (11)	0.0183 (11)	-0.0138 (10)
C2	0.097 (2)	0.0503 (14)	0.0836 (18)	-0.0367 (14)	0.0304 (16)	-0.0141 (13)
C3	0.0840 (18)	0.0588 (15)	0.0724 (16)	-0.0314 (14)	0.0309 (14)	-0.0004 (12)
C4	0.0608 (14)	0.0522 (12)	0.0550 (13)	-0.0138 (11)	0.0225 (11)	-0.0006 (10)
C5	0.0384 (10)	0.0400 (10)	0.0384 (10)	-0.0056 (8)	0.0051 (8)	0.0000 (8)
C6	0.0361 (9)	0.0350 (9)	0.0362 (9)	-0.0015 (7)	0.0062 (7)	-0.0028 (7)
C7	0.0587 (13)	0.0326 (10)	0.0659 (14)	0.0109 (9)	0.0079 (11)	0.0020 (9)
C8	0.0549 (12)	0.0283 (9)	0.0450 (10)	0.0014 (8)	0.0083 (9)	0.0069 (8)
C9	0.0400 (9)	0.0329 (9)	0.0313 (8)	-0.0043 (7)	0.0034 (7)	-0.0007 (7)
C10	0.0396 (10)	0.0512 (12)	0.0371 (10)	-0.0055 (9)	0.0090 (8)	-0.0025 (8)
C11	0.0558 (14)	0.0774 (17)	0.0714 (15)	-0.0124 (13)	0.0249 (12)	0.0100 (13)
C12	0.0458 (14)	0.122 (3)	0.091 (2)	-0.0025 (16)	0.0318 (14)	0.0096 (19)
C13	0.0408 (13)	0.106 (2)	0.087 (2)	0.0129 (14)	0.0168 (13)	0.0048 (18)
C14	0.0410 (12)	0.0697 (16)	0.0651 (15)	0.0102 (10)	0.0054 (10)	0.0038 (11)
C15	0.0460 (10)	0.0327 (9)	0.0335 (9)	0.0025 (8)	0.0009 (7)	0.0030 (7)
C16	0.0419 (10)	0.0295 (9)	0.0362 (9)	0.0008 (7)	-0.0006 (8)	-0.0026 (7)
C17	0.0382 (10)	0.0358 (9)	0.0364 (9)	-0.0010 (7)	-0.0016 (7)	0.0053 (7)
C18	0.0420 (10)	0.0329 (9)	0.0308 (8)	-0.0017 (8)	0.0027 (7)	0.0020 (7)

Geometric parameters (Å, °)

Co1—O1	2.0989 (13)	O6—C18	1.258 (2)
Co1—O2	2.0905 (13)	O7—C18	1.254 (2)
Co1—O3	2.0396 (13)	C1—C2	1.369 (3)
Co1—N1	2.0790 (15)	C1—H1A	0.9300
Co1—N3	2.0624 (14)	C2—C3	1.390 (4)
Co1—N5	2.0803 (16)	C2—H2A	0.9300
N1—C5	1.335 (2)	C3—C4	1.361 (3)
N1—C1	1.351 (3)	C3—H3A	0.9300
N2—C6	1.378 (2)	C4—C5	1.396 (3)
N2—C5	1.387 (2)	C4—H4	0.9300
N2—H2	0.8600	C7—C8	1.352 (3)
N3—C6	1.352 (2)	C7—H7	0.9300
N3—C9	1.355 (2)	C8—C9	1.368 (3)
N4—C9	1.368 (2)	C8—H8	0.9300
N4—C10	1.381 (3)	C10—C11	1.405 (3)
N4—H4A	0.8600	C11—C12	1.381 (4)
N5—C10	1.327 (3)	C11—H11	0.9300
N5—C14	1.358 (3)	C12—C13	1.380 (4)
N6—C6	1.347 (2)	C12—H12	0.9300
N6—C7	1.350 (3)	C13—C14	1.358 (4)
O1—H1C	0.832 (10)	C13—H13	0.9300
O1—H1D	0.829 (10)	C14—H14	0.9300

supplementary materials

O2—H2C	0.841 (10)	C15—C15 ⁱ	1.317 (4)
O2—H2D	0.836 (10)	C15—C16	1.503 (3)
O3—H3D	0.832 (10)	C15—H15	0.9300
O3—H3C	0.840 (9)	C17—C17 ⁱⁱ	1.308 (4)
O4—C16	1.235 (2)	C17—C18	1.497 (2)
O5—C16	1.237 (2)	C17—H17	0.9300
O3—Co1—N3	174.38 (6)	C4—C3—H3A	120.2
O3—Co1—N1	92.41 (7)	C2—C3—H3A	120.2
N3—Co1—N1	89.63 (6)	C3—C4—C5	118.6 (2)
O3—Co1—N5	89.11 (7)	C3—C4—H4	120.7
N3—Co1—N5	89.35 (6)	C5—C4—H4	120.7
N1—Co1—N5	174.48 (6)	N1—C5—N2	120.50 (17)
O3—Co1—O2	83.24 (5)	N1—C5—C4	122.78 (19)
N3—Co1—O2	91.44 (5)	N2—C5—C4	116.69 (18)
N1—Co1—O2	92.79 (6)	N6—C6—N3	125.42 (17)
N5—Co1—O2	92.66 (6)	N6—C6—N2	114.11 (16)
O3—Co1—O1	91.31 (6)	N3—C6—N2	120.46 (16)
N3—Co1—O1	94.07 (6)	N6—C7—C8	122.84 (19)
N1—Co1—O1	85.23 (6)	N6—C7—H7	118.6
N5—Co1—O1	89.44 (6)	C8—C7—H7	118.6
O2—Co1—O1	174.13 (5)	C7—C8—C9	117.28 (18)
C5—N1—C1	117.16 (17)	C7—C8—H8	121.4
C5—N1—Co1	121.31 (12)	C9—C8—H8	121.4
C1—N1—Co1	119.33 (14)	N3—C9—N4	120.86 (16)
C6—N2—C5	130.39 (16)	N3—C9—C8	123.00 (17)
C6—N2—H2	114.8	N4—C9—C8	116.13 (16)
C5—N2—H2	114.8	N5—C10—N4	120.42 (17)
C6—N3—C9	115.20 (15)	N5—C10—C11	122.6 (2)
C6—N3—Co1	123.13 (11)	N4—C10—C11	117.0 (2)
C9—N3—Co1	120.93 (11)	C12—C11—C10	118.2 (3)
C9—N4—C10	131.96 (16)	C12—C11—H11	120.9
C9—N4—H4A	114.0	C10—C11—H11	120.9
C10—N4—H4A	114.0	C13—C12—C11	119.5 (2)
C10—N5—C14	117.34 (18)	C13—C12—H12	120.3
C10—N5—Co1	121.56 (13)	C11—C12—H12	120.3
C14—N5—Co1	120.41 (15)	C14—C13—C12	118.4 (3)
C6—N6—C7	116.15 (17)	C14—C13—H13	120.8
Co1—O1—H1C	117 (2)	C12—C13—H13	120.8
Co1—O1—H1D	118 (2)	N5—C14—C13	123.9 (2)
H1C—O1—H1D	109.1 (16)	N5—C14—H14	118.1
Co1—O2—H2C	114.8 (18)	C13—C14—H14	118.1
Co1—O2—H2D	124.7 (19)	C15 ⁱ —C15—C16	124.5 (2)
H2C—O2—H2D	106.8 (15)	C15 ⁱ —C15—H15	117.8
Co1—O3—H3D	121.7 (17)	C16—C15—H15	117.8
Co1—O3—H3C	129.8 (17)	O4—C16—O5	125.24 (18)
H3D—O3—H3C	108.4 (15)	O4—C16—C15	117.70 (16)
N1—C1—C2	123.4 (2)	O5—C16—C15	117.05 (16)
N1—C1—H1A	118.3	C17 ⁱⁱ —C17—C18	124.2 (2)

C2—C1—H1A	118.3	C17 ⁱⁱ —C17—H17	117.9
C1—C2—C3	118.3 (2)	C18—C17—H17	117.9
C1—C2—H2A	120.8	O7—C18—O6	123.72 (17)
C3—C2—H2A	120.8	O7—C18—C17	119.26 (16)
C4—C3—C2	119.5 (2)	O6—C18—C17	117.01 (16)
O3—Co1—N1—C5	-151.20 (15)	C3—C4—C5—N2	-174.2 (2)
N3—Co1—N1—C5	34.03 (15)	C7—N6—C6—N3	-1.9 (3)
O2—Co1—N1—C5	125.45 (15)	C7—N6—C6—N2	179.18 (18)
O1—Co1—N1—C5	-60.08 (15)	C9—N3—C6—N6	-0.5 (3)
O3—Co1—N1—C1	11.43 (17)	Co1—N3—C6—N6	169.80 (15)
N3—Co1—N1—C1	-163.33 (17)	C9—N3—C6—N2	178.32 (16)
O2—Co1—N1—C1	-71.91 (17)	Co1—N3—C6—N2	-11.4 (2)
O1—Co1—N1—C1	102.55 (17)	C5—N2—C6—N6	-144.6 (2)
N1—Co1—N3—C6	-15.88 (14)	C5—N2—C6—N3	36.5 (3)
N5—Co1—N3—C6	158.70 (14)	C6—N6—C7—C8	1.9 (3)
O2—Co1—N3—C6	-108.66 (14)	N6—C7—C8—C9	0.5 (3)
O1—Co1—N3—C6	69.31 (14)	C6—N3—C9—N4	-178.14 (16)
N1—Co1—N3—C9	153.86 (14)	Co1—N3—C9—N4	11.3 (2)
N5—Co1—N3—C9	-31.56 (14)	C6—N3—C9—C8	3.1 (3)
O2—Co1—N3—C9	61.08 (14)	Co1—N3—C9—C8	-167.37 (15)
O1—Co1—N3—C9	-120.95 (13)	C10—N4—C9—N3	26.2 (3)
O3—Co1—N5—C10	-141.78 (15)	C10—N4—C9—C8	-155.0 (2)
N3—Co1—N5—C10	32.82 (15)	C7—C8—C9—N3	-3.2 (3)
O2—Co1—N5—C10	-58.59 (15)	C7—C8—C9—N4	178.03 (18)
O1—Co1—N5—C10	126.90 (15)	C14—N5—C10—N4	176.3 (2)
O3—Co1—N5—C14	28.44 (17)	Co1—N5—C10—N4	-13.2 (2)
N3—Co1—N5—C14	-156.96 (17)	C14—N5—C10—C11	-4.0 (3)
O2—Co1—N5—C14	111.63 (17)	Co1—N5—C10—C11	166.54 (18)
O1—Co1—N5—C14	-62.88 (17)	C9—N4—C10—N5	-25.1 (3)
C5—N1—C1—C2	3.8 (4)	C9—N4—C10—C11	155.2 (2)
Co1—N1—C1—C2	-159.5 (2)	N5—C10—C11—C12	1.5 (4)
N1—C1—C2—C3	0.4 (5)	N4—C10—C11—C12	-178.8 (2)
C1—C2—C3—C4	-2.7 (5)	C10—C11—C12—C13	1.8 (5)
C2—C3—C4—C5	0.7 (4)	C11—C12—C13—C14	-2.5 (5)
C1—N1—C5—N2	171.9 (2)	C10—N5—C14—C13	3.3 (4)
Co1—N1—C5—N2	-25.1 (2)	Co1—N5—C14—C13	-167.3 (2)
C1—N1—C5—C4	-6.0 (3)	C12—C13—C14—N5	-0.1 (5)
Co1—N1—C5—C4	157.03 (17)	C15 ⁱ —C15—C16—O4	-155.6 (2)
C6—N2—C5—N1	-15.7 (3)	C15 ⁱ —C15—C16—O5	25.1 (4)
C6—N2—C5—C4	162.4 (2)	C17 ⁱⁱ —C17—C18—O7	11.0 (3)
C3—C4—C5—N1	3.8 (4)	C17 ⁱⁱ —C17—C18—O6	-167.7 (2)

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

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2D \cdots O4 ⁱⁱⁱ	0.836 (10)	1.943 (14)	2.7396 (19)	159 (2)

supplementary materials

O2—H2C···O6 ^{iv}	0.841 (10)	1.898 (10)	2.7374 (18)	176 (3)
O3—H3C···O7 ^{iv}	0.840 (9)	1.858 (11)	2.6929 (18)	172 (3)
O3—H3D···O5 ⁱ	0.832 (10)	1.734 (11)	2.559 (2)	171 (2)
O1—H1D···O6 ^v	0.829 (10)	1.930 (13)	2.7374 (19)	165 (3)
O1—H1C···O4 ⁱ	0.832 (10)	2.001 (13)	2.8143 (19)	166 (2)
N4—H4A···O5 ^{vi}	0.86	1.93	2.782 (2)	169
N2—H2···O7 ^{vii}	0.86	2.28	3.002 (2)	141

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

Fig. 1

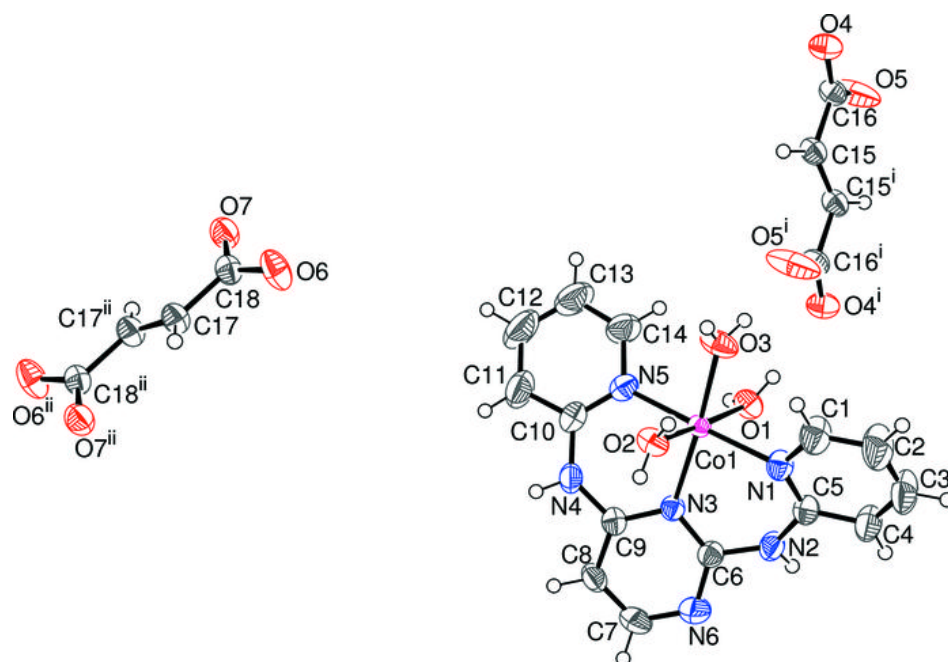


Fig. 2

