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Crystal structure of tetraaquabis(3,5-diamino-4*H*-1,2,4-triazol-1-ium)cobalt(II) bis[bis(pyridine-2,6-dicarboxylato)cobaltate(II)] dihydrate

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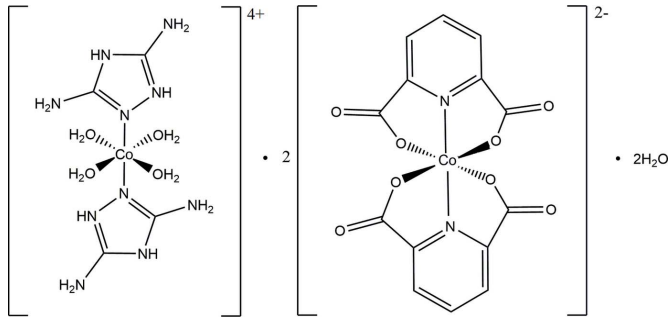
The asymmetric unit of the title compound, $[Co(C_2H_6N_5)_2(H_2O)_4][Co(C_7H_3NO_4)_2]_2\cdot 2H_2O$, features 1.5 Co^{II} ions (one anionic complex and one half cationic complex) and one water molecule. In the cationic complex, the Co^{II} atom is located on an inversion centre and is coordinated by two triazolium cations and four water molecules, adopting an octahedral geometry where the N atoms of the two triazolium cations occupy the axial positions and the O atoms of the four water molecules the equatorial positions. The two triazole ligands are parallel offset (with a distance of 1.38 Å between their planes). In the anionic complex, the Co^{II} ion is six-coordinated by two N and four O atoms of the two pyridine-2,6-dicarboxylate anions, exhibiting a slightly distorted octahedral coordination geometry in which the mean plane of the two pyridine-2,6-dicarboxylate anions are almost perpendicular to each other, making a dihedral angle of 85.87 (2)°. In the crystal, molecules are linked into a three-dimensional network *via* C—H···O, C—H···N, O—H···O and N—H···O hydrogen bonds.

Keywords: crystal structure; pyridine-2,6-dicarboxylate; triazolium; Co^{II} complex; hydrogen bonding.

CCDC reference: 1402526

1. Related literature

For the different coordination modes of transition metal–dipicolinate complexes, see: Håkansson *et al.* (1993); Okabe & Oya (2000); Aghajani *et al.* (2009). For crystal structures of related complexes, see: Yousuf *et al.* (2011*a*,*b*); Aghabozorg *et al.* (2009); Ramos Silva *et al.* (2008); Wang *et al.* (2004); MacDonald *et al.* (2004). For studies on proton transfer from carboxylic acids to both heterocyclic and substituted amine N atoms, see: Aghabozorg *et al.* (2008); Moghimi *et al.* (2002, 2005, 2007); Pasdar *et al.* (2011); Tabatabaee *et al.* (2009).



2. Experimental

2.1. Crystal data

$[Co(C_2H_6N_5)_2(H_2O)_4][Co(C_7H_3NO_4)_2]_2\cdot 2H_2O$
M_r = 1145.54
Monoclinic, $P2_1/c$
a = 7.1499 (2) Å
b = 10.8807 (2) Å
c = 26.6877 (6) Å
β = 90.649 (1)°
V = 2076.06 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.29 mm^{-1}
T = 100 K
0.43 × 0.28 × 0.28 mm

2.2. Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.607, T_{max} = 0.718
35534 measured reflections
9081 independent reflections
8203 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.068
S = 1.05
9081 reflections
370 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H1*N*4···O1^{i}	0.88 (2)	1.74 (2)	2.6044 (12)	165 (2)
N5—H1*N*5···O7^{ii}	0.89 (2)	1.77 (2)	2.6402 (12)	169 (2)
N6—H1*N*6···O2	0.84 (2)	2.15 (2)	2.9117 (12)	151.1 (19)
N6—H2*N*6···O1*W*^{ii}	0.92 (2)	1.85 (2)	2.7645 (12)	173.6 (19)
N7—H2*N*7···O6^{iii}	0.80 (2)	2.24 (2)	2.9956 (13)	158.4 (18)
O1*W*—H1*W*1···O3	0.83 (2)	1.90 (2)	2.7354 (13)	171 (3)
O1*W*—H2*W*1···O6^{iv}	0.79 (2)	2.09 (2)	2.8711 (12)	175 (2)

‡ Thomson Reuters ResearcherID: C-7581-2009.
§ Thomson Reuters ResearcherID: A-3561-2009.

D—H···A	D—H	H···A	D···A	D—H···A
O2W—H1W2···O5^{i}	0.86 (2)	1.80 (2)	2.6666 (11)	173 (2)
O2W—H2W2···O4	0.82 (2)	2.00 (2)	2.8206 (11)	175 (2)
O3W—H1W3···O4^{i}	0.79 (2)	2.19 (2)	2.9602 (11)	163 (2)
O3W—H2W3···O8^{v}	0.83 (2)	1.76 (2)	2.5795 (11)	173 (2)
C3—H3A···O5^{vi}	0.95	2.25	3.1816 (13)	167
C5—H5A···N7^{vii}	0.95	2.50	3.4265 (15)	164
C10—H10A···O6^{ii}	0.95	2.44	3.3898 (13)	177

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: ZL2619).

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supporting information

Acta Cryst. (2015). E**71**, m139–m140 [doi:10.1107/S2056989015010014]

Crystal structure of tetraaquabis(3,5-diamino-4*H*-1,2,4-triazol-1-ium)cobalt(II) bis[bis(pyridine-2,6-dicarboxylato)cobaltate(II)] dihydrate

Atim Johnson, Justina Mbonu, Zahid Hussain, Wan-Sin Loh and Hoong-Kun Fun

S1. Chemical context

Among different multidentate species, compounds bearing carboxylate functions are widely studied ligands for producing stable transition metals coordination polymers and supramolecular architectures, mostly because of the versatile ligating abilities of the -COO moieties and also due to the enhanced affinity of these metal ions towards such O donors. There have been a number of successful attempts at utilizing proton transfer from carboxylic acids to both heterocyclic and substituted amine nitrogens (Moghimi *et al.*, 2002; Moghimi *et al.*, 2005; Moghimi *et al.*, 2007; Aghabozorg *et al.*, 2008; Aghabozorg *et al.*, 2009; Tabatabaee *et al.*, 2009, Pasdar *et al.*, 2011, Yousuf *et al.*, 2011*b*). Dicarboxylic acids possess a good potential to be used as proton donors in the synthesis of proton transfer compounds. In continuation of our work, we report herein the trinuclear complex of Co^{II} with pyridine-2,6-dicarboxylic acid as proton donor and 3,5-diamino-1,2,4-triazole as proton acceptor.

S2. Structural commentary

The asymmetric unit consits of half whole repeating unit of the title compound (Fig. 1) and is composed of 1.5 Co^{II} ions (one anionic complex and one half cationic complex) and one water molecule. In the cationic complex, the Co^{II} atom (Co2) is located on an inversion centre and is coordinated by two triazolium cations and four water molecules, adopting an octahedral geometry where the N atoms of the two triazolium cations (N3 & N3A) occupy the axial positions (Co–N = 2.2016 (7) Å) and the O atoms of the four water molecules (O2W, O2WA, O3W & O3WA) occupy the equatorial positions (Co–O = 2.0590 (7) - 2.1080 (7) Å). Atoms with suffix A were generated by the symmetry operation *-x*, *-y*, *-z*. The two triazole ligands are parallel offset (with a distance of 1.377 Å between the exact parallel planes). The angle between the Co–N bond and the centroid of the triazole plane is 158.56°. The bond distances are comparable with those reported for similar complexes (Aghabozorg *et al.*, 2008; Prasad & Rajasekharan, 2007; Colak *et al.*, 2009). In the anionic complex, the Co^{II} ion (Co1) is six-coordinated by two N (Co–N = 2.0273 (9) - 2.0308 (9) Å) and four O (Co–O = 2.1471 (7) - 2.2223 (7) Å) atoms of the two pyridine-2,6-dicarboxylate anions, exhibiting a slightly distorted octahedral coordination geometry where the mean plane of the two pyridine-2,6-dicarboxylate anions (maximum deviation = 0.0851 (9) Å at C7) are almost perpendicular to each other with a dihedral angle of 85.87 (2)°.

S3. Supramolecular features

In the crystal packing (Fig. 2), the molecules are linked into a three dimensional network *via* intermolecular C—H···O, C—H···N, O—H···O and N—H···O hydrogen bonds (Table 1).

S4. Synthesis and crystallization

An aqueous solution (10 ml) containing 0.5mmol (0.0496 g) of 3,5-diamino-1,2,4-triazole was added to a hot and stirring aqueous solution (20 ml) containing 1mmol (0.167 g) of pyridine-2,6-dicarboxylic acid and 1mmol (0.238 g) of $CoCl_2.6H_2O$. The resulting pink solution was stirred for 30 min and allowed to stand at room temperature. Crystals formed after 3 days but single crystals suitable for X-ray analysis were separated after one month.

S5. Refinement details

N- and O- bound H atoms were located from the difference Fourier map and were refined freely [N—H = 0.79 (2) to 0.92 (2) Å; O—H = 0.79 (2) to 0.86 (2) Å]. The remaining H atoms were calculated geometrically and were refined using a riding model with U_{iso} = 1.2 U_{eq}(C), with the bond lengths of C–H being 0.95 Å.

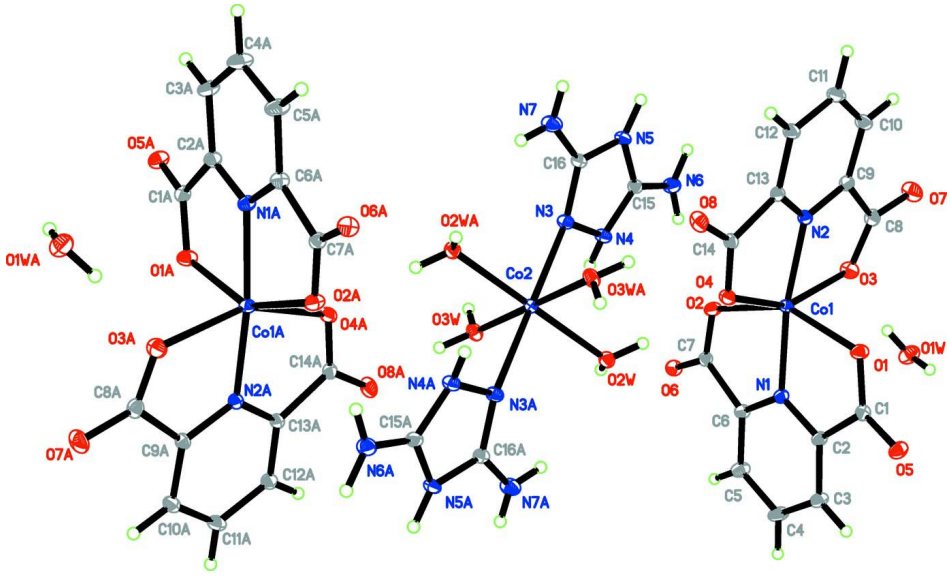

Figure 1

The molecular structure of the title compound with atom labels and 50% probability displacement ellipsoids. Atoms with suffix A were generated by the symmetry operation *-x*, *-y*, *-z*.

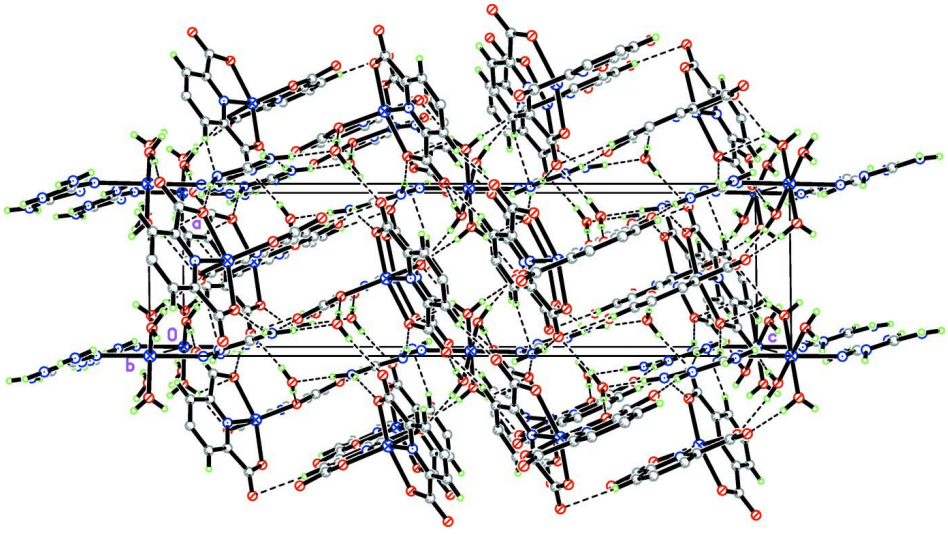

Figure 2

Crystal packing of the title compound, showing the three-dimensional network. H atoms not involved in the intermolecular interactions (dashed lines) have been omitted for clarity.

Tetraaquabis(3,5-diamino-4*H*-1,2,4-triazol-1-ium)cobalt(II) bis[bis(pyridine-2,6-dicarboxylato)cobaltate(II)] dihydrate

Crystal data

$[Co(C_2H_6N_5)_2(H_2O)_4][Co(C_7H_3NO_4)_2]_2{\cdot}2H_2O$
M_r = 1145.54
Monoclinic, $P2_1/c$
a = 7.1499 (2) Å
b = 10.8807 (2) Å
c = 26.6877 (6) Å
β = 90.649 (1)°
V = 2076.06 (8) Å^3
Z = 2
$F(000)$ = 1166
D_x = 1.833 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9904 reflections
θ = 2.4–35.0°
μ = 1.29 mm^{-1}
T = 100 K
Block, purple
0.43 × 0.28 × 0.28 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.607, T_{max} = 0.718
35534 measured reflections
9081 independent reflections
8203 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 35.1°, θ_{min} = 1.5°
h = −9→11
k = −17→17
l = −42→41

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.068
S = 1.05
9081 reflections
370 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 1.0292P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.55162 (2)	0.25891 (2)	0.13399 (2)	0.00894 (3)
Co2	0.0000	0.0000	0.0000	0.00821 (4)
O1	0.82104 (10)	0.26153 (6)	0.09788 (3)	0.01282 (12)
O2	0.27767 (10)	0.33471 (6)	0.14695 (3)	0.01253 (12)
O3	0.65732 (11)	0.31798 (7)	0.20566 (3)	0.01412 (12)
O4	0.46908 (10)	0.11281 (6)	0.07992 (2)	0.01164 (11)
O5	0.98594 (10)	0.35876 (7)	0.03895 (3)	0.01370 (12)
O6	0.11089 (10)	0.50933 (6)	0.13722 (3)	0.01255 (12)
O7	0.79218 (12)	0.24719 (7)	0.27668 (3)	0.01834 (14)
O8	0.44182 (11)	−0.09334 (7)	0.07506 (3)	0.01482 (13)
N1	0.54987 (11)	0.41617 (7)	0.09324 (3)	0.00998 (12)
N2	0.59941 (11)	0.09926 (7)	0.17147 (3)	0.00943 (12)
N3	−0.00429 (11)	−0.02963 (7)	0.08158 (3)	0.01012 (12)
N4	0.03927 (11)	0.07247 (7)	0.11156 (3)	0.01056 (12)
N5	0.08642 (11)	−0.08746 (7)	0.15824 (3)	0.01057 (12)
N6	0.13643 (13)	0.11292 (8)	0.19445 (3)	0.01373 (14)
N7	−0.00180 (14)	−0.24234 (8)	0.09908 (3)	0.01487 (15)
C1	0.85009 (12)	0.34939 (8)	0.06704 (3)	0.01023 (14)
C2	0.69856 (12)	0.44549 (8)	0.06584 (3)	0.01026 (14)
C3	0.70679 (14)	0.55422 (9)	0.03875 (4)	0.01333 (15)
H3A	0.8119	0.5733	0.0187	0.016*
C4	0.55548 (15)	0.63436 (9)	0.04196 (4)	0.01642 (17)
H4A	0.5576	0.7105	0.0246	0.020*
C5	0.40079 (14)	0.60293 (9)	0.07070 (4)	0.01499 (16)
H5A	0.2967	0.6568	0.0730	0.018*
C6	0.40236 (13)	0.49099 (8)	0.09586 (3)	0.01047 (14)
C7	0.24820 (12)	0.44216 (8)	0.12908 (3)	0.00996 (13)
C8	0.71223 (13)	0.23375 (9)	0.23540 (3)	0.01208 (15)
C9	0.67492 (13)	0.10389 (8)	0.21746 (3)	0.01040 (14)
C10	0.71742 (14)	−0.00249 (9)	0.24395 (3)	0.01303 (15)
H10A	0.7708	0.0016	0.2767	0.016*
C11	0.67989 (14)	−0.11541 (9)	0.22139 (4)	0.01395 (15)
H11A	0.7070	−0.1896	0.2388	0.017*
C12	0.60241 (13)	−0.11954 (8)	0.17318 (3)	0.01207 (15)
H12A	0.5762	−0.1957	0.1572	0.014*
C13	0.56501 (12)	−0.00872 (8)	0.14938 (3)	0.00955 (13)

C14	0.48503 (12)	0.00302 (8)	0.09707 (3)	0.00989 (14)
C15	0.09005 (12)	0.03737 (8)	0.15732 (3)	0.01009 (14)
C16	0.02562 (12)	−0.12445 (8)	0.11143 (3)	0.00985 (13)
O1W	0.81160 (12)	0.54803 (8)	0.20623 (3)	0.01822 (14)
O2W	0.16935 (10)	0.15580 (6)	0.01259 (3)	0.01110 (11)
O3W	−0.23235 (10)	0.11122 (7)	0.00395 (3)	0.01179 (11)
H1N4	−0.017 (2)	0.1420 (17)	0.1043 (6)	0.024 (4)*
H1N5	0.124 (3)	−0.1360 (19)	0.1831 (7)	0.037 (5)*
H1N6	0.147 (2)	0.1885 (17)	0.1873 (7)	0.026 (4)*
H2N6	0.151 (3)	0.0852 (17)	0.2268 (7)	0.030 (5)*
H1N7	−0.047 (3)	−0.2572 (17)	0.0707 (8)	0.030 (5)*
H2N7	0.024 (2)	−0.2988 (17)	0.1167 (6)	0.023 (4)*
H1W1	0.753 (3)	0.482 (2)	0.2054 (8)	0.043 (6)*
H2W1	0.899 (3)	0.5365 (19)	0.1887 (8)	0.038 (5)*
H1W2	0.113 (3)	0.2197 (18)	0.0235 (7)	0.030 (5)*
H2W2	0.261 (3)	0.1440 (18)	0.0306 (7)	0.032 (5)*
H1W3	−0.295 (3)	0.1150 (18)	0.0282 (7)	0.035 (5)*
H2W3	−0.308 (3)	0.1054 (18)	−0.0198 (7)	0.033 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01044 (5)	0.00761 (5)	0.00876 (5)	0.00044 (4)	0.00033 (4)	0.00075 (4)
Co2	0.00864 (7)	0.00831 (7)	0.00767 (7)	0.00067 (5)	−0.00032 (5)	0.00030 (5)
O1	0.0124 (3)	0.0111 (3)	0.0150 (3)	0.0025 (2)	0.0028 (2)	0.0036 (2)
O2	0.0126 (3)	0.0105 (3)	0.0145 (3)	0.0007 (2)	0.0027 (2)	0.0029 (2)
O3	0.0188 (3)	0.0109 (3)	0.0126 (3)	−0.0005 (2)	−0.0018 (2)	−0.0012 (2)
O4	0.0143 (3)	0.0100 (3)	0.0106 (3)	0.0002 (2)	−0.0021 (2)	0.0011 (2)
O5	0.0120 (3)	0.0122 (3)	0.0170 (3)	0.0011 (2)	0.0051 (2)	0.0012 (2)
O6	0.0118 (3)	0.0128 (3)	0.0132 (3)	0.0027 (2)	0.0025 (2)	0.0001 (2)
O7	0.0262 (4)	0.0160 (3)	0.0126 (3)	−0.0015 (3)	−0.0069 (3)	−0.0036 (2)
O8	0.0184 (3)	0.0113 (3)	0.0146 (3)	0.0006 (2)	−0.0057 (2)	−0.0035 (2)
N1	0.0101 (3)	0.0093 (3)	0.0105 (3)	0.0005 (2)	0.0017 (2)	0.0006 (2)
N2	0.0102 (3)	0.0097 (3)	0.0084 (3)	−0.0006 (2)	−0.0005 (2)	−0.0002 (2)
N3	0.0127 (3)	0.0083 (3)	0.0093 (3)	0.0014 (2)	−0.0004 (2)	0.0004 (2)
N4	0.0143 (3)	0.0086 (3)	0.0088 (3)	0.0013 (2)	−0.0007 (2)	0.0005 (2)
N5	0.0129 (3)	0.0102 (3)	0.0086 (3)	0.0006 (2)	−0.0010 (2)	0.0019 (2)
N6	0.0190 (4)	0.0125 (3)	0.0097 (3)	−0.0029 (3)	−0.0009 (3)	−0.0002 (2)
N7	0.0210 (4)	0.0088 (3)	0.0147 (3)	0.0004 (3)	−0.0025 (3)	0.0008 (3)
C1	0.0099 (3)	0.0093 (3)	0.0116 (3)	0.0001 (3)	0.0004 (3)	−0.0006 (3)
C2	0.0103 (3)	0.0090 (3)	0.0115 (3)	0.0007 (3)	0.0017 (3)	0.0006 (3)
C3	0.0135 (4)	0.0095 (3)	0.0170 (4)	0.0003 (3)	0.0046 (3)	0.0027 (3)
C4	0.0166 (4)	0.0112 (4)	0.0216 (4)	0.0031 (3)	0.0070 (3)	0.0059 (3)
C5	0.0146 (4)	0.0107 (4)	0.0198 (4)	0.0032 (3)	0.0058 (3)	0.0040 (3)
C6	0.0107 (3)	0.0097 (3)	0.0111 (3)	0.0014 (3)	0.0018 (3)	0.0006 (3)
C7	0.0104 (3)	0.0104 (3)	0.0091 (3)	−0.0003 (3)	0.0007 (3)	−0.0002 (3)
C8	0.0133 (4)	0.0122 (4)	0.0108 (3)	−0.0013 (3)	0.0000 (3)	−0.0027 (3)
C9	0.0116 (3)	0.0115 (3)	0.0081 (3)	−0.0011 (3)	−0.0007 (3)	−0.0006 (3)

C10	0.0155 (4)	0.0137 (4)	0.0099 (3)	−0.0011 (3)	−0.0022 (3)	0.0015 (3)
C11	0.0172 (4)	0.0117 (4)	0.0129 (4)	−0.0004 (3)	−0.0024 (3)	0.0037 (3)
C12	0.0143 (4)	0.0094 (3)	0.0125 (3)	−0.0012 (3)	−0.0022 (3)	0.0011 (3)
C13	0.0101 (3)	0.0094 (3)	0.0091 (3)	−0.0010 (3)	−0.0009 (3)	0.0000 (3)
C14	0.0097 (3)	0.0100 (3)	0.0100 (3)	0.0002 (3)	−0.0008 (3)	−0.0006 (3)
C15	0.0103 (3)	0.0110 (3)	0.0090 (3)	0.0005 (3)	0.0008 (3)	0.0012 (3)
C16	0.0101 (3)	0.0098 (3)	0.0097 (3)	0.0010 (3)	0.0006 (3)	0.0010 (3)
O1W	0.0221 (4)	0.0180 (3)	0.0146 (3)	−0.0055 (3)	0.0041 (3)	−0.0028 (3)
O2W	0.0109 (3)	0.0105 (3)	0.0118 (3)	0.0005 (2)	−0.0007 (2)	0.0000 (2)
O3W	0.0110 (3)	0.0155 (3)	0.0088 (3)	0.0026 (2)	−0.0005 (2)	−0.0011 (2)

Geometric parameters (Å, º)

Co1—N1	2.0275 (8)	N6—C15	1.3269 (12)
Co1—N2	2.0315 (8)	N6—H1N6	0.848 (19)
Co1—O3	2.1471 (7)	N6—H2N6	0.921 (18)
Co1—O2	2.1567 (7)	N7—C16	1.3383 (12)
Co1—O1	2.1640 (7)	N7—H1N7	0.84 (2)
Co1—O4	2.2223 (7)	N7—H2N7	0.795 (18)
Co2—O3W	2.0590 (7)	C1—C2	1.5058 (13)
Co2—O3W^{i}	2.0590 (7)	C2—C3	1.3880 (13)
Co2—O2W^{i}	2.1080 (7)	C3—C4	1.3929 (14)
Co2—O2W	2.1080 (7)	C3—H3A	0.9500
Co2—N3^{i}	2.2015 (7)	C4—C5	1.3957 (13)
Co2—N3	2.2016 (7)	C4—H4A	0.9500
O1—C1	1.2800 (11)	C5—C6	1.3908 (13)
O2—C7	1.2792 (11)	C5—H5A	0.9500
O3—C8	1.2715 (12)	C6—C7	1.5183 (12)
O4—C14	1.2840 (11)	C8—C9	1.5146 (13)
O5—C1	1.2378 (11)	C9—C10	1.3881 (13)
O6—C7	1.2451 (11)	C10—C11	1.3928 (14)
O7—C8	1.2440 (11)	C10—H10A	0.9500
O8—C14	1.2392 (11)	C11—C12	1.3959 (13)
N1—C6	1.3347 (12)	C11—H11A	0.9500
N1—C2	1.3358 (11)	C12—C13	1.3873 (12)
N2—C13	1.3361 (11)	C12—H12A	0.9500
N2—C9	1.3363 (11)	C13—C14	1.5080 (12)
N3—C16	1.3194 (11)	O1W—H1W1	0.83 (2)
N3—N4	1.4020 (11)	O1W—H2W1	0.79 (2)
N4—C15	1.3261 (11)	O2W—H1W2	0.86 (2)
N4—H1N4	0.877 (18)	O2W—H2W2	0.817 (19)
N5—C15	1.3587 (12)	O3W—H1W3	0.79 (2)
N5—C16	1.3781 (12)	O3W—H2W3	0.830 (19)
N5—H1N5	0.89 (2)		
N1—Co1—N2	170.32 (3)	O5—C1—O1	125.80 (9)
N1—Co1—O3	103.02 (3)	O5—C1—C2	119.95 (8)
N2—Co1—O3	76.22 (3)	O1—C1—C2	114.23 (8)

N1—Co1—O2	76.30 (3)	N1—C2—C3	121.83 (8)
N2—Co1—O2	113.33 (3)	N1—C2—C1	113.54 (8)
O3—Co1—O2	93.09 (3)	C3—C2—C1	124.62 (8)
N1—Co1—O1	75.53 (3)	C2—C3—C4	117.64 (8)
N2—Co1—O1	94.87 (3)	C2—C3—H3A	121.2
O3—Co1—O1	94.97 (3)	C4—C3—H3A	121.2
O2—Co1—O1	151.77 (3)	C3—C4—C5	120.09 (9)
N1—Co1—O4	104.80 (3)	C3—C4—H4A	120.0
N2—Co1—O4	75.52 (3)	C5—C4—H4A	120.0
O3—Co1—O4	151.74 (3)	C6—C5—C4	118.54 (9)
O2—Co1—O4	98.20 (3)	C6—C5—H5A	120.7
O1—Co1—O4	87.21 (3)	C4—C5—H5A	120.7
O3W—Co2—O3W^{i}	180.0	N1—C6—C5	120.72 (8)
O3W—Co2—O2W^{i}	91.06 (3)	N1—C6—C7	113.36 (8)
O3W^{i}—Co2—O2W^{i}	88.94 (3)	C5—C6—C7	125.90 (8)
O3W—Co2—O2W	88.94 (3)	O6—C7—O2	126.75 (8)
O3W^{i}—Co2—O2W	91.06 (3)	O6—C7—C6	118.39 (8)
O2W^{i}—Co2—O2W	180.0	O2—C7—C6	114.83 (8)
O3W—Co2—N3^{i}	89.13 (3)	O7—C8—O3	127.12 (9)
O3W^{i}—Co2—N3^{i}	90.87 (3)	O7—C8—C9	117.84 (8)
O2W^{i}—Co2—N3^{i}	88.54 (3)	O3—C8—C9	115.04 (8)
O2W—Co2—N3^{i}	91.46 (3)	N2—C9—C10	121.34 (8)
O3W—Co2—N3	90.87 (3)	N2—C9—C8	113.16 (8)
O3W^{i}—Co2—N3	89.13 (3)	C10—C9—C8	125.47 (8)
O2W^{i}—Co2—N3	91.46 (3)	C9—C10—C11	118.39 (8)
O2W—Co2—N3	88.54 (3)	C9—C10—H10A	120.8
N3^{i}—Co2—N3	180.0	C11—C10—H10A	120.8
C1—O1—Co1	116.61 (6)	C10—C11—C12	119.95 (8)
C7—O2—Co1	115.83 (6)	C10—C11—H11A	120.0
C8—O3—Co1	116.32 (6)	C12—C11—H11A	120.0
C14—O4—Co1	114.34 (6)	C13—C12—C11	117.80 (8)
C6—N1—C2	121.15 (8)	C13—C12—H12A	121.1
C6—N1—Co1	119.12 (6)	C11—C12—H12A	121.1
C2—N1—Co1	119.68 (6)	N2—C13—C12	121.93 (8)
C13—N2—C9	120.58 (8)	N2—C13—C14	113.57 (7)
C13—N2—Co1	120.38 (6)	C12—C13—C14	124.50 (8)
C9—N2—Co1	118.95 (6)	O8—C14—O4	126.69 (8)
C16—N3—N4	103.98 (7)	O8—C14—C13	117.20 (8)
C16—N3—Co2	135.05 (6)	O4—C14—C13	116.11 (8)
N4—N3—Co2	116.28 (5)	N4—C15—N6	124.95 (9)
C15—N4—N3	110.73 (7)	N4—C15—N5	107.43 (8)
C15—N4—H1N4	124.9 (11)	N6—C15—N5	127.62 (8)
N3—N4—H1N4	117.3 (11)	N3—C16—N7	125.34 (8)
C15—N5—C16	106.34 (7)	N3—C16—N5	111.49 (8)
C15—N5—H1N5	127.1 (13)	N7—C16—N5	123.16 (8)
C16—N5—H1N5	126.4 (13)	H1W1—O1W—H2W1	104 (2)
C15—N6—H1N6	117.0 (12)	Co2—O2W—H1W2	115.8 (13)
C15—N6—H2N6	121.6 (12)	Co2—O2W—H2W2	115.0 (14)

H1N6—N6—H2N6	121.3 (17)	H1W2—O2W—H2W2	107.6 (18)
C16—N7—H1N7	117.6 (13)	Co2—O3W—H1W3	122.4 (14)
C16—N7—H2N7	124.3 (13)	Co2—O3W—H2W3	115.8 (13)
H1N7—N7—H2N7	118.2 (18)	H1W3—O3W—H2W3	104.9 (18)
C16—N3—N4—C15	−0.82 (10)	C13—N2—C9—C8	177.27 (8)
Co2—N3—N4—C15	−160.26 (6)	Co1—N2—C9—C8	0.78 (10)
Co1—O1—C1—O5	−171.62 (7)	O7—C8—C9—N2	−176.02 (9)
Co1—O1—C1—C2	7.05 (10)	O3—C8—C9—N2	3.74 (12)
C6—N1—C2—C3	−0.26 (14)	O7—C8—C9—C10	2.07 (14)
Co1—N1—C2—C3	−177.65 (7)	O3—C8—C9—C10	−178.16 (9)
C6—N1—C2—C1	−179.43 (8)	N2—C9—C10—C11	0.15 (14)
Co1—N1—C2—C1	3.18 (10)	C8—C9—C10—C11	−177.80 (9)
O5—C1—C2—N1	172.01 (8)	C9—C10—C11—C12	0.38 (14)
O1—C1—C2—N1	−6.75 (12)	C10—C11—C12—C13	−0.15 (14)
O5—C1—C2—C3	−7.13 (14)	C9—N2—C13—C12	1.16 (13)
O1—C1—C2—C3	174.11 (9)	Co1—N2—C13—C12	177.60 (7)
N1—C2—C3—C4	1.55 (15)	C9—N2—C13—C14	−178.31 (8)
C1—C2—C3—C4	−179.38 (9)	Co1—N2—C13—C14	−1.88 (10)
C2—C3—C4—C5	−1.50 (16)	C11—C12—C13—N2	−0.62 (14)
C3—C4—C5—C6	0.24 (16)	C11—C12—C13—C14	178.80 (9)
C2—N1—C6—C5	−1.10 (14)	Co1—O4—C14—O8	177.20 (8)
Co1—N1—C6—C5	176.31 (7)	Co1—O4—C14—C13	−2.90 (10)
C2—N1—C6—C7	−179.62 (8)	N2—C13—C14—O8	−176.90 (8)
Co1—N1—C6—C7	−2.21 (10)	C12—C13—C14—O8	3.64 (14)
C4—C5—C6—N1	1.09 (15)	N2—C13—C14—O4	3.20 (12)
C4—C5—C6—C7	179.41 (9)	C12—C13—C14—O4	−176.26 (9)
Co1—O2—C7—O6	−170.41 (8)	N3—N4—C15—N6	−178.78 (9)
Co1—O2—C7—C6	7.75 (10)	N3—N4—C15—N5	1.67 (10)
N1—C6—C7—O6	174.41 (8)	C16—N5—C15—N4	−1.82 (10)
C5—C6—C7—O6	−4.03 (14)	C16—N5—C15—N6	178.65 (9)
N1—C6—C7—O2	−3.91 (11)	N4—N3—C16—N7	178.47 (9)
C5—C6—C7—O2	177.65 (9)	Co2—N3—C16—N7	−27.99 (15)
Co1—O3—C8—O7	173.50 (9)	N4—N3—C16—N5	−0.36 (10)
Co1—O3—C8—C9	−6.24 (10)	Co2—N3—C16—N5	153.18 (7)
C13—N2—C9—C10	−0.92 (13)	C15—N5—C16—N3	1.37 (10)
Co1—N2—C9—C10	−177.40 (7)	C15—N5—C16—N7	−177.50 (9)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H1*N*4···O1^{ii}	0.88 (2)	1.74 (2)	2.6044 (12)	165 (2)
N5—H1*N*5···O7^{iii}	0.89 (2)	1.77 (2)	2.6402 (12)	169 (2)
N6—H1*N*6···O2	0.84 (2)	2.15 (2)	2.9117 (12)	151.1 (19)
N6—H2*N*6···O1*W*^{iii}	0.92 (2)	1.85 (2)	2.7645 (12)	173.6 (19)
N7—H2*N*7···O6^{iv}	0.80 (2)	2.24 (2)	2.9956 (13)	158.4 (18)

O1*W*—H1*W*1···O3	0.83 (2)	1.90 (2)	2.7354 (13)	171 (3)
O1*W*—H2*W*1···O6^{v}	0.79 (2)	2.09 (2)	2.8711 (12)	175 (2)
O2*W*—H1*W*2···O5^{ii}	0.86 (2)	1.80 (2)	2.6666 (11)	173 (2)
O2*W*—H2*W*2···O4	0.82 (2)	2.00 (2)	2.8206 (11)	175 (2)
O3*W*—H1*W*3···O4^{ii}	0.79 (2)	2.19 (2)	2.9602 (11)	163 (2)
O3*W*—H2*W*3···O8^{i}	0.83 (2)	1.76 (2)	2.5795 (11)	173 (2)
C3—H3*A*···O5^{vi}	0.95	2.25	3.1816 (13)	167
C5—H5*A*···N7^{vii}	0.95	2.50	3.4265 (15)	164
C10—H10*A*···O6^{iii}	0.95	2.44	3.3898 (13)	177

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