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Diaquabis(1*H*-imidazole-4-carboxylato- κ^2N^3,O)cobalt(II)

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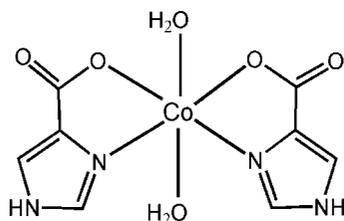
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.027; wR factor = 0.073; data-to-parameter ratio = 14.2.

In the title compound, $[Co(C_4H_3N_2O_2)_2(H_2O)_2]$, the Co^{II} ion is located on a twofold rotation axis and shows a distorted octahedral coordination configuration, defined by two N,O -bidentate 1*H*-imidazole-4-carboxylate ligands in the equatorial plane and two water molecules in the axial positions. In the crystal, $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds link the molecules into a three-dimensional supramolecular network. $\pi-\pi$ stacking interactions between the imidazole rings [centroid-centroid distances = 3.4914 (15) and 3.6167 (15) Å] further stabilize the crystal structure.

Related literature

For related structures, see: Cai *et al.* (2012); Gryz *et al.* (2007); Haggag (2005); Shuai *et al.* (2011); Starosta & Leciejewicz (2006); Yin *et al.* (2009); Zheng *et al.* (2011).



Experimental

Crystal data

$[Co(C_4H_3N_2O_2)_2(H_2O)_2]$ $a = 7.1216$ (18) Å
 $M_r = 317.13$ $b = 11.780$ (3) Å
Orthorhombic, *Pccn* $c = 13.536$ (3) Å

$V = 1135.6$ (5) Å³
 $Z = 4$
Mo $K\alpha$ radiation

$\mu = 1.54$ mm⁻¹
 $T = 298$ K
 $0.35 \times 0.33 \times 0.30$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
 $T_{min} = 0.614$, $T_{max} = 0.655$

6171 measured reflections
1238 independent reflections
1050 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.073$
 $S = 1.08$
1238 reflections

87 parameters
H-atom parameters constrained
 $\Delta\rho_{max} = 0.29$ e Å⁻³
 $\Delta\rho_{min} = -0.25$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1WA\cdots O2^i$	0.87	1.99	2.827 (2)	162
$O1W-H1WB\cdots O2^{ii}$	0.86	1.93	2.771 (2)	166
$N2-H2\cdots O2^{iii}$	0.86	1.92	2.771 (2)	173

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *S SAINT* (Bruker, 2007); data reduction: *S SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2579).

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supporting information

Acta Cryst. (2012). E68, m1246 [https://doi.org/10.1107/S1600536812037579]

Diaquabis(1*H*-imidazole-4-carboxylato- κ^2 N³,O)cobalt(II)**Wen-Sen Chen****S1. Comment**

There is currently much interest in adopting heterocyclic carboxylic acids as multidentate ligands to prepare new metal coordination polymers. The main reason is that they have versatile coordination behaviors and can form high-dimensional polymers via hydrogen-bonding interactions in the process of self-assembly. 1*H*-Imidazole-4-carboxylic acid (H₂imc), containing two N atoms of an imidazole group and one carboxylate group, is an excellent candidate for the construction of new coordination polymers. Up to this date, one-, two- and three-dimensional coordination polymers based on the H₂imc ligand have been documented (Cai *et al.*, 2012; Haggag, 2005; Gryz *et al.*, 2007; Shuai *et al.*, 2011; Starosta & Leciejewicz, 2006; Yin *et al.*, 2009; Zheng *et al.*, 2011). For example, the mononuclear complexes [Cd(Himc)₂(H₂O)₂] and [Zn(Himc)₂(H₂O)₂] have been reported by Yin *et al.* (2009) and Shuai *et al.* (2011), respectively. In this work, we report a Co(II) coordination polymer, [Co(Himc)₂(H₂O)₂], which is isomorphous with the Cd(II) and Zn(II) analogs.

The asymmetric unit of the title compound contains a half of Co^{II} ion, lying on a twofold rotation axis, one Himc anion and one coordinated water molecule. As illustrated in Fig. 1, the Co^{II} ion is six-coordinated by two N and two O atoms from two *cis*-oriented *N,O*-bidentate Himc ligands in the equatorial plane, and two water molecules in the axial positions, forming a slightly distorted octahedral geometry. The Co—N bond length is 2.0786 (16) Å and the Co—O distances are 2.1088 (15) and 2.1793 (14) Å, which are comparable to those of the Cd^{II} and Zn^{II} analogs. In the crystal structure, a pairs of intermolecular O—H...O hydrogen bonds (Table 1) involving the coordinated water (O1W) and the carboxylate O atom (O2) link the molecules into a two-dimensional network in the *ab* plane (Fig. 2). In addition, there exist strong π – π stacking interactions between the imidazole rings in the layer, with a centroid–centroid distance of 3.4914 (15) Å. These layers are further connected by N—H...O hydrogen bonds (Table 1) involving the imidazole N atom (N2) and the carboxylate O atom (O2), generating a three-dimensional supramolecular network. Another type of π – π stacking interactions with a centroid–centroid distance of 3.6167 (15) Å also can be observed between the neighbouring layers (Fig. 3).

S2. Experimental

A mixture of CoCl₂·6H₂O (0.20 mmol), H₂imc (0.20 mmol) and 6 ml EtOH/H₂O (v/v 1:1) was sealed into a 10 ml sample bottle reactor and heated at 373 K for 48 h under autogenous pressure, and then slowly cooled to room temperature at a rate of 2 K/h. Red block crystals of the title compound were isolated, washed with distilled water, and dried in air (yield: 45%).

S3. Refinement

C- and N-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 and N—H = 0.86 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. H atoms of the water molecule were located from a difference Fourier map and refined as riding, with O—H bond lengths restrained to 0.86 Å.

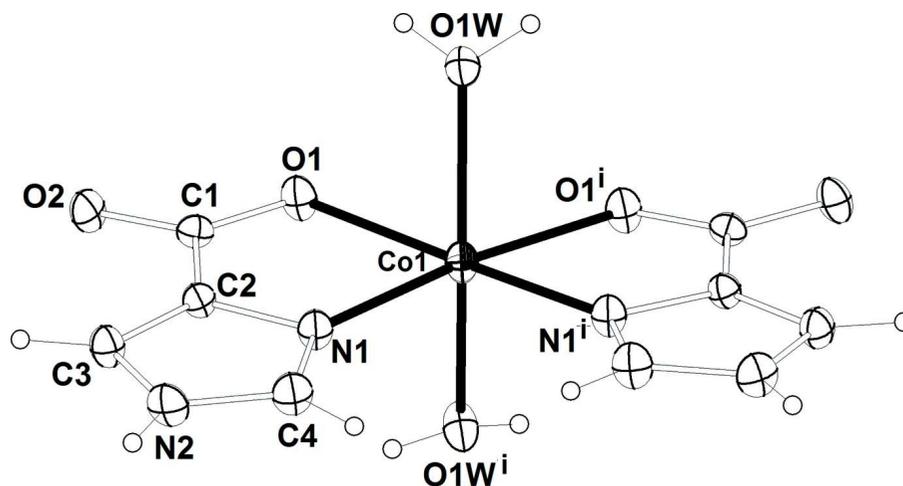


Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

[Symmetry code: (i) $-x+3/2, -y+1/2, z$.]

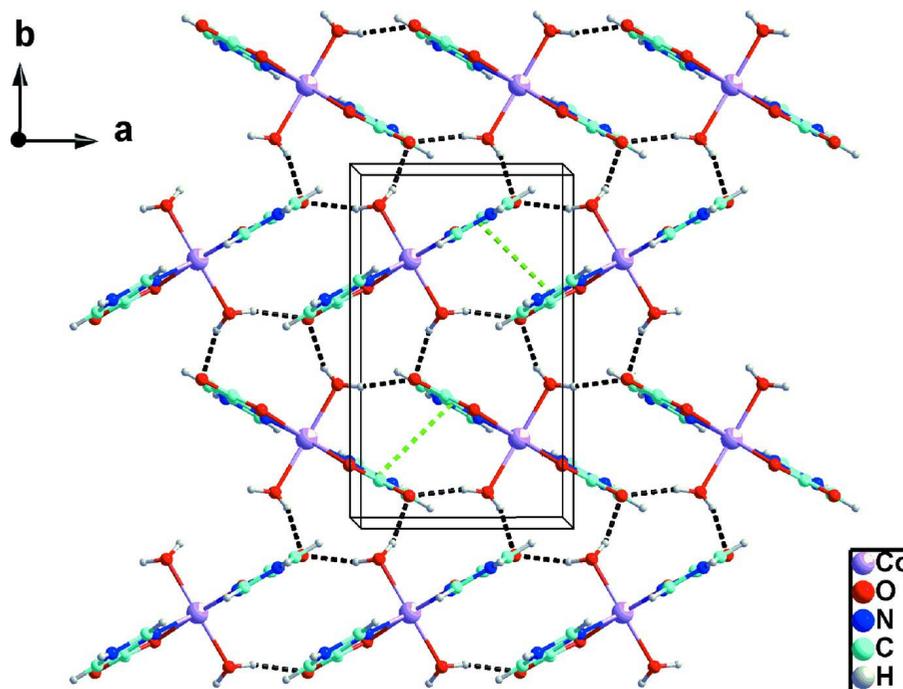


Figure 2

The crystal packing of the title compound, showing the two-dimensional network. Hydrogen bonds and π - π stacking interactions are shown as dashed lines.

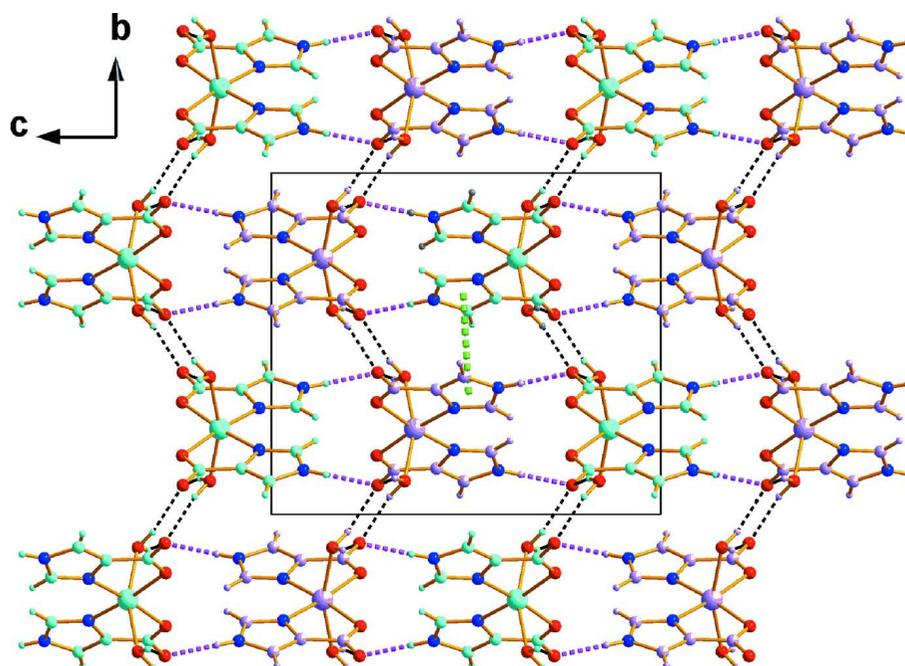


Figure 3

The crystal packing of the title compound, showing the three-dimensional supramolecular network. Hydrogen bonds and π - π stacking interactions are shown as dashed lines.

Diaquabis(1*H*-imidazole-4-carboxylato- κ^2N^3,O)cobalt(II)

Crystal data

$[\text{Co}(\text{C}_4\text{H}_3\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2]$

$M_r = 317.13$

Orthorhombic, *Pccn*

Hall symbol: -P 2ab 2ac

$a = 7.1216$ (18) Å

$b = 11.780$ (3) Å

$c = 13.536$ (3) Å

$V = 1135.6$ (5) Å³

$Z = 4$

$F(000) = 644$

$D_x = 1.855$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2075 reflections

$\theta = 3.0$ – 27.3°

$\mu = 1.54$ mm⁻¹

$T = 298$ K

Block, red

$0.35 \times 0.33 \times 0.30$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2001)

$T_{\min} = 0.614$, $T_{\max} = 0.655$

6171 measured reflections

1238 independent reflections

1050 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -9 \rightarrow 9$

$k = -12 \rightarrow 15$

$l = -17 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.073$

$S = 1.08$

1238 reflections

87 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 0.7299P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.7500	0.2500	0.13193 (2)	0.02397 (14)
O1	0.95746 (19)	0.17187 (13)	0.22880 (10)	0.0305 (3)
O1W	0.8973 (2)	0.40251 (13)	0.15738 (11)	0.0351 (4)
O2	1.23719 (18)	0.08486 (12)	0.22678 (10)	0.0302 (3)
N1	0.9449 (2)	0.18857 (14)	0.03090 (11)	0.0270 (4)
C3	1.2150 (3)	0.09661 (18)	0.00537 (15)	0.0304 (4)
H3	1.3262	0.0569	0.0155	0.036*
C1	1.0961 (3)	0.12982 (16)	0.18488 (14)	0.0243 (4)
C2	1.0934 (3)	0.13421 (16)	0.07551 (14)	0.0235 (4)
C4	0.9791 (3)	0.18410 (18)	-0.06466 (14)	0.0314 (5)
H4	0.9018	0.2150	-0.1131	0.038*
N2	1.1403 (2)	0.12911 (15)	-0.08276 (12)	0.0327 (4)
H2	1.1882	0.1166	-0.1401	0.039*
H1WA	0.8364	0.4481	0.1962	0.039*
H1WB	1.0072	0.3950	0.1833	0.039*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0206 (2)	0.0304 (2)	0.0209 (2)	0.00483 (15)	0.000	0.000
O1	0.0258 (8)	0.0427 (8)	0.0230 (7)	0.0060 (6)	0.0011 (6)	-0.0005 (6)
O1W	0.0241 (8)	0.0367 (8)	0.0445 (9)	0.0039 (6)	-0.0032 (6)	-0.0095 (7)
O2	0.0225 (7)	0.0413 (8)	0.0267 (7)	0.0027 (6)	-0.0034 (6)	0.0047 (6)
N1	0.0252 (9)	0.0331 (9)	0.0226 (8)	0.0046 (7)	0.0017 (6)	0.0016 (7)
C3	0.0258 (10)	0.0356 (11)	0.0297 (10)	0.0038 (8)	0.0005 (8)	-0.0026 (9)

C1	0.0233 (10)	0.0246 (9)	0.0251 (9)	-0.0032 (7)	-0.0019 (8)	0.0010 (8)
C2	0.0218 (10)	0.0251 (9)	0.0237 (9)	0.0005 (7)	-0.0002 (7)	0.0007 (7)
C4	0.0303 (11)	0.0408 (12)	0.0230 (10)	0.0041 (9)	0.0004 (8)	0.0031 (9)
N2	0.0327 (10)	0.0424 (10)	0.0231 (8)	0.0023 (8)	0.0073 (7)	-0.0015 (7)

Geometric parameters (Å, °)

Co1—N1	2.0786 (16)	N1—C2	1.376 (2)
Co1—O1W	2.1088 (15)	C3—C2	1.359 (3)
Co1—O1	2.1793 (14)	C3—N2	1.361 (3)
O1—C1	1.254 (2)	C3—H3	0.9300
O1W—H1WA	0.87	C1—C2	1.482 (3)
O1W—H1WB	0.86	C4—N2	1.341 (3)
O2—C1	1.269 (2)	C4—H4	0.9300
N1—C4	1.317 (2)	N2—H2	0.8600
N1 ⁱ —Co1—N1	97.72 (9)	C4—N1—C2	105.69 (16)
N1 ⁱ —Co1—O1W	98.23 (6)	C4—N1—Co1	141.57 (14)
N1—Co1—O1W	94.12 (6)	C2—N1—Co1	112.73 (12)
N1 ⁱ —Co1—O1W ⁱ	94.12 (6)	C2—C3—N2	105.76 (18)
N1—Co1—O1W ⁱ	98.23 (6)	C2—C3—H3	127.1
O1W—Co1—O1W ⁱ	161.19 (9)	N2—C3—H3	127.1
N1 ⁱ —Co1—O1	174.63 (6)	O1—C1—O2	125.17 (18)
N1—Co1—O1	78.23 (6)	O1—C1—C2	116.70 (16)
O1W—Co1—O1	85.65 (6)	O2—C1—C2	118.13 (17)
O1W ⁱ —Co1—O1	83.06 (6)	C3—C2—N1	109.55 (17)
N1 ⁱ —Co1—O1 ⁱ	78.23 (6)	C3—C2—C1	132.70 (18)
N1—Co1—O1 ⁱ	174.63 (6)	N1—C2—C1	117.72 (16)
O1W—Co1—O1 ⁱ	83.06 (6)	N1—C4—N2	110.91 (18)
O1W ⁱ —Co1—O1 ⁱ	85.65 (6)	N1—C4—H4	124.5
O1—Co1—O1 ⁱ	106.02 (7)	N2—C4—H4	124.5
C1—O1—Co1	114.54 (12)	C4—N2—C3	108.07 (17)
Co1—O1W—H1WA	112.2	C4—N2—H2	126.0
Co1—O1W—H1WB	115.5	C3—N2—H2	126.0
H1WA—O1W—H1WB	105.7		
N1—Co1—O1—C1	1.74 (14)	N2—C3—C2—N1	0.4 (2)
O1W—Co1—O1—C1	-93.39 (14)	N2—C3—C2—C1	-177.63 (19)
O1W ⁱ —Co1—O1—C1	101.68 (14)	C4—N1—C2—C3	-0.5 (2)
O1 ⁱ —Co1—O1—C1	-174.89 (15)	Co1—N1—C2—C3	-179.88 (13)
N1 ⁱ —Co1—N1—C4	4.6 (2)	C4—N1—C2—C1	177.83 (17)
O1W—Co1—N1—C4	-94.3 (2)	Co1—N1—C2—C1	-1.5 (2)
O1W ⁱ —Co1—N1—C4	99.9 (2)	O1—C1—C2—C3	-179.0 (2)
O1—Co1—N1—C4	-179.0 (2)	O2—C1—C2—C3	1.4 (3)
N1 ⁱ —Co1—N1—C2	-176.42 (16)	O1—C1—C2—N1	3.1 (2)
O1W—Co1—N1—C2	84.68 (14)	O2—C1—C2—N1	-176.53 (17)
O1W ⁱ —Co1—N1—C2	-81.10 (14)	C2—N1—C4—N2	0.5 (2)
O1—Co1—N1—C2	0.00 (13)	Co1—N1—C4—N2	179.49 (16)

Co1—O1—C1—O2	176.63 (15)	N1—C4—N2—C3	-0.2 (2)
Co1—O1—C1—C2	-3.0 (2)	C2—C3—N2—C4	-0.1 (2)

Symmetry code: (i) $-x+3/2, -y+1/2, z$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1 <i>W</i> —H1 <i>WA</i> ...O2 ⁱⁱ	0.87	1.99	2.827 (2)	162
O1 <i>W</i> —H1 <i>WB</i> ...O2 ⁱⁱⁱ	0.86	1.93	2.771 (2)	166
N2—H2...O2 ^{iv}	0.86	1.92	2.771 (2)	173

Symmetry codes: (ii) $-x+2, y+1/2, -z+1/2$; (iii) $-x+5/2, -y+1/2, z$; (iv) $-x+5/2, y, z-1/2$.