

Diaquabis[5-(2-pyridyl)-1*H*-tetrazolato- κ^2N^1,N^5]cobalt(II)

Zhen-Hai Sun, Ling-Bo Meng* and Hua Lin

School of Chemistry and Life Sciences, Harbin University, Harbin 150080, People's Republic of China

Correspondence e-mail: menglb_hu@sina.com

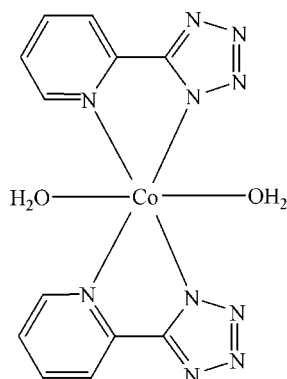
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.026; wR factor = 0.073; data-to-parameter ratio = 11.0.

In the title compound, $[Co(C_6H_4N_5)_2(H_2O)_2]$, the Co atom is bonded to two water molecules and two bidentate 5-(2-pyridyl)tetrazolate ligands resulting in a slightly distorted octahedral CoN_4O_2 coordination geometry. The Co^{II} cation is situated on a crystallographic center of inversion. The asymmetric unit therefore comprises one-half of the molecule. The four N atoms belonging to two bidentate 5-(2-pyridyl)tetrazolate ligands lie in the equatorial plane and the two associated water molecules are observed in the axial coordination sites. The crystal structure exhibits a three-dimensional supramolecular network assembled by intermolecular $O-H \cdots N$ hydrogen bonds.

Related literature

For general background, see: Caneschi *et al.* (1989); Tsukuda *et al.* (2002); Vostrikova *et al.* (2000); Kuchar *et al.* (2003)



Experimental

Crystal data

$[Co(C_6H_4N_5)_2(H_2O)_2]$
 $M_r = 387.25$
 Monoclinic, $P2_1/c$
 $a = 7.999$ (2) Å
 $b = 12.870$ (3) Å
 $c = 7.168$ (2) Å
 $\beta = 95.99$ (1)°

$V = 733.8$ (3) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.20$ mm⁻¹
 $T = 296$ K
 $0.12 \times 0.10 \times 0.08$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{min} = 0.869$, $T_{max} = 0.910$

3854 measured reflections
 1346 independent reflections
 1270 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.012$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.073$
 $S = 1.00$
 1346 reflections
 122 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.29$ e Å⁻³
 $\Delta\rho_{min} = -0.39$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1W-H2W \cdots N2^i$	0.82 (1)	2.00 (1)	2.798 (2)	168 (4)
$O1W-H1W \cdots N1^{ii}$	0.82 (1)	1.92 (1)	2.736 (2)	179 (3)

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; 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: IM2097).

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supplementary materials

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Diaquabis[5-(2-pyridyl)-1*H*-tetrazolato- κ^2 N¹,N⁵]cobalt(II)

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Comment

The design of different kinds of paramagnetic metal coordination architectures with appropriate organic radicals and coligands has been an important subject during the last decade because of its potential usages for molecule-based magnetic materials and optical devices (Caneschi *et al.*, 1989; Tsukuda *et al.*, 2002; Vostrikova *et al.*, 2000; Kuchar *et al.*, 2003). If organic radicals such as the tridentate nitronyl nitroxide radical or the bidentate nitroxide radical are used as an integral part of a ligand system a large number of building blocks with various potential applications may be achieved. In this paper, we report the structure of the title compound, (I).

The molecular structure of the title compound is shown in Fig. 1. The Co^{II} atom (site symmetry $\bar{1}$) is bonded to two water molecules and two bidentate 5-(2-pyridyl)tetrazolato ligands resulting in a slightly distorted octahedral CoN₄O₂ coordination geometry. The Co^{II} cation is situated on a crystallographic center of inversion. The asymmetric unit therefore comprises one half of the molecule. The four nitrogen atoms belonging to two bidentate 5-(2-pyridyl)tetrazolato ligands lie in the equatorial plane and the two associated water molecules are observed in the axial coordination sites. In the equatorial plane, the Co—N bond lengths are in the range of 2.142 (2)–2.173 (2) Å. The Co—O axial bond length is 2.093 (2) Å. It is also worth noticing that the three-dimensional supramolecular structure is assembled *via* complicated hydrogen bonds, shown in Fig. 2. The hydrogen bonds are listed in Table 1.

Experimental

A mixture of cobalt(II) dichloride hexhydrate (1 mmol), 5-(2-pyridyl)tetrazolate (1 mmol) in 20 ml mixed solvate(1:1) of methanol and water was refluxed for several hours. After cooling down the solution was filtered and the filtrate was kept in the ice box. One week later, red blocks of (I) were obtained with a yield of *ca* 56%. Anal. Calc. for C₁₂H₁₂CoN₁₀O₂: C 37.19, H 3.10, N 36.15%; Found: C 37.22, H 3.08, N 36.11%.

Refinement

All H atoms were placed in calculated positions with C—H = 0.93 Å and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the water molecule were located from difference density maps and were refined with distance restraints of $d(\text{H}—\text{H}) = 1.38$ (2) Å, $d(\text{O}—\text{H}) = 0.82$ (1) Å.

Figures

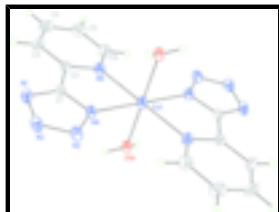


Fig. 1. The molecular structure of (I), around Co^{II}, displacement ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

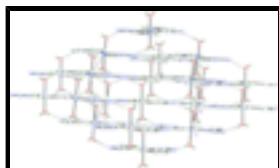


Fig. 2. Packing diagram of (I) showing the hydrogen bond interaction.

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Crystal data

[Co(C₆H₄N₅)₂(H₂O)₂]

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Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

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$b = 12.870$ (3) Å

$c = 7.168$ (2) Å

$\beta = 95.99$ (1)°

$V = 733.8$ (3) Å³

$Z = 2$

$F_{000} = 394$

$D_x = 1.752$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1346 reflections

$\theta = 2.6$ – 25.5 °

$\mu = 1.20$ mm⁻¹

$T = 296$ K

Block, red

$0.12 \times 0.10 \times 0.08$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2001)

$T_{\min} = 0.869$, $T_{\max} = 0.910$

3854 measured reflections

1346 independent reflections

1270 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.012$

$\theta_{\max} = 25.5$ °

$\theta_{\min} = 2.6$ °

$h = -9 \rightarrow 7$

$k = -15 \rightarrow 12$

$l = -8 \rightarrow 7$

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
$wR(F^2) = 0.073$	$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.7827P]$
$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
1346 reflections	$(\Delta/\sigma)_{\max} < 0.001$
122 parameters	$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
3 restraints	$\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.032 (2)

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	1.0000	0.0000	0.0000	0.02558 (17)
C1	0.9245 (2)	0.22105 (14)	0.0495 (2)	0.0238 (4)
C2	0.7797 (2)	0.17179 (15)	0.1175 (2)	0.0252 (4)
C3	0.6476 (3)	0.22658 (19)	0.1749 (3)	0.0362 (5)
H3	0.6448	0.2988	0.1690	0.043*
C4	0.5198 (3)	0.1717 (2)	0.2411 (3)	0.0459 (6)
H7	0.4276	0.2062	0.2805	0.055*
C5	0.5285 (3)	0.0653 (2)	0.2492 (4)	0.0473 (6)
H6	0.4434	0.0273	0.2963	0.057*
C6	0.6639 (3)	0.01547 (19)	0.1872 (3)	0.0377 (5)
H5	0.6690	-0.0567	0.1921	0.045*
N1	0.9563 (2)	0.32120 (13)	0.0376 (2)	0.0303 (4)
N2	1.1049 (2)	0.32543 (13)	-0.0308 (2)	0.0316 (4)
N3	1.1587 (2)	0.23204 (13)	-0.0591 (2)	0.0290 (4)
N4	1.0465 (2)	0.16372 (12)	-0.0086 (2)	0.0246 (4)
N5	0.7867 (2)	0.06737 (13)	0.1208 (2)	0.0270 (4)
O1W	1.13421 (19)	-0.00907 (10)	0.2663 (2)	0.0275 (3)
H1W	1.108 (5)	-0.0604 (13)	0.324 (4)	0.080*
H2W	1.141 (5)	0.0450 (12)	0.326 (4)	0.080*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0296 (2)	0.0178 (2)	0.0309 (2)	-0.00067 (13)	0.01065 (16)	-0.00120 (13)
C1	0.0315 (10)	0.0199 (9)	0.0195 (8)	0.0036 (7)	0.0005 (7)	-0.0013 (7)
C2	0.0291 (10)	0.0273 (10)	0.0190 (9)	0.0042 (8)	0.0011 (7)	-0.0026 (7)
C3	0.0361 (12)	0.0399 (12)	0.0325 (11)	0.0140 (9)	0.0033 (9)	-0.0038 (9)
C4	0.0289 (11)	0.0691 (18)	0.0408 (13)	0.0128 (11)	0.0090 (9)	-0.0086 (12)
C5	0.0300 (12)	0.0680 (18)	0.0465 (13)	-0.0078 (11)	0.0160 (10)	-0.0051 (12)
C6	0.0344 (12)	0.0375 (12)	0.0431 (13)	-0.0079 (9)	0.0125 (10)	-0.0014 (9)
N1	0.0448 (10)	0.0194 (8)	0.0263 (9)	0.0029 (7)	0.0020 (7)	0.0005 (7)
N2	0.0447 (10)	0.0207 (8)	0.0295 (9)	-0.0039 (7)	0.0038 (7)	0.0018 (7)
N3	0.0371 (9)	0.0218 (8)	0.0289 (8)	-0.0062 (7)	0.0070 (7)	0.0005 (7)
N4	0.0304 (8)	0.0177 (8)	0.0267 (8)	-0.0016 (7)	0.0081 (6)	-0.0003 (6)
N5	0.0271 (8)	0.0272 (9)	0.0278 (8)	0.0000 (7)	0.0084 (7)	-0.0021 (6)
O1W	0.0340 (8)	0.0203 (7)	0.0289 (7)	-0.0014 (6)	0.0073 (6)	-0.0008 (5)

Geometric parameters (\AA , $^\circ$)

Co1—O1W ⁱ	2.0932 (16)	C3—H3	0.9300
Co1—O1W	2.0932 (16)	C4—C5	1.372 (4)
Co1—N4 ⁱ	2.1416 (16)	C4—H7	0.9300
Co1—N4	2.1416 (16)	C5—C6	1.371 (3)
Co1—N5 ⁱ	2.1726 (16)	C5—H6	0.9300
Co1—N5	2.1726 (16)	C6—N5	1.317 (3)
C1—N1	1.318 (3)	C6—H5	0.9300
C1—N4	1.325 (3)	N1—N2	1.333 (3)
C1—C2	1.448 (3)	N2—N3	1.300 (3)
C2—N5	1.345 (3)	N3—N4	1.333 (2)
C2—C3	1.369 (3)	O1W—H1W	0.817 (10)
C3—C4	1.368 (4)	O1W—H2W	0.815 (10)
O1W ⁱ —Co1—O1W	180.00 (8)	C2—C3—H3	121.1
O1W ⁱ —Co1—N4 ⁱ	90.41 (6)	C3—C4—C5	119.6 (2)
O1W—Co1—N4 ⁱ	89.59 (6)	C3—C4—H7	120.2
O1W ⁱ —Co1—N4	89.59 (6)	C5—C4—H7	120.2
O1W—Co1—N4	90.41 (6)	C6—C5—C4	119.4 (2)
N4 ⁱ —Co1—N4	180.000 (15)	C6—C5—H6	120.3
O1W ⁱ —Co1—N5 ⁱ	90.47 (6)	C4—C5—H6	120.3
O1W—Co1—N5 ⁱ	89.53 (6)	N5—C6—C5	121.6 (2)
N4 ⁱ —Co1—N5 ⁱ	76.39 (6)	N5—C6—H5	119.2
N4—Co1—N5 ⁱ	103.61 (6)	C5—C6—H5	119.2
O1W ⁱ —Co1—N5	89.53 (6)	C1—N1—N2	104.43 (16)
O1W—Co1—N5	90.47 (6)	N3—N2—N1	110.03 (15)
N4 ⁱ —Co1—N5	103.61 (6)	N2—N3—N4	108.90 (16)
N4—Co1—N5	76.39 (6)	C1—N4—N3	104.89 (16)

N5 ⁱ —Co1—N5	180.00 (11)	C1—N4—Co1	113.77 (13)
N1—C1—N4	111.76 (18)	N3—N4—Co1	141.31 (13)
N1—C1—C2	128.05 (18)	C6—N5—C2	118.81 (18)
N4—C1—C2	120.19 (18)	C6—N5—Co1	126.01 (15)
N5—C2—C3	122.8 (2)	C2—N5—Co1	115.11 (13)
N5—C2—C1	114.22 (17)	Co1—O1W—H1W	112 (2)
C3—C2—C1	123.0 (2)	Co1—O1W—H2W	115 (2)
C4—C3—C2	117.8 (2)	H1W—O1W—H2W	115.5 (19)
C4—C3—H3	121.1		

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

Hydrogen-bond geometry (Å, °)

<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>
O1W—H2W \cdots N2 ⁱⁱ	0.82 (1)	2.00 (1)	2.798 (2)	168 (4)
O1W—H1W \cdots N1 ⁱⁱⁱ	0.82 (1)	1.92 (1)	2.736 (2)	179 (3)

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

Fig. 1

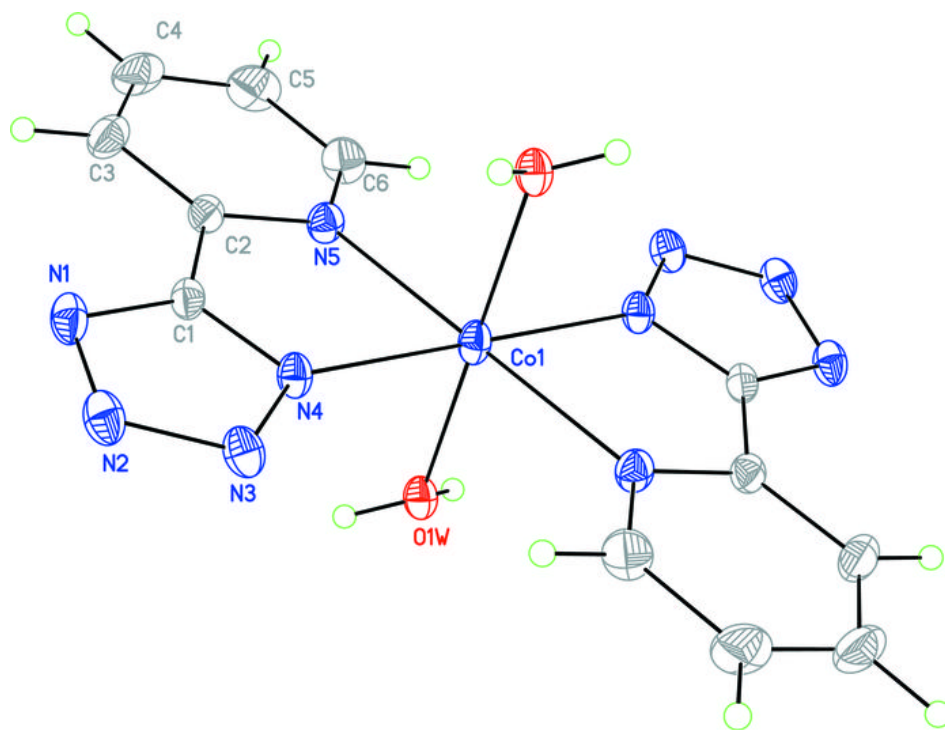


Fig. 2

