

Diaquabis(2-oxidopyridinium-3-carboxylato- κ^2O^2,O^3)cobalt(II)

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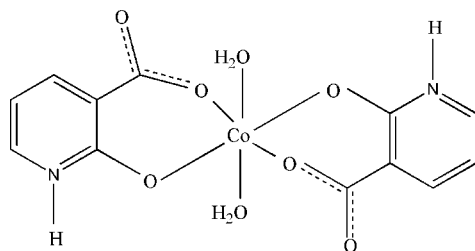
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.034; wR factor = 0.083; data-to-parameter ratio = 12.6.

In the title mononuclear complex, $[Co(C_6H_4NO_3)_2(H_2O)_2]$, the six-coordinate Co^{II} atom assumes an octahedral geometry and is located on an inversion centre. There is a weak $\pi-\pi$ stacking interaction between adjacent pyridyl rings [centroid-to-centroid distance = 3.8067 (17) Å and perpendicular distance = 3.533 Å]. O—H...O, N—H...O and C—H...O hydrogen bonds connect the mononuclear complexes and form a supramolecular three-dimensional structure.

Related literature

 For a relevant crystal structure, see: Sakai *et al.* (2006).


Experimental

Crystal data

 $[Co(C_6H_4NO_3)_2(H_2O)_2]$
 $M_r = 371.17$

 Monoclinic, $P2_1/c$
 $a = 7.4216$ (19) Å

 $b = 12.330$ (3) Å

 $c = 7.550$ (2) Å

 $\beta = 99.921$ (4)°

 $V = 680.6$ (3) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 1.31$ mm⁻¹
 $T = 298$ (2) K

 $0.26 \times 0.20 \times 0.05$ mm

Data collection

Bruker SMART APEX CCD

diffractometer

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\min} = 0.727$, $T_{\max} = 0.937$

3627 measured reflections

1331 independent reflections

 1151 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.083$
 $S = 1.02$

1331 reflections

106 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³
Table 1

Selected bond lengths (Å).

O1—Co1	2.0155 (17)	Co1—O4	2.1065 (19)
Co1—O3	2.1016 (17)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H5...O2 ⁱ	0.89	1.80	2.686 (2)	175
O4—H6...O2 ⁱⁱ	0.89	1.91	2.772 (2)	165
N1—H1...O3 ⁱⁱⁱ	0.86	2.06	2.886 (3)	162
C3—H2...O1 ^{iv}	0.93	2.56	3.100 (3)	118
C3—H2...O2 ^v	0.93	2.56	3.318 (3)	139

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

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2023).

References

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- Sheldrick, G. M. (1996). SADABS. Version 2.10. University of Göttingen, Germany.

supplementary materials

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Diaquabis(2-oxidopyridinium-3-carboxylato- κ^2O^2,O^3)cobalt(II)

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Comment

Metal complexes containing N-heterocyclic ligands play a pivotal role in the area of modern coordination chemistry, and it has been reported that complex containing 3-hydroxypicolinamide ligand displays strong fluorescent emission (Sakai *et al.*, 2006). The interest in this area led us to synthesize the title complex, and here we report its crystal structure, (I).

Fig. 1 shows the molecular structure of (I), the Co^{II} atom lies in an inversion centre and assumes a little distorted octahedral geometry (Table 1). There is a weak π - π stacking interaction between adjacent pyridyl rings of the neighboring complexes; the relevant distances are $Cg1 \cdots Cg1^i = 3.8067(17)$ Å and $Cg1 \cdots Cg1^i_{\text{perp}} = 3.533$ Å [symmetry codes: (i) $X, 3/2-Y, -1/2+Z$; Cg1 is the centroid of pyridyl ring; $Cg1 \cdots Cg1^i_{\text{perp}}$ is the perpendicular distance from ring Cg1 to ring $Cg1^i$]. Table 2 and Fig. 2 show the information of O—H \cdots O, N—H \cdots O and C—H \cdots O hydrogen bonds, and it is the hydrogen bonds that led to the connection of adjacent mononuclear complexes and to the formation of a super-molecular three-dimensional polymer.

Experimental

Diluted sodium hydroxide H₂O solution was added in drops into 30 ml H₂O solution containing Co(ClO₄)₂·6H₂O (0.1830 g, 0.500 mmol) and 2-hydroxyl-3-carboxypyridine (0.1390 g, 1.13 mmol) until the pH value reached 4, and the solution was stirred for another a few minutes. The red single crystals were obtained after the mixed solution had been allowed to stand at room temperature for one week.

Refinement

H atoms of water molecule were located in a difference Fourier map and included in the refinements as riding in their as-found positions, with O—H = 0.886–0.889 Å, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$; the rest of the H atoms were placed in calculated positions with C—H = 0.93 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$; N—H = 0.86 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

Figures

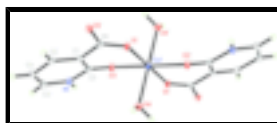


Fig. 1. The coordination structure of (I) showing the atom numbering scheme with thermal ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $-x, -y + 2, -z$].

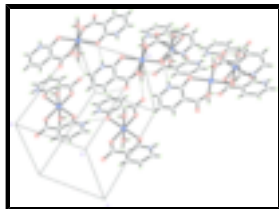


Fig. 2. Unit cell and hydrogen bonds (line of dashes).

Diaquabis(2-oxidopyridinium-3-carboxylate)cobalt(II)

Crystal data

[Co(C₆H₄NO₃)₂(H₂O)₂]

$M_r = 371.17$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.4216$ (19) Å

$b = 12.330$ (3) Å

$c = 7.550$ (2) Å

$\beta = 99.921$ (4)°

$V = 680.6$ (3) Å³

$Z = 2$

$F_{000} = 378$

$D_x = 1.811$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1158 reflections

$\theta = 2.8$ – 26.7 °

$\mu = 1.31$ mm⁻¹

$T = 298$ (2) K

Prism, red

$0.26 \times 0.20 \times 0.05$ mm

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ (2) K

φ and ω scans

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

$T_{\min} = 0.727$, $T_{\max} = 0.937$

3627 measured reflections

1331 independent reflections

1151 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\text{max}} = 26.0$ °

$\theta_{\text{min}} = 2.8$ °

$h = -8$ → 9

$k = -15$ → 8

$l = -9$ → 8

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.083$

$S = 1.02$

1331 reflections

106 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.5342P]$$

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

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

$\Delta\rho_{\text{max}} = 0.39$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.29$ e Å⁻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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	−0.0608 (2)	0.84059 (13)	−0.0153 (2)	0.0183 (4)
C6	0.0373 (3)	0.7569 (2)	0.0071 (3)	0.0153 (5)
Co1	0.0000	1.0000	0.0000	0.01392 (16)
O3	0.2707 (2)	0.95557 (14)	−0.0135 (2)	0.0185 (4)
N1	0.5220 (3)	0.86194 (17)	0.1087 (3)	0.0195 (5)
H1	0.5827	0.9211	0.1047	0.023*
O2	−0.0295 (2)	0.66277 (14)	−0.0126 (2)	0.0194 (4)
C1	0.2408 (3)	0.7664 (2)	0.0610 (3)	0.0158 (5)
C5	0.3400 (4)	0.6753 (2)	0.1223 (3)	0.0198 (6)
H4	0.2783	0.6098	0.1246	0.024*
O4	0.0769 (3)	0.99441 (13)	0.2817 (2)	0.0239 (4)
H6	0.0545	1.0547	0.3380	0.036*
H5	0.0372	0.9411	0.3444	0.036*
C2	0.3378 (3)	0.8659 (2)	0.0496 (3)	0.0157 (5)
C3	0.6169 (4)	0.7728 (2)	0.1729 (3)	0.0235 (6)
H2	0.7427	0.7769	0.2115	0.028*
C4	0.5282 (4)	0.6769 (2)	0.1809 (4)	0.0245 (6)
H3	0.5913	0.6145	0.2241	0.029*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0140 (9)	0.0112 (9)	0.0291 (10)	0.0005 (7)	0.0023 (7)	−0.0004 (7)
C6	0.0171 (13)	0.0169 (14)	0.0124 (11)	0.0000 (9)	0.0041 (10)	0.0001 (10)
Co1	0.0123 (3)	0.0098 (3)	0.0198 (3)	0.00027 (18)	0.00311 (18)	0.00043 (19)
O3	0.0146 (9)	0.0132 (9)	0.0285 (10)	0.0006 (7)	0.0055 (7)	0.0025 (8)
N1	0.0135 (11)	0.0200 (12)	0.0251 (12)	−0.0025 (8)	0.0031 (9)	0.0012 (9)
O2	0.0194 (10)	0.0111 (10)	0.0269 (10)	−0.0022 (7)	0.0020 (8)	−0.0005 (7)
C1	0.0171 (13)	0.0153 (13)	0.0152 (11)	−0.0011 (10)	0.0036 (10)	0.0005 (10)
C5	0.0203 (14)	0.0191 (14)	0.0209 (13)	−0.0001 (10)	0.0056 (11)	0.0030 (10)
O4	0.0371 (12)	0.0128 (9)	0.0223 (9)	−0.0003 (8)	0.0064 (8)	0.0011 (7)

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C2	0.0138 (13)	0.0191 (14)	0.0148 (12)	-0.0004 (10)	0.0041 (10)	-0.0015 (10)
C3	0.0152 (13)	0.0317 (16)	0.0230 (13)	0.0024 (11)	0.0013 (11)	0.0075 (12)
C4	0.0207 (15)	0.0230 (15)	0.0294 (14)	0.0081 (11)	0.0033 (11)	0.0101 (11)

Geometric parameters (Å, °)

O1—C6	1.257 (3)	N1—C2	1.364 (3)
O1—Co1	2.0155 (17)	N1—H1	0.8600
C6—O2	1.261 (3)	C1—C5	1.379 (3)
C6—C1	1.500 (3)	C1—C2	1.432 (3)
Co1—O1 ⁱ	2.0155 (17)	C5—C4	1.390 (4)
Co1—O3 ⁱ	2.1016 (17)	C5—H4	0.9300
Co1—O3	2.1016 (17)	O4—H6	0.8862
Co1—O4 ⁱ	2.1065 (19)	O4—H5	0.8893
Co1—O4	2.1065 (19)	C3—C4	1.359 (4)
O3—C2	1.271 (3)	C3—H2	0.9300
N1—C3	1.350 (3)	C4—H3	0.9300
C6—O1—Co1	132.40 (16)	C3—N1—H1	117.3
O1—C6—O2	122.2 (2)	C2—N1—H1	117.3
O1—C6—C1	120.3 (2)	C5—C1—C2	118.3 (2)
O2—C6—C1	117.5 (2)	C5—C1—C6	118.8 (2)
O1 ⁱ —Co1—O1	180.0	C2—C1—C6	122.9 (2)
O1 ⁱ —Co1—O3 ⁱ	87.10 (7)	C1—C5—C4	123.0 (2)
O1—Co1—O3 ⁱ	92.90 (7)	C1—C5—H4	118.5
O1 ⁱ —Co1—O3	92.90 (7)	C4—C5—H4	118.5
O1—Co1—O3	87.10 (7)	Co1—O4—H6	114.6
O3 ⁱ —Co1—O3	180.0	Co1—O4—H5	120.3
O1 ⁱ —Co1—O4 ⁱ	92.57 (7)	H6—O4—H5	105.0
O1—Co1—O4 ⁱ	87.43 (7)	O3—C2—N1	117.4 (2)
O3 ⁱ —Co1—O4 ⁱ	86.87 (7)	O3—C2—C1	126.8 (2)
O3—Co1—O4 ⁱ	93.13 (7)	N1—C2—C1	115.8 (2)
O1 ⁱ —Co1—O4	87.43 (7)	N1—C3—C4	119.8 (2)
O1—Co1—O4	92.57 (7)	N1—C3—H2	120.1
O3 ⁱ —Co1—O4	93.13 (7)	C4—C3—H2	120.1
O3—Co1—O4	86.87 (7)	C3—C4—C5	117.8 (2)
O4 ⁱ —Co1—O4	180.00 (9)	C3—C4—H3	121.1
C2—O3—Co1	121.63 (15)	C5—C4—H3	121.1
C3—N1—C2	125.3 (2)	O2—C6—C1—C2	165.8 (2)
Co1—O1—C6—O2	-178.61 (15)	C2—C1—C5—C4	3.0 (4)
Co1—O1—C6—C1	2.1 (3)	C6—C1—C5—C4	-177.8 (2)
C6—O1—Co1—O1 ⁱ	9(13)	Co1—O3—C2—N1	-151.59 (17)
C6—O1—Co1—O3 ⁱ	-164.1 (2)	Co1—O3—C2—C1	30.4 (3)
C6—O1—Co1—O3	15.9 (2)	C3—N1—C2—O3	-177.3 (2)
C6—O1—Co1—O4 ⁱ	109.2 (2)	C3—N1—C2—C1	1.0 (4)
C6—O1—Co1—O4	-70.8 (2)		

O1 ⁱ —Co1—O3—C2	149.27 (18)	C5—C1—C2—O3	175.4 (2)
O1—Co1—O3—C2	-30.73 (18)	C6—C1—C2—O3	-3.8 (4)
O3 ⁱ —Co1—O3—C2	-15 (93)	C5—C1—C2—N1	-2.6 (3)
O4 ⁱ —Co1—O3—C2	-117.99 (18)	C6—C1—C2—N1	178.2 (2)
O4—Co1—O3—C2	62.01 (18)	C2—N1—C3—C4	0.5 (4)
O1—C6—C1—C5	166.0 (2)	N1—C3—C4—C5	-0.3 (4)
O2—C6—C1—C5	-13.3 (3)	C1—C5—C4—C3	-1.4 (4)
O1—C6—C1—C2	-14.8 (3)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H5...O2 ⁱⁱ	0.89	1.80	2.686 (2)	175
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Symmetry codes: (ii) $x, -y+3/2, z+1/2$; (iii) $-x, y+1/2, -z+1/2$; (iv) $-x+1, -y+2, -z$; (v) $x+1, y, z$; (vi) $x+1, -y+3/2, z+1/2$.

Fig. 1

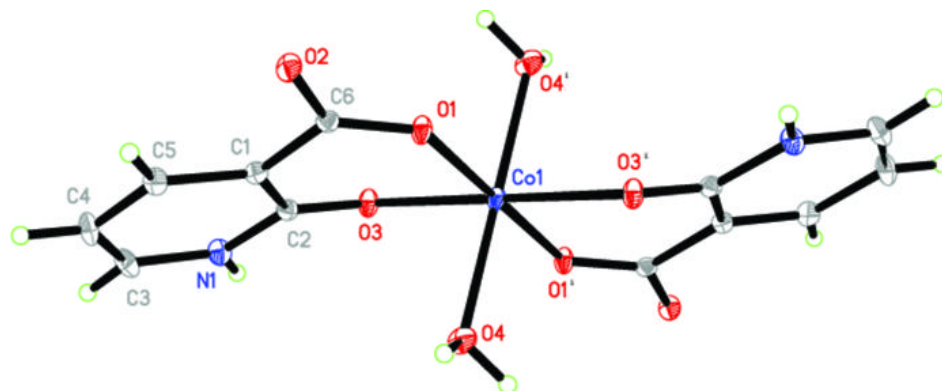


Fig. 2

