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Diaquabis(pyrimidine-2-carboxylic acid- κ^2N,O)cobalt(II) dichloride

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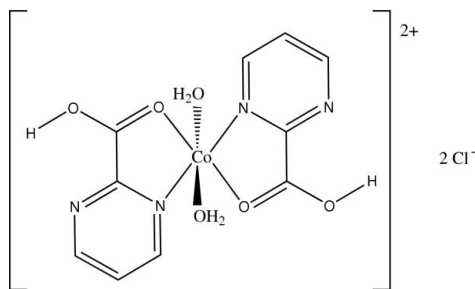
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.006$ Å; R factor = 0.040; wR factor = 0.119; data-to-parameter ratio = 16.5.

In the title salt, $[Co(C_5H_4N_2O_2)_2(H_2O)_2]Cl_2$, the Co^{II} ion is located on an inversion center. It is chelated by two neutral pyrimidine-2-carboxylic acid molecules and is coordinated by two water molecules in an octahedral coordination geometry. The cations and anions are linked *via* $O-H\cdots Cl$ hydrogen bonds into a layer structure; an intramolecular $O-H\cdots N$ hydrogen bond connects the carboxylic acid group to the pyrimidine N atom.

Related literature

For general background, see: Cheng *et al.* (2000); Wu *et al.* (2003). For related structures, see: Rodriguez-Dieguez *et al.* (2007); Zhang *et al.* (2008).



Experimental

Crystal data

 $[Co(C_5H_4N_2O_2)_2(H_2O)_2]Cl_2$
 $M_r = 414.07$

 Monoclinic, $P2_1/n$
 $a = 6.2803$ (8) Å

 $b = 10.361$ (2) Å

 $c = 11.906$ (2) Å

 $\beta = 95.254$ (15)°

 $V = 771.5$ (2) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 1.49$ mm⁻¹
 $T = 293$ (2) K

 $0.25 \times 0.12 \times 0.10$ mm

Data collection

Rigaku R-Axis RAPID IP

diffractometer

Absorption correction: multi-scan

(ABSCOR; Higashi, 1995)

 $T_{min} = 0.726$, $T_{max} = 0.862$

7413 measured reflections

1763 independent reflections

 1178 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.052$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.119$
 $S = 1.12$

1763 reflections

107 parameters

H-atom parameters constrained

 $\Delta\rho_{max} = 0.70$ e Å⁻³
 $\Delta\rho_{min} = -0.72$ e Å⁻³
Table 1

Selected geometric parameters (Å, °).

Co—O1	2.077 (3)	Co—N1	2.085 (3)
Co—O3	2.123 (3)		
O1—Co—N1	78.92 (11)	N1—Co—O3	87.84 (12)
O1—Co—O3	91.01 (12)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots N2	0.82	2.32	2.784 (5)	116
O3—H3A \cdots Cl1 ¹	0.95	2.20	3.140 (4)	168
O3—H3B \cdots Cl1	0.97	2.34	3.273 (3)	161

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2402).

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supporting information

Acta Cryst. (2008). E64, m77 [https://doi.org/10.1107/S1600536807063258]

Diaquabis(pyrimidine-2-carboxylic acid- κ^2N,O)cobalt(II) dichloride**Duan-Jun Xu, Bing-Yu Zhang, Qian Yang and Jing-Jing Nie****S1. Comment**

As part of our ongoing investigation on the nature of aromatic stacking (Cheng *et al.*, 2000; Wu *et al.*, 2003), the title Co^{II} compound has recently been prepared and its crystal structure is presented here.

The molecular structure of the title compound is shown in Fig. 1. The crystal of the title compound consists of complex cations and Cl⁻ anions. The Co^{II} located on an inversion center is coordinated by two neutral pyrimidine-2-carboxylic acid and two water molecules with an octahedral geometry (Table 1). The Cl⁻ anions link with the complex cations *via* O—H \cdots Cl hydrogen bonding (Table 2 and Fig. 1). The charge balance indicates that the pyrimidine-2-carboxylic acid is a neutral ligand but not an anion; and the significant difference in C—O bond distances (Table 1) also suggests that the carboxyl group is not deprotonated. This is obviously owing to the acidified solution environment in the preparation of the compound (see `_publ_section_exptl_prep`). The intra-molecular O—H \cdots N hydrogen bonding exists between the carboxyl group and adjacent pyrimidine-N atom (Fig. 1). Thus the pyrimidine-2-carboxylic acid can not play a role of bridge ligand in this structure, contrast to that found in pyrimidine-2-carboxylate complex of Co(II) reported previously (Rodríguez-Dieguez *et al.*, 2007).

π - π stacking is not observed in this crystal structure, which is different from the situation in a related Cu^{II} complex with pyrimidine-2-carboxylate (Zhang *et al.*, 2008). It may be due to extensive hydrogen bonding network involving coordinated water molecules and counter Cl⁻ anions.

S2. Experimental

2-Cyanopyrimidine (0.19 g, 1.8 mmol), CoCl₂·6(H₂O) (0.24 g, 1 mmol) were dissolved in a mixture solution of water (15 ml) and ethanol (5 ml), then hydrochloric acid solution (3 ml, 37%) was added into the solution. The solution was refluxed for 5 h. Single crystals of the title compound were obtained after about one month.

S3. Refinement

Hydroxy and water H atoms were located in a difference Fourier map and refined as riding in as-found relative positions, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Other H atoms were placed in calculated positions with C—H = 0.93 Å and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

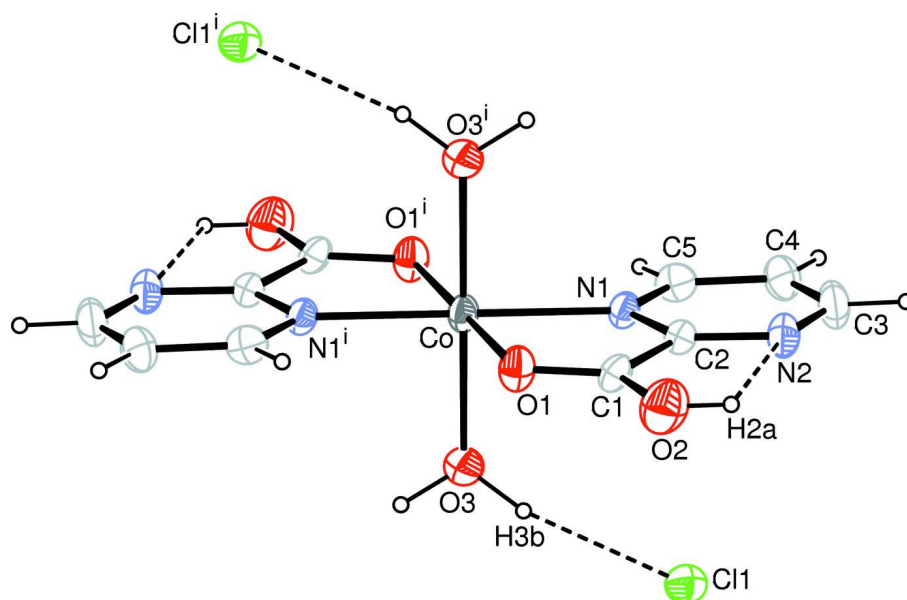


Figure 1

The molecular structure of the title compound with 30% probability displacement (arbitrary spheres for H atoms), dashed lines indicate hydrogen bonding [symmetry codes: (i) $1 - x, 1 - y, 1 - z$].

Diaquabis(pyrimidine-2-carboxylic acid- κ^2N,O)cobalt(II) dichloride

Crystal data

$[\text{Co}(\text{C}_5\text{H}_4\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_2$

$M_r = 414.07$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 6.2803$ (8) Å

$b = 10.361$ (2) Å

$c = 11.906$ (2) Å

$\beta = 95.254$ (15)°

$V = 771.5$ (2) Å³

$Z = 2$

$F(000) = 418$

$D_x = 1.782$ Mg m⁻³

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

Cell parameters from 2668 reflections

$\theta = 3.5$ – 24.5 °

$\mu = 1.49$ mm⁻¹

$T = 293$ K

Prism, pink

$0.25 \times 0.12 \times 0.10$ mm

Data collection

Rigaku R-AXIS RAPID IP

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 10.0 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.726$, $T_{\max} = 0.862$

7413 measured reflections

1763 independent reflections

1178 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 27.4$ °, $\theta_{\min} = 3.4$ °

$h = -8 \rightarrow 8$

$k = -12 \rightarrow 13$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.119$

$S = 1.12$

1763 reflections

107 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

$$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 1.9784P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.72 \text{ e } \text{\AA}^{-3}$

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.

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co	0.5000	0.5000	0.5000	0.0257 (2)
Cl1	0.83609 (17)	0.85016 (10)	0.65401 (9)	0.0367 (3)
N1	0.6455 (5)	0.6498 (3)	0.4186 (3)	0.0250 (7)
N2	0.5891 (6)	0.8696 (3)	0.3695 (3)	0.0340 (8)
O1	0.3012 (4)	0.6537 (3)	0.5310 (2)	0.0329 (7)
O2	0.2425 (6)	0.8657 (3)	0.4995 (3)	0.0541 (9)
H2	0.2993	0.9247	0.4674	0.081*
O3	0.7051 (5)	0.5443 (3)	0.6466 (3)	0.0397 (7)
H3A	0.7018	0.4951	0.7142	0.060*
H3B	0.7642	0.6288	0.6649	0.060*
C1	0.3501 (6)	0.7589 (3)	0.4885 (3)	0.0268 (8)
C2	0.5395 (6)	0.7618 (4)	0.4203 (3)	0.0258 (8)
C3	0.7628 (8)	0.8641 (5)	0.3124 (4)	0.0415 (11)
H3	0.8027	0.9374	0.2746	0.050*
C4	0.8852 (7)	0.7540 (4)	0.3075 (4)	0.0381 (10)
H4	1.0058	0.7524	0.2677	0.046*
C5	0.8217 (6)	0.6467 (4)	0.3637 (3)	0.0323 (9)
H5	0.9021	0.5713	0.3635	0.039*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co	0.0300 (4)	0.0184 (4)	0.0294 (4)	0.0009 (3)	0.0068 (3)	0.0022 (3)
Cl1	0.0399 (6)	0.0365 (6)	0.0339 (6)	-0.0014 (5)	0.0045 (4)	-0.0036 (4)
N1	0.0274 (16)	0.0192 (15)	0.0289 (17)	-0.0015 (14)	0.0056 (13)	-0.0003 (13)
N2	0.0376 (19)	0.0261 (18)	0.039 (2)	-0.0039 (16)	0.0045 (16)	0.0076 (15)
O1	0.0352 (15)	0.0248 (14)	0.0410 (17)	0.0033 (13)	0.0157 (13)	0.0007 (13)
O2	0.058 (2)	0.0387 (19)	0.067 (3)	0.0051 (18)	0.0102 (19)	-0.0011 (18)
O3	0.0529 (19)	0.0332 (16)	0.0317 (16)	-0.0045 (15)	-0.0028 (14)	0.0010 (13)
C1	0.030 (2)	0.0167 (17)	0.034 (2)	0.0004 (16)	0.0038 (17)	-0.0033 (16)
C2	0.031 (2)	0.0210 (18)	0.025 (2)	-0.0024 (17)	0.0017 (16)	0.0000 (15)

C3	0.047 (3)	0.037 (2)	0.041 (3)	-0.010 (2)	0.007 (2)	0.014 (2)
C4	0.037 (2)	0.042 (3)	0.037 (2)	-0.007 (2)	0.0124 (19)	0.005 (2)
C5	0.028 (2)	0.036 (2)	0.033 (2)	0.0004 (19)	0.0047 (17)	-0.0040 (18)

Geometric parameters (Å, °)

Co—O1	2.077 (3)	O2—C1	1.309 (5)
Co—O1 ⁱ	2.077 (3)	O2—H2	0.8200
Co—O3 ⁱ	2.123 (3)	O3—H3A	0.9545
Co—O3	2.123 (3)	O3—H3B	0.9674
Co—N1 ⁱ	2.085 (3)	C1—C2	1.501 (5)
Co—N1	2.085 (3)	C3—C4	1.379 (7)
N1—C5	1.337 (5)	C3—H3	0.9300
N1—C2	1.338 (5)	C4—C5	1.375 (6)
N2—C2	1.321 (5)	C4—H4	0.9300
N2—C3	1.338 (6)	C5—H5	0.9300
O1—C1	1.252 (5)		
O1—Co—O1 ⁱ	180.00 (16)	C1—O2—H2	109.5
O1—Co—N1 ⁱ	101.08 (11)	Co—O3—H3A	121.3
O1 ⁱ —Co—N1 ⁱ	78.92 (11)	Co—O3—H3B	124.9
O1—Co—N1	78.92 (11)	H3A—O3—H3B	109.3
O1 ⁱ —Co—N1	101.08 (11)	O1—C1—O2	123.2 (4)
N1 ⁱ —Co—N1	180.00 (11)	O1—C1—C2	118.2 (3)
O1—Co—O3 ⁱ	88.99 (12)	O2—C1—C2	118.6 (3)
O1 ⁱ —Co—O3 ⁱ	91.01 (12)	N2—C2—N1	126.0 (4)
N1 ⁱ —Co—O3 ⁱ	87.84 (12)	N2—C2—C1	119.7 (3)
N1—Co—O3 ⁱ	92.16 (12)	N1—C2—C1	114.3 (3)
O1—Co—O3	91.01 (12)	N2—C3—C4	122.7 (4)
O1 ⁱ —Co—O3	88.99 (12)	N2—C3—H3	118.6
N1 ⁱ —Co—O3	92.16 (12)	C4—C3—H3	118.6
N1—Co—O3	87.84 (12)	C5—C4—C3	117.4 (4)
O3 ⁱ —Co—O3	180.000 (1)	C5—C4—H4	121.3
C5—N1—C2	117.6 (3)	C3—C4—H4	121.3
C5—N1—Co	128.8 (3)	N1—C5—C4	120.5 (4)
C2—N1—Co	113.5 (2)	N1—C5—H5	119.7
C2—N2—C3	115.7 (4)	C4—C5—H5	119.7
C1—O1—Co	115.0 (2)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.*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>
O2—H2 \cdots N2	0.82	2.32	2.784 (5)	116
O3—H3A \cdots C11 ⁱⁱ	0.95	2.20	3.140 (4)	168

O3—H3B···C11	0.97	2.34	3.273 (3)	161
C4—H4···C11 ⁱⁱⁱ	0.93	2.79	3.670 (5)	159

Symmetry codes: (ii) $-x+3/2, y-1/2, -z+3/2$; (iii) $x+1/2, -y+3/2, z-1/2$.