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Diaquabis(4-oxidopyridinium-3-sulfonato-κ^2O,O')cobalt(II) hexahydrate

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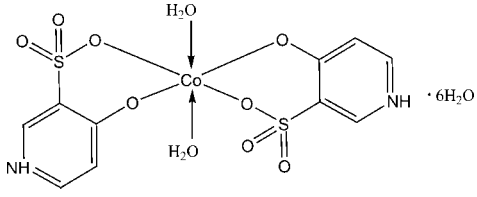
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; R factor = 0.030; wR factor = 0.115; data-to-parameter ratio = 14.6.

The Co^{II} atom in the title zwitterionic compound, $[Co(C_5H_4NO_4S)_2(H_2O)_2]\cdot 6H_2O$, is located on an inversion centre, and exists in an octahedral coordination geometry owing to chelation by the monoanion and coordination by water. A three-dimensional hydrogen-bonding framework is formed through O—H···O and N—H···O hydrogen-bonding interactions.

Related literature

There are no crystallographic reports to date of complexes of hydroxypyridinesulfonic acid. For metal complexes of the related pyridinesulfonic acid, see: Delgado *et al.* (2006); Cotton *et al.* (1992); Lu *et al.* (2007).



Experimental

Crystal data

$[Co(C_5H_4NO_4S)_2(H_2O)_2]\cdot 6H_2O$
M_r = 551.36
Triclinic, $P\overline{1}$
a = 7.7825 (16) Å
b = 8.4697 (17) Å
c = 8.7952 (18) Å
α = 90.97 (3)°
β = 110.17 (3)°
γ = 106.65 (3)°
V = 517.0 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.12 mm^{-1}
T = 295 (2) K
0.36 × 0.24 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.690, T_{max} = 0.825
5086 measured reflections
2344 independent reflections
2180 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.115
S = 1.19
2344 reflections
160 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1W	2.0551 (19)	Co1—O4	2.0833 (17)
Co1—O1	2.1349 (18)		
O1W^i—Co1—O1W	180	O4—Co1—O1^i	91.40 (7)
O1W—Co1—O4^i	91.22 (8)	O1W—Co1—O1	86.70 (8)
O4—Co1—O4^i	180	O4—Co1—O1	88.60 (7)
O1W—Co1—O4	88.78 (8)	O1^i—Co1—O1	180
O1W—Co1—O1^i	93.30 (8)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O2^{ii}	0.847 (10)	2.19 (3)	2.896 (3)	140 (3)
O1W—H1W1···O2^i	0.847 (10)	2.37 (2)	2.982 (3)	130 (3)
O1W—H1W2···O2W	0.840 (10)	1.905 (16)	2.714 (3)	161 (4)
O2W—H2W1···O4W^{iii}	0.86 (3)	1.96 (3)	2.809 (3)	168 (4)
O2W—H2W2···O4W^{ii}	0.85 (5)	2.04 (4)	2.880 (4)	170 (5)
O3W—H3W1···O3^{iv}	0.85	2.37	3.175 (3)	158
O3W—H3W2···O1^{iii}	0.85	2.18	2.978 (3)	157
O4W—H4W1···O3	0.84 (3)	2.046 (17)	2.827 (3)	154 (3)
O4W—H4W2···O4^v	0.85 (3)	1.96 (3)	2.805 (3)	174 (4)
N1—H1N···O3W	0.86	1.90	2.752 (3)	169

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); 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: NG2374).

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supplementary materials

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Diaquabis(4-oxidopyridinium-3-sulfonato-κ^2O,O')cobalt(II) hexahydrate

Z.-B. Zhu, S. Gao, L.-H. Huo and H. Zhao

Comment

Recently, pyridinesulfonates have been widely used to synthesize metal complexes, such as 2-pyridinesulfonate (Delgado *et al.*, 2006), 3-pyridinesulfonate (Cotton *et al.*, 1992), 4-pyridinesulfonate (Lu *et al.*, 2007) However, there is no report based on hydroxypyridonesulfonic acid which is derivated from pyridinesulfonate. Herein, we reported the synthesis and structure of a new complex, $[Co(4\text{-}HPSH)_2(H_2O)_2]\cdot 6H_2O$, obtained by the reaction of 4-hydroxypyridone-3-sulfonic acid ($4\text{-}HPSH_2$) and cobalt chloride hexahydrate in aqueous solution.

As illustrated in Fig. 1, the Co^{II} atom lies on an inversion center and displays an octahedral geometry defined by two sulfonyl O atoms and hydroxyl O atoms of different $4\text{-}HPSH^-$ ligands and two water molecules. The distances of $Co1—O_{sulfonato}$ bonds are slightly longer than that of $Co1—O_{hydroxyl}$ and $Co—O_{water}$. A three-dimensional supramolecular network structure is formed through the extended hydrogen-bonding interactions between water molecules and N,*O* atoms of $4\text{-}HPSH^-$ ligands (Table 2).

Experimental

The title complex was prepared by the addition of cobalt chloride hexahydrate (2.38 g, 10 mmol) to a hot aqueous solution of 4-hydroxypyridone-3-sulfonaic acid (1.75 g, 10 mmol); the pH was adjusted to 6 with 0.1 *M* sodium hydroxide. The solution was allowed to evaporate at room temperature. Pink prismatic crystals separated from the filtered solution after several days. CH&N analysis. Calc. for $C_{10}H_{24}N_2O_{16}S_2Co$: C 21.78, H 4.39, N 5.08%; Found: C 21.75, H 4.34, N 5.11%.

Refinement

Carbon-bond H atoms were placed in calculated positions, C—H = 0.93 and $U_{iso}(H) = 1.2U_{eq}(C)$, and were included in the refinement in the riding-model approximation. The H atoms of water molecules and nitrogen atoms of $4\text{-}HPSH_2$ were located in difference Fourier map and refined with the O—H and N—H distance restrained to 0.85 (1) and 0.86 (1) Å, and with $U_{iso}(H) = 1.5U_{eq}(O,N)$.

Figures

Fig. 1. Molecular structure of the title compound with 30% probability ellipsoid for the non-H atoms.

Diaqua(4-oxidopyridinium-3-sulfonato-κ^2*O*,*O*^{1})cobaltate(II) hexahydrate

Crystal data

$[Co(C_5H_4N_1O_4S)_2(H_2O)_2]\cdot 6H_2O$	$Z = 1$
$M_r = 551.36$	$F_{000} = 285$
Triclinic, $P\overline{1}$	$D_x = 1.771$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.7825$ (16) Å	Cell parameters from 4752 reflections
$b = 8.4697$ (17) Å	$\theta = 3.1$–27.5º
$c = 8.7952$ (18) Å	$\mu = 1.12$ mm^{-1}
$\alpha = 90.97$ (3)º	$T = 295$ (2) K
$\beta = 110.17$ (3)º	Prism, pink
$\gamma = 106.65$ (3)º	0.36 × 0.24 × 0.18 mm
$V = 517.0$ (2) Å^3	

Data collection

Rigaku R-AXIS RAPID diffractometer	2344 independent reflections
Radiation source: fine-focus sealed tube	2180 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.018$
Detector resolution: 10.000 pixels mm^{-1}	$\theta_{max} = 27.5$º
$T = 295$(2) K	$\theta_{min} = 3.1$º
ω scans	$h = -10\rightarrow 9$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$k = -10\rightarrow 10$
$T_{min} = 0.690$, $T_{max} = 0.825$	$l = -11\rightarrow 11$
5086 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.115$	$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.2777P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.19$	$(\Delta/\sigma)_{max} < 0.001$
2344 reflections	$\Delta\rho_{max} = 0.49$ e Å^{-3}
160 parameters	$\Delta\rho_{min} = -0.51$ e Å^{-3}
9 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.5000	0.0000	0.0000	0.02233 (15)
S1	0.92641 (8)	0.15049 (7)	0.25659 (7)	0.02739 (17)
O1W	0.3658 (3)	0.1085 (3)	0.1158 (2)	0.0408 (5)
H1W1	0.249 (2)	0.057 (4)	0.098 (4)	0.061*
H1W2	0.420 (4)	0.165 (4)	0.209 (2)	0.061*
O2W	0.5537 (4)	0.3487 (3)	0.3767 (3)	0.0561 (6)
H2W1	0.559 (7)	0.448 (3)	0.355 (5)	0.084*
H2W2	0.506 (7)	0.330 (5)	0.451 (4)	0.084*
O3W	1.2937 (3)	0.9351 (3)	0.4386 (3)	0.0503 (5)
H3W1	1.2279	1.0011	0.4081	0.076*
H3W2	1.3059	0.9221	0.5370	0.076*
O4W	1.4313 (3)	0.3181 (3)	0.6517 (3)	0.0473 (5)
H4W1	1.318 (3)	0.254 (4)	0.606 (4)	0.071*
H4W2	1.489 (5)	0.286 (5)	0.740 (3)	0.071*
O1	0.7299 (2)	0.0442 (2)	0.23120 (19)	0.0287 (4)
O2	1.0019 (3)	0.0900 (3)	0.1464 (3)	0.0456 (5)
O3	1.0490 (3)	0.1798 (3)	0.4275 (2)	0.0464 (5)
O4	0.6346 (2)	0.2346 (2)	−0.0464 (2)	0.0314 (4)
N1	1.0347 (3)	0.6376 (3)	0.2655 (3)	0.0407 (5)
H1N	1.1202	0.7233	0.3298	0.049*
C1	1.0364 (4)	0.4848 (3)	0.3030 (3)	0.0343 (5)
H1	1.1288	0.4733	0.3991	0.041*
C2	0.9046 (3)	0.3462 (3)	0.2023 (3)	0.0252 (4)
C3	0.7598 (3)	0.3593 (3)	0.0541 (3)	0.0257 (4)
C4	0.7656 (4)	0.5256 (3)	0.0240 (3)	0.0376 (6)
H4	0.6744	0.5434	−0.0695	0.045*
C5	0.9011 (4)	0.6580 (3)	0.1287 (4)	0.0419 (6)
H5	0.9017	0.7648	0.1055	0.050*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0205 (2)	0.0197 (2)	0.0217 (2)	0.00253 (15)	0.00473 (16)	0.00120 (15)
S1	0.0201 (3)	0.0250 (3)	0.0310 (3)	0.0059 (2)	0.0029 (2)	0.0034 (2)
O1W	0.0252 (9)	0.0478 (11)	0.0439 (10)	0.0069 (8)	0.0105 (8)	−0.0119 (9)
O2W	0.0698 (16)	0.0414 (12)	0.0494 (13)	0.0074 (11)	0.0211 (11)	−0.0064 (10)
O3W	0.0423 (11)	0.0433 (12)	0.0565 (13)	0.0059 (9)	0.0136 (9)	−0.0001 (9)
O4W	0.0455 (12)	0.0397 (11)	0.0385 (11)	0.0036 (9)	0.0011 (9)	0.0093 (8)
O1	0.0230 (8)	0.0310 (8)	0.0260 (8)	0.0041 (6)	0.0048 (6)	0.0068 (6)
O2	0.0384 (10)	0.0407 (10)	0.0684 (14)	0.0170 (8)	0.0286 (10)	0.0066 (10)
O3	0.0366 (10)	0.0378 (10)	0.0386 (10)	0.0030 (8)	−0.0109 (8)	0.0065 (8)
O4	0.0317 (9)	0.0227 (8)	0.0269 (8)	−0.0003 (6)	0.0021 (6)	0.0039 (6)
N1	0.0416 (12)	0.0235 (10)	0.0412 (12)	−0.0029 (9)	0.0073 (10)	−0.0059 (9)
C1	0.0303 (12)	0.0306 (12)	0.0313 (11)	0.0025 (9)	0.0041 (9)	−0.0014 (9)

C2	0.0231 (10)	0.0215 (10)	0.0269 (10)	0.0037 (8)	0.0069 (8)	0.0014 (8)
C3	0.0238 (10)	0.0241 (10)	0.0256 (10)	0.0035 (8)	0.0079 (8)	0.0034 (8)
C4	0.0399 (14)	0.0272 (12)	0.0374 (13)	0.0067 (10)	0.0067 (11)	0.0085 (10)
C5	0.0500 (16)	0.0227 (11)	0.0462 (15)	0.0054 (11)	0.0140 (12)	0.0041 (10)

Geometric parameters (Å, °)

Co1—O1W	2.0551 (19)	O3W—H3W2	0.8500
Co1—O1	2.1349 (18)	O4W—H4W1	0.84 (3)
Co1—O4	2.0833 (17)	O4W—H4W2	0.85 (3)
Co1—O1W^{i}	2.0551 (19)	O4—C3	1.277 (3)
Co1—O4^{i}	2.0833 (17)	N1—C1	1.343 (4)
Co1—O1^{i}	2.1349 (18)	N1—C5	1.344 (4)
S1—O3	1.447 (2)	N1—H1N	0.8600
S1—O2	1.448 (2)	C1—C2	1.365 (3)
S1—O1	1.4722 (17)	C1—H1	0.9300
S1—C2	1.771 (2)	C2—C3	1.430 (3)
O1W—H1W1	0.847 (10)	C3—C4	1.429 (3)
O1W—H1W2	0.840 (10)	C4—C5	1.354 (4)
O2W—H2W1	0.86 (3)	C4—H4	0.9300
O2W—H2W2	0.85 (5)	C5—H5	0.9300
O3W—H3W1	0.8500		
O1W^{i}—Co1—O1W	180.00 (9)	H2W1—O2W—H2W2	108 (5)
O1W—Co1—O4^{i}	91.22 (8)	H3W1—O3W—H3W2	107.8
O4—Co1—O4^{i}	180.00 (10)	H4W1—O4W—H4W2	111 (4)
O1W—Co1—O4	88.78 (8)	S1—O1—Co1	121.86 (10)
O1W—Co1—O1^{i}	93.30 (8)	C3—O4—Co1	129.23 (15)
O4—Co1—O1^{i}	91.40 (7)	C1—N1—C5	120.8 (2)
O1W—Co1—O1	86.70 (8)	C1—N1—H1N	119.6
O4—Co1—O1	88.60 (7)	C5—N1—H1N	119.6
O1^{i}—Co1—O1	180.00 (11)	N1—C1—C2	121.1 (2)
O1W^{i}—Co1—O4^{i}	88.78 (8)	N1—C1—H1	119.5
O1W^{i}—Co1—O4	91.22 (8)	C2—C1—H1	119.5
O1W^{i}—Co1—O1^{i}	86.70 (8)	C1—C2—C3	121.0 (2)
O4^{i}—Co1—O1^{i}	88.60 (7)	C1—C2—S1	117.73 (18)
O1W^{i}—Co1—O1	93.30 (8)	C3—C2—S1	121.24 (17)
O4^{i}—Co1—O1	91.40 (7)	O4—C3—C4	121.4 (2)
O3—S1—O2	115.28 (14)	O4—C3—C2	123.9 (2)
O3—S1—O1	111.26 (12)	C4—C3—C2	114.7 (2)
O2—S1—O1	111.36 (12)	C5—C4—C3	121.4 (2)
O3—S1—C2	105.95 (12)	C5—C4—H4	119.3
O2—S1—C2	106.48 (12)	C3—C4—H4	119.3
O1—S1—C2	105.79 (10)	N1—C5—C4	121.1 (2)
Co1—O1W—H1W1	117 (2)	N1—C5—H5	119.4
Co1—O1W—H1W2	125 (2)	C4—C5—H5	119.4
H1W1—O1W—H1W2	111.0 (17)		

O3—S1—O1—Co1	171.90 (12)	O2—S1—C2—C1	−105.7 (2)
O2—S1—O1—Co1	−57.99 (15)	O1—S1—C2—C1	135.74 (19)
C2—S1—O1—Co1	57.30 (14)	O3—S1—C2—C3	−165.5 (2)
O1W^{i}—Co1—O1—S1	61.02 (13)	O2—S1—C2—C3	71.3 (2)
O1W—Co1—O1—S1	−118.98 (13)	O1—S1—C2—C3	−47.2 (2)
O4—Co1—O1—S1	−30.12 (12)	Co1—O4—C3—C4	−146.7 (2)
O4^{i}—Co1—O1—S1	149.88 (12)	Co1—O4—C3—C2	33.9 (3)
O1W^{i}—Co1—O4—C3	−113.9 (2)	C1—C2—C3—O4	178.8 (2)
O1W—Co1—O4—C3	66.1 (2)	S1—C2—C3—O4	1.9 (3)
O1^{i}—Co1—O4—C3	159.4 (2)	C1—C2—C3—C4	−0.6 (3)
O1—Co1—O4—C3	−20.6 (2)	S1—C2—C3—C4	−177.48 (19)
C5—N1—C1—C2	1.0 (4)	O4—C3—C4—C5	−178.5 (3)
N1—C1—C2—C3	−0.4 (4)	C2—C3—C4—C5	0.9 (4)
N1—C1—C2—S1	176.6 (2)	C1—N1—C5—C4	−0.6 (5)
O3—S1—C2—C1	17.5 (2)	C3—C4—C5—N1	−0.4 (5)

Symmetry codes: (i) −*x*+1, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1W1···O2^{ii}	0.847 (10)	2.19 (3)	2.896 (3)	140 (3)
O1W—H1W1···O2^{i}	0.847 (10)	2.37 (2)	2.982 (3)	130 (3)
O1W—H1W2···O2W	0.840 (10)	1.905 (16)	2.714 (3)	161 (4)
O2W—H2W1···O4W^{iii}	0.86 (3)	1.96 (3)	2.809 (3)	168 (4)
O2W—H2W2···O4W^{ii}	0.85 (5)	2.04 (4)	2.880 (4)	170 (5)
O3W—H3W1···O3^{iv}	0.85	2.37	3.175 (3)	158
O3W—H3W2···O1^{iii}	0.85	2.18	2.978 (3)	157
O4W—H4W1···O3	0.84 (3)	2.046 (17)	2.827 (3)	154 (3)
O4W—H4W2···O4^{v}	0.85 (3)	1.96 (3)	2.805 (3)	174 (4)
N1—H1N···O3W	0.86	1.90	2.752 (3)	169

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

Fig. 1