trans-Tetraaquabis(2,6-dimethylpyridinium-3,5-dicarboxylato-κO)cobalt(II) tetrahydrate

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In the title compound, $[Co(C_9H_8NO_4)_2(H_2O)_4]\cdot4H_2O$, the Co atom lies on an inversion centre in an octahedral environment that is formed from two O atoms of two 2,6-dimethylpyridinium-3,5-dicarboxylate monoanions and four water molecules. Hydrogen bonds that involve the pyridinium NH groups and both coordinated and uncoordinated water molecules give rise to an infinite three-dimensional network.

Related literature

For the synthesis of the ligand, see: Checchi (1959). For the crystal structure of the copper compound (which is not isostructural), see: Shi *et al.* (2007)
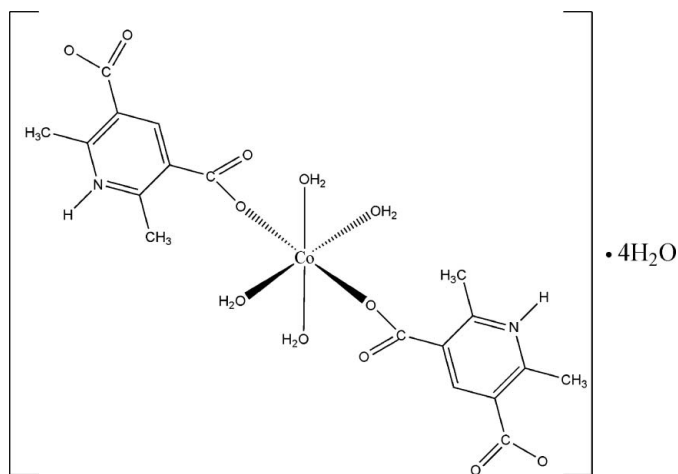
$\cdot4H_2O$

Experimental

Crystal data

$[Co(C_9H_8NO_4)_2(H_2O)_4]\cdot4H_2O$
$M_r = 591.39$

Triclinic, $P\bar{1}$
$a = 7.597\ (5)$ Å

$b = 8.651\ (7)$ Å
$c = 10.715\ (7)$ Å
$\alpha = 69.90\ (3)°$
$\beta = 69.75\ (2)°$
$\gamma = 83.58\ (2)°$
$V = 620.4\ (8)$ Å^3

$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.77$ mm^{-1}
$T = 295\ (2)$ K
$0.48 \times 0.39 \times 0.31$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.706$, $T_{max} = 0.794$

6106 measured reflections
2803 independent reflections
2631 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.100$
$S = 1.21$
2803 reflections
175 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1—H4···O8	0.84 (3)	1.89 (3)	2.726 (3)	175 (2)
O5—H8···O2	0.85	1.91	2.712 (3)	156
O5—H9···O7^i	0.85	1.92	2.769 (3)	179
O6—H11···O3^{ii}	0.85	1.91	2.740 (2)	165
O6—H10···O3^{iii}	0.85	1.92	2.743 (2)	163
O7—H13···O4^{iv}	0.85	1.97	2.814 (3)	171
O7—H12···O4^{ii}	0.85	2.05	2.862 (3)	160
O8—H14···O3^{iv}	0.85	2.08	2.914 (3)	165
O8—H15···O5^v	0.85	2.02	2.861 (3)	171

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXL97*.

References

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supplementary materials

trans-Tetraaquabis(2,6-dimethylpyridinium-3,5-dicarboxylato-*κO*)cobalt(II) tetrahydrate

J.-S. Gao, Y.-M. Zhang, B.-Y. Li and G.-F. Hou

Comment

Recently, we reported the crystal structure of *trans*-tetraaqua-bis(2,6-dimethylpyridinium-3,5-dicarboxylato) copper(II) tetrahydrate (Shi *et al.* 2007). The title cobalt analog (Fig. 1) is centrosymmetric, and the metal exists in an octahedral co-ordination geometry. Molecules are linked by O—H···O and N—H···O hydrogen bonds involving allpotential donors to generate infinite three-dimensional network. (Table 1; Fig. 2). The two compounds are not isostructural although both have the same formula.

Experimental

2,6-Dimethylpyridine-3,5-dicarboxylic acid was prepared by basic hydrolysis of diethyl 2,6-dimethylpyridine-3,5-di-carboxylate (Checchi, 1959). Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (25.1 g, 0.1 mol) and potassium hydroxide (13.44 g, 0.24 mol) were dissolved in 150 ml e thanol and 150 ml water. The solution was stirred for three hours under reflux conditions. 2,6-Dimethylpyridine-3,5-dicarboxylic acid (10.5 g), a white precipitate, was formed by adjusting the pH of the solution to 3 with 0.1 *M* HCl after ethanol was removed by evaporation.

The complex was synthesized with cobalt(II) dinitrate hexahydrate (0.582 g, 2 mmol) and 2,6-dimethylpyridine-3,5-di-carboxylic acid (0.390 g, 2 mmol) in water; the pH was adjusted to 6 with 0.01 *M* sodium hydroxide. Pink crystals separated from the filtered solution after several days.

Refinement

H atoms bound to C atoms were placed in calculated positions and treated as riding on their parent atoms, with C—H = 0.93 Å, 0.97 Å for aromatic and methyl H atoms respectively; $U_{iso}(H)$ was set to = $1.2U_{eq}$ of the carrier atom (1.5 U_{eq} for methyl H atoms). Water H atoms were initially located in a difference Fourier map; they were treated as riding on their parent atoms. The H4 atom bond to N1 atoms was located in a difference Fourier map and refined isotropically.

Figures
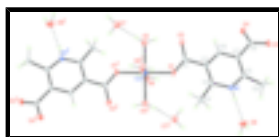
Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement el-lipsoids for all atoms. H atoms are represented as spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines; [symmetry codes: (i): −*x* + 2,-*y* + 1,-*z*].

Fig. 2. Packing diagram for the crystal of the title compound, showing the three-dimensional hydrogen-bonding network. H-bonds are drawn as dashed lines; H atoms not involved in hy-drogen bonds have been omitted for clarity.

supplementary materials

***trans*-Tetraaquabis(2,6-dimethylpyridinium-3,5-dicarboxylato- κ*O*)cobalt(II) tetrahydrate**

Crystal data

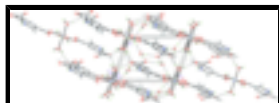|	
$[Co(C_9H_8NO_4)_2(H_2O)_4]\cdot4H_2O$	$Z = 1$
$M_r = 591.39$	$F_{000} = 309$
Triclinic, $P\bar{1}$	$D_x = 1.583$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.597$ (5) Å	Cell parameters from 5838 reflections
$b = 8.651$ (7) Å	$\theta = 3.4–27.5º$
$c = 10.715$ (7) Å	$\mu = 0.77$ mm^{-1}
$\alpha = 69.90$ (3)º	$T = 295$ (2) K
$\beta = 69.75$ (2)º	Block, pink
$\gamma = 83.58$ (2)º	$0.48 \times 0.39 \times 0.31$ mm
$V = 620.4$ (8) Å^3	

Data collection

Rigaku R-AXIS RAPID diffractometer	2803 independent reflections
Radiation source: fine-focus sealed tube	2631 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.015$
$T = 295(2)$ K	$\theta_{max} = 27.5º$
ω scans	$\theta_{min} = 3.4º$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$h = -9\rightarrow8$
$T_{min} = 0.706$, $T_{max} = 0.794$	$k = -11\rightarrow11$
6106 measured reflections	$l = -13\rightarrow13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.2698P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.21$	$(\Delta/\sigma)_{max} = 0.004$
2803 reflections	$\Delta\rho_{max} = 0.46$ e Å^{-3}
175 parameters	$\Delta\rho_{min} = -0.30$ 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 ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
O7	0.6205 (2)	0.66640 (19)	0.29668 (15)	0.0360 (3)
Co1	1.0000	0.5000	0.0000	0.01986 (12)
O1	0.9067 (2)	0.33848 (17)	0.20120 (14)	0.0325 (3)
O2	0.9725 (3)	0.08988 (19)	0.17835 (15)	0.0469 (4)
O3	0.5899 (2)	−0.39084 (16)	0.78211 (14)	0.0282 (3)
O4	0.5555 (2)	−0.34851 (18)	0.57558 (15)	0.0348 (3)
O6	0.7258 (2)	0.5352 (2)	0.00197 (15)	0.0364 (4)
H11	0.6395	0.4893	0.0785	0.055*
H10	0.6940	0.5771	−0.0713	0.055*
O5	1.0344 (2)	0.30316 (17)	−0.08666 (14)	0.0291 (3)
H8	1.0355	0.2192	−0.0163	0.044*
H9	1.1412	0.3114	−0.1501	0.044*
N1	0.7321 (2)	0.11394 (18)	0.63709 (16)	0.0228 (3)
H4	0.728 (4)	0.167 (3)	0.691 (3)	0.029 (6)*
C1	0.9123 (3)	0.1843 (2)	0.24754 (18)	0.0239 (4)
C2	0.8308 (2)	0.1072 (2)	0.40626 (17)	0.0205 (3)
C3	0.8208 (2)	0.1904 (2)	0.49864 (18)	0.0212 (3)
C4	0.9000 (3)	0.3567 (2)	0.4621 (2)	0.0319 (4)
H2	0.8069	0.4388	0.4462	0.048*
H1	1.0078	0.3772	0.3783	0.048*
H3	0.9364	0.3610	0.5382	0.048*
C5	0.6508 (3)	−0.0367 (2)	0.69532 (18)	0.0221 (3)
C6	0.5440 (3)	−0.0842 (3)	0.8498 (2)	0.0356 (5)
H6	0.6258	−0.1405	0.9019	0.053*
H7	0.4413	−0.1555	0.8723	0.053*
H5	0.4963	0.0129	0.8740	0.053*
C7	0.6681 (2)	−0.1265 (2)	0.60701 (17)	0.0197 (3)
C8	0.5976 (2)	−0.3021 (2)	0.65888 (18)	0.0213 (3)
C9	0.7573 (2)	−0.0511 (2)	0.46273 (17)	0.0211 (3)
H16	0.7677	−0.1096	0.4021	0.025*
O8	0.7410 (3)	0.2787 (2)	0.81069 (18)	0.0437 (4)
H14	0.6800	0.3662	0.8155	0.066*
H15	0.8350	0.2779	0.8367	0.066*

H13	0.5924	0.6709	0.3793	0.066*	
H12	0.5774	0.5721	0.3141	0.066*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O7	0.0431 (8)	0.0336 (8)	0.0282 (7)	−0.0047 (6)	−0.0064 (6)	−0.0101 (6)
Co1	0.02236 (19)	0.01968 (18)	0.01346 (17)	−0.00420 (12)	−0.00471 (12)	−0.00036 (12)
O1	0.0482 (9)	0.0219 (7)	0.0171 (6)	−0.0023 (6)	−0.0052 (6)	0.0013 (5)
O2	0.0793 (13)	0.0293 (8)	0.0188 (7)	−0.0015 (8)	−0.0021 (7)	−0.0054 (6)
O3	0.0373 (7)	0.0235 (6)	0.0198 (6)	−0.0074 (5)	−0.0110 (6)	0.0015 (5)
O4	0.0510 (9)	0.0302 (7)	0.0246 (7)	−0.0152 (6)	−0.0114 (6)	−0.0070 (6)
O6	0.0247 (7)	0.0553 (10)	0.0211 (6)	−0.0045 (6)	−0.0080 (5)	−0.0007 (6)
O5	0.0333 (7)	0.0284 (7)	0.0221 (6)	−0.0036 (5)	−0.0051 (6)	−0.0067 (5)
N1	0.0297 (8)	0.0188 (7)	0.0193 (7)	−0.0003 (6)	−0.0066 (6)	−0.0069 (6)
C1	0.0259 (9)	0.0239 (8)	0.0165 (8)	−0.0053 (7)	−0.0050 (7)	−0.0003 (6)
C2	0.0241 (8)	0.0188 (8)	0.0157 (7)	0.0002 (6)	−0.0069 (6)	−0.0016 (6)
C3	0.0230 (8)	0.0168 (8)	0.0210 (8)	−0.0002 (6)	−0.0073 (7)	−0.0026 (6)
C4	0.0420 (11)	0.0203 (9)	0.0313 (10)	−0.0068 (8)	−0.0102 (9)	−0.0059 (7)
C5	0.0261 (8)	0.0192 (8)	0.0179 (8)	−0.0001 (6)	−0.0055 (7)	−0.0040 (6)
C6	0.0512 (13)	0.0297 (10)	0.0173 (8)	−0.0049 (9)	0.0006 (8)	−0.0077 (7)
C7	0.0225 (8)	0.0174 (7)	0.0166 (7)	−0.0017 (6)	−0.0052 (6)	−0.0031 (6)
C8	0.0231 (8)	0.0182 (8)	0.0190 (8)	−0.0026 (6)	−0.0038 (6)	−0.0040 (6)
C9	0.0259 (8)	0.0196 (8)	0.0159 (7)	−0.0012 (6)	−0.0061 (6)	−0.0039 (6)
O8	0.0581 (10)	0.0410 (9)	0.0516 (10)	0.0106 (7)	−0.0325 (9)	−0.0276 (8)

Geometric parameters (Å, °)

O7—H13	0.8497	N1—H4	0.84 (3)
O7—H12	0.8491	C1—C2	1.518 (2)
Co1—O1	2.0483 (18)	C2—C9	1.386 (3)
Co1—O1^i	2.0483 (18)	C2—C3	1.389 (2)
Co1—O6^i	2.0652 (19)	C3—C4	1.492 (3)
Co1—O6	2.0652 (19)	C4—H2	0.9600
Co1—O5	2.1562 (19)	C4—H1	0.9600
Co1—O5^i	2.1562 (19)	C4—H3	0.9600
O1—C1	1.254 (2)	C5—C7	1.384 (2)
O2—C1	1.235 (3)	C5—C6	1.498 (3)
O3—C8	1.263 (2)	C6—H6	0.9600
O4—C8	1.238 (2)	C6—H7	0.9600
O6—H11	0.8500	C6—H5	0.9600
O6—H10	0.8500	C7—C9	1.398 (2)
O5—H8	0.8499	C7—C8	1.516 (3)
O5—H9	0.8500	C9—H16	0.9300
N1—C5	1.350 (2)	O8—H14	0.8499
N1—C3	1.351 (2)	O8—H15	0.8501
H13—O7—H12	101.1	C9—C2—C1	119.22 (15)
O1—Co1—O1^i	180.00 (8)	C3—C2—C1	122.83 (16)

O1—Co1—O6[i]	90.73 (7)	N1—C3—C2	117.51 (16)
O1[i]—Co1—O6[i]	89.28 (7)	N1—C3—C4	115.52 (16)
O1—Co1—O6	89.27 (7)	C2—C3—C4	126.97 (17)
O1[i]—Co1—O6	90.73 (7)	C3—C4—H2	109.5
O6[i]—Co1—O6	180.00 (8)	C3—C4—H1	109.5
O1—Co1—O5	91.39 (8)	H2—C4—H1	109.5
O1[i]—Co1—O5	88.61 (8)	C3—C4—H3	109.5
O6[i]—Co1—O5	88.52 (7)	H2—C4—H3	109.5
O6—Co1—O5	91.48 (7)	H1—C4—H3	109.5
O1—Co1—O5[i]	88.61 (8)	N1—C5—C7	117.54 (16)
O1[i]—Co1—O5[i]	91.39 (8)	N1—C5—C6	115.12 (16)
O6[i]—Co1—O5[i]	91.48 (7)	C7—C5—C6	127.28 (17)
O6—Co1—O5[i]	88.52 (7)	C5—C6—H6	109.5
O5—Co1—O5[i]	180.0	C5—C6—H7	109.5
C1—O1—Co1	131.02 (13)	H6—C6—H7	109.5
Co1—O6—H11	117.8	C5—C6—H5	109.5
Co1—O6—H10	124.3	H6—C6—H5	109.5
H11—O6—H10	116.9	H7—C6—H5	109.5
Co1—O5—H8	101.7	C5—C7—C9	117.86 (16)
Co1—O5—H9	109.8	C5—C7—C8	123.42 (15)
H8—O5—H9	108.2	C9—C7—C8	118.72 (15)
C5—N1—C3	126.27 (16)	O4—C8—O3	124.96 (17)
C5—N1—H4	118.0 (17)	O4—C8—C7	117.14 (16)
C3—N1—H4	115.7 (17)	O3—C8—C7	117.87 (16)
O2—C1—O1	127.22 (17)	C2—C9—C7	122.72 (16)
O2—C1—C2	117.17 (17)	C2—C9—H16	118.6
O1—C1—C2	115.59 (16)	C7—C9—H16	118.6
C9—C2—C3	117.92 (16)	H14—O8—H15	107.8

Symmetry codes: (i) −x+2, −y+1, −z.

Hydrogen-bond geometry (Å, °)

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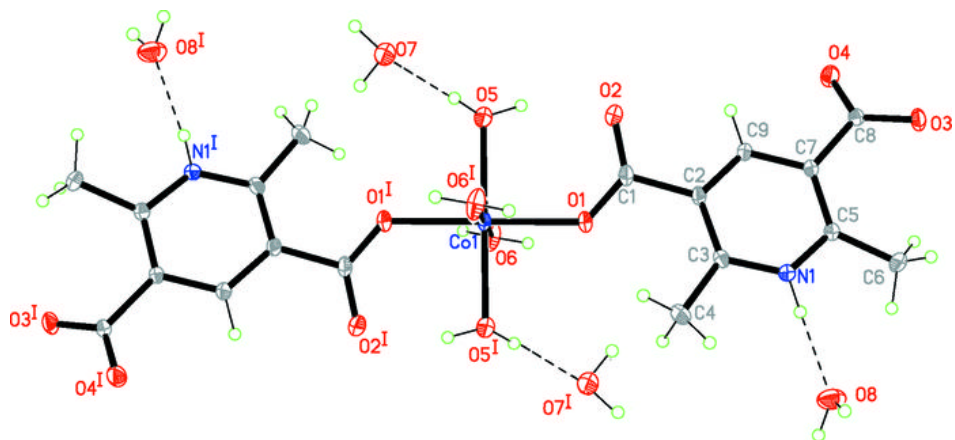
Fig. 1

Fig. 2