Crystal structure of diaqua-*bis*-(2-ethyl-1*H*-imidazole-4,5-dicarboxylato-O,N)-cobalt(II) trihydrate, $[Co(C_6H_4N_2O_4)_2(H_2O)_2]\cdot 2(H_2O)O$, $C_{14}H_{22}CoN_4O_{13}$

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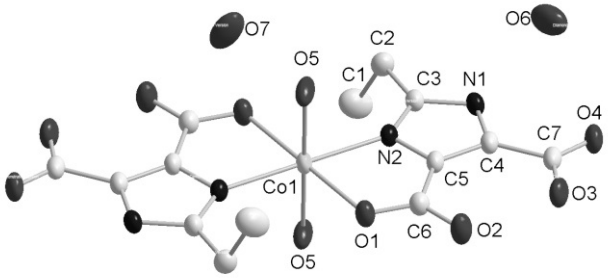

Abstract

$C_{14}H_{22}CoN_4O_{13}$, triclinic, $P\bar{1}$ (no. 2), a = 7.153(1) Å, b = 8.882(2) Å, c = 9.338(2) Å, α = 66.055(2)°, β = 88.411(2)°, γ = 70.870(2)°, V = 508.4 Å^3, Z = 1, $R_{gt}(F)$ = 0.0326, $wR_{ref}(F^2)$ = 0.0940, T = 293 K.

Table 1. Data collection and handling.

Crystal:	red blocks, size 0.21×0.23×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.15 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	50.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3911, 1885
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1851
$N(param)_{refined}$:	154
Programs:	SHELXS-97 [15]

Source of material

The title compound was synthesized by a hydrothermal method under autogenous pressure. A mixture of $CoCl_2\cdot 6H_2O$ (0.036 g, 0.1 mmol), 2-ethyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3EIDA) (0.037 g, 0.2 mmol) and distilled water (15 mL) was sealed in a teflon-lined stainless reactor (25 mL) and heated at 120 °C for 72 h, and then cooled to room temperature. The red block crystals were filtered and washed with water and ethanol. Yield 80 % (based on H_3EIDA).

Analysis calculated for $C_{14}H_{22}CoN_4O_{13}$: C 32.76%, H 4.32%, N 11.48%; found: C 32.70%, H 4.36%, N 11.42%.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C–H = 0.96-0.97 Å, O–H = 0.81-0.84 Å and N–H = 0.86 Å, with $U_{iso}(H) = 1.5\ U_{eq}(C)$ for methyl H atoms and 1.2 $U_{eq}(C)$ for all other H atoms. O7 is the oxygen atom of a crystal water molecule. Since no suitable electron densities corresponding to the two hydrogen atoms attached to O7 were found in the DIF-fourier maps, no hydrogen atoms were added for O7.

Discussion

Over the past few years, extensive investigation has focused on the construction of coordination polymers using 4,5-imidazole-dicarboxylic acid and derivatives as bridges of interest [1-4]. Recently, our group also reported five coordination polymers with 2-methyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3MIA) ligand [5-9]. The reported coordination polymers with H_3MIA do not only show beautiful and interesting topological structures with various dimensionalities but also exhibit very flexible coordination modes [1-8]. To explore the effect of 2-position substituents of imidazole for dominating the self-assembly of metal-organic networks, we synthesised another new analogue ligand of 2-ethyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3EIDA), to prepare novel MOFs. To the best of our knowledge, in contrast to the ligand H_3MIA, coordination polymers with H_3EIDA have been rarely reported so far [8-14]. Herein we report the hydrothermal synthesis and crystal structure of a new cobalt (II) complex incorporating H_3EIDA. The title complex consists of $[Co(C_7H_7N_2O_4)_2(H_2O)_2]\cdot 2(H_2O)O$, consists of one cobalt(II) ion, two 4-carboxy-2-ethyl-1*H*-imidazole-5-carboxylate anion, two coordinated water molecule, three free water molecule. Each cobalt(II) is six coordinated with four oxygen atoms [O(1), O(1A), N(2), N(2A)] from two individual H_2EIDA^- ligands and two oxygen atoms [O(5) and O(5A)] from two coordinated water molecules, forming a distorted octahedral coordination configuration. Each ligand is stabilized by a strong, almost symmetrical, hydrogen bond with a short O···O distance of 2.476(3) Å [O(2) and O(3)]. Intermolecular O–H···O hydrogen bonds between the two uncoordinated carboxyl O atom [O(3) and O(4)] and the O atom [O(5)] of coordinated water molecule link the molecules into a two-dimensional hydrogen bonds network. The 2-D networks are further linked into a three-dimensional hydrogen bonds supramolecular framework through N–H···O and O–H···O hydrogen-bonding interactions involving the free water molecules. The structure of the title compound is isomorphous to previously reported cadmium (II) complexe constructed by Cd(II) and H_2EIDA^- [14]. The Cd(II) complex crystallizes in Monoclinic, space group $C2/c$ whereas the Co (II) complex belongs to the Triclinic, $P\bar{1}$ space group. The mean distances Co–O and Co–N of 2.0616 Å and 2.1587 Å, respectively, are smaller than that of Cd–O (2.368 Å) and Cd–N (2.270 Å).

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	2*i*	0.0309	0.4829	0.3552	0.078
H(1B)	2*i*	0.1685	0.2931	0.4694	0.078
H(1C)	2*i*	0.1890	0.3663	0.2884	0.078
H(2A)	2*i*	0.2936	0.4919	0.4968	0.040
H(2B)	2*i*	0.4479	0.3835	0.4210	0.040
H(1)	2*i*	0.1788	0.8184	0.3437	0.034
H(2W)	2*i*	0.2368	0.4328	–0.0997	0.064
H(1W)	2*i*	0.1154	0.5932	–0.1043	0.064
H(3W)	2*i*	0.1357	0.8195	0.6368	0.103
H(4W)	2*i*	0.2472	0.8896	0.5251	0.103
H(2)	2*i*	0.298(6)	1.085(6)	–0.158(5)	0.09(1)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.1618(4)	0.3962(4)	0.3766(3)	0.068(2)	0.050(2)	0.043(1)	–0.035(1)	0.005(1)	–0.013(1)
C(2)	2*i*	0.3156(3)	0.4699(3)	0.4030(2)	0.040(1)	0.028(1)	0.029(1)	–0.0082(8)	0.0020(8)	–0.0108(8)
C(3)	2*i*	0.3053(3)	0.6361(2)	0.2660(2)	0.0271(9)	0.0235(9)	0.0291(9)	–0.0049(7)	0.0015(7)	–0.0147(8)
C(4)	2*i*	0.2335(3)	0.9198(2)	0.1204(2)	0.0263(9)	0.022(1)	0.034(1)	–0.0048(7)	0.0001(7)	–0.0158(8)
C(5)	2*i*	0.3196(3)	0.8268(2)	0.0348(2)	0.0258(9)	0.0192(9)	0.030(1)	–0.0053(7)	0.0011(7)	–0.0130(7)
C(6)	2*i*	0.3674(3)	0.8809(3)	–0.1286(2)	0.0309(9)	0.0242(9)	0.030(1)	–0.0080(8)	0.0031(8)	–0.0134(8)
C(7)	2*i*	0.1531(3)	1.1114(3)	0.0778(3)	0.0283(9)	0.0228(9)	0.041(1)	–0.0042(7)	–0.0032(8)	–0.0181(9)
Co(1)	1e	½	½	0	0.0284(2)	0.0182(2)	0.0274(2)	–0.0041(2)	0.0030(1)	–0.0136(2)
N(1)	2*i*	0.2260(2)	0.7970(2)	0.2656(2)	0.0316(8)	0.0269(8)	0.0290(8)	–0.0054(7)	0.0046(7)	–0.0182(7)
N(2)	2*i*	0.3634(2)	0.6504(2)	0.1264(2)	0.0286(8)	0.0202(8)	0.0281(8)	–0.0055(6)	0.0024(6)	–0.0129(7)
O(1)	2*i*	0.4431(2)	0.7648(2)	–0.1761(2)	0.0439(8)	0.0257(7)	0.0316(7)	–0.0083(6)	0.0087(6)	–0.0161(6)
O(2)	2*i*	0.3296(3)	1.0438(2)	–0.2165(2)	0.066(1)	0.0236(8)	0.0341(8)	–0.0131(7)	0.0124(8)	–0.0117(7)
O(3)	2*i*	0.1808(2)	1.2110(2)	–0.0600(2)	0.0512(9)	0.0212(7)	0.0469(9)	–0.0090(7)	0.0048(7)	–0.0169(7)
O(4)	2*i*	0.0655(2)	1.1635(2)	0.1727(2)	0.0452(9)	0.0294(8)	0.0484(9)	–0.0021(7)	0.0048(7)	–0.0256(7)
O(5)	2*i*	0.2243(2)	0.5162(2)	–0.0783(2)	0.0310(7)	0.0273(8)	0.072(1)	–0.0027(6)	–0.0056(7)	–0.0287(8)
O(6)	2*i*	0.1671(3)	0.8357(3)	0.5463(2)	0.063(1)	0.097(2)	0.052(1)	–0.014(1)	0.0094(9)	–0.048(1)
O(7)	2*f*	½	0	½	0.54(3)	0.29(2)	0.23(1)	–0.01(2)	0.13(2)	0.04(1)

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