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Crystal structure of diaquabis(hydrogen 2-ethyl-1*H*-imidazole-4,5-dicarboxylato-$\kappa^2 N,O$)cobalt(II) dihydrate, $Co(H_2O)_2(C_7H_7N_2O_4)_2 \cdot 2H_2O$

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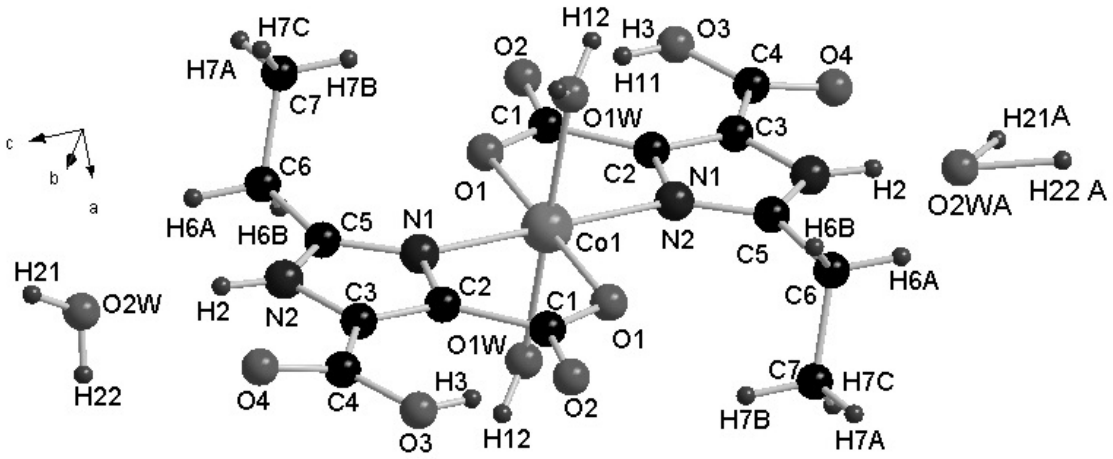

Abstract

$C_{14}H_{22}CoN_4O_{12}$, triclinic, $P\bar{1}$ (no. 2), a = 7.1485(8) Å, b = 8.8837(9) Å, c = 9.346(1) Å, α = 66.036(1)°, β = 88.452(1)°, γ = 70.882(1)°, V = 508.6 Å^3, Z = 1, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.142, T = 293 K.

Source of material

Cobalt(II) acetate dihydrate (0.112 g, 0.5 mmol) and $NaN(CN)_2$ (0.090 g, 1.0 mmol) were refluxed in anhydrous methanol (10 ml) for 50 min, followed by dropwise addition of a methanol solution containing 2-ethyl-1*H*-imidazole-4,5-dicarboxylic acid (0.186 g, 1.0 mmol). After stirring for 20 min in air, the pH value was adjusted to 6.0 with triethylenamine, and the mixture was placed into a 25 ml Teflon-lined autoclave under autogenous pressure being heated at 150 °C for 72 h. Then the autoclave was cooled over a period of 24 h at a rate of 5 °C/h. After filtration, the product was washed with distilled water and then dried, red crystals were obtained (yield 0.014 g, 52 %).

Elemental analysis — found: C, 34.92 %; H, 4.18 %; N, 11.74 %; calculated for $C_{14}H_{20}CoN_4O_{11}$: C, 35.09 %; H, 4.21 %; N, 11.68 %. IR data are available in the CIF file.

Experimental details

Positions of hydrogen atoms of water were located from the difference Fourier maps and refined. All U_{iso} values were restrained on U_{eq} values of the parent atoms.

Discussion

During the past two decades, the study of metal-organic supramolecules has gained great recognition as an important interface between synthetic chemistry and materials science. It provides a solid foundation for understanding how molecules can be organized and how functions can be achieved [1-3]. The multifunctional ligands containing N- and O- donors such as 2-ethyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3Eimda) have attracted attention because they may provide a variety of topological architectures due to their remarkably versatile coordination modes and potential application [4,5]. In order to further study the coordination behavior and role of the late transition cation in the self-assembly processes in the presence of nitrogen-heterocyclic dicarboxylate, the title complex has been synthesized and has been characterized.

The crystal structure reveals mononuclear symmetric complex units and free water molecules. The complex contains one cobalt(II) cation, two 2-ethyl-1*H*-imidazole-4,5-dicarboxylate ligands, and two coordinated water molecules, among which the singly deprotonated 2-ethyl-imidazole-4,5-dicarboxylate acts as bridging ligand. It is generated through the deprotonation of H_3Eimda ligand under hydrothermal conditions, while the sodium dicyanamide does not present in the final product. Center Co(II) ion adopts a sixfold coordination [CoN_2O_4] in a slightly distorted octahedral configuration. The configuration of the title complex is neither comparable to that of $[Fe(H_2IDC)_2]_n$ [6], in which there are no water molecules in the sphere of the central ion and the imidazole-4,5-dicarboxylic acid adopts a two coordination mode, although the iron ion has the same octahedral environment, nor to that of $4d^{10}$ metal Cd complex containing the analogous ligand H_3Pimda (H_3Pimda = 2-propyl-1*H*-imidazole-4,5-dicarboxylic acid) [7]. It is even different from that complex containing the same metal central with the analogous ligand H_3pimda, in which there are two water molecules taking part in the coordination; maybe this is due to the difference of synthesis conditions [8]. The equatorial planes of the octahedron are occu-

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pied by the two nitrogen atoms of the imidazole rings and two oxygen atoms which are from the two carboxylate groups of H_3Eimda ligands. Among the latter, two H_3Eimda ligands coordinate Co(II) in an *N*,*O* chelate coordination mode (O1 and N1) through carboxylate oxygen atoms and form two stable five-membered rings N1-C2-C1-O1-Co1. Two oxygen atoms belonging to the water molecules in the axial position complete an octahedron coordination sphere of cobalt(II): *d*(Co1—N1) = 2.120(2) Å and *d*(Co1—O) = 2.062(2)-2.160(2) Å. Interestingly, the apical *d*(Co1—OW) is shorter than that of the equatorial ones. The slight distortion of the octahedron is verified by the angles of O1W–Co1–O1 , N1–Co1–O1, O1W–Co1–O1 and N1–Co1–O1, which are 88.73(10)°, 78.08(9)°, 91.27(10)° and 101.92(9)°, respectively. Both the imidazole rings and the dicarboxylate groups are almost coplanar, and the atoms in the imidazole deviate out of the mean plane defined by the imidazole ring by less than 0.1°. In addition, a series of hydrogen bond interactions between the oxygen atoms of the carboxylate groups, uncoordinated and coordinated water molecules are found. All the hydrogen atoms of coordinated water participate in the hydrogen bond, contributing to packing stability [9,10]. These cobalt complex units were connected by the hydrogen bond interactions, resulting in an infinite three-dimensional architecture.

Table 1. Data collection and handling.

Crystal:	red block, size 0.18 × 0.19 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.15 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	54.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3007, 2188
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2020
$N(param)_{refined}$:	161
Programs:	SHELXS-97, SHELXL-97 [11]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	2*i*	0.223(6)	1.166(5)	0.378(4)	0.063
H(11)	2*i*	0.126(4)	0.608(3)	0.400(5)	0.067
H(12)	2*i*	0.191(5)	0.444(4)	0.402(5)	0.067
H(21)	2*i*	0.081(6)	0.872(7)	0.098(6)	0.108
H(22)	2*i*	0.257(6)	0.881(7)	0.040(7)	0.108
H(2)	2*i*	0.189(5)	0.821(4)	0.846(3)	0.041
H(6A)	2*i*	0.2928	0.4921	0.9970	0.044
H(6B)	2*i*	0.4470	0.3831	0.9218	0.044
H(7A)	2*i*	0.1721	0.2903	0.9675	0.084
H(7B)	2*i*	0.1834	0.3728	0.7854	0.084
H(7C)	2*i*	0.0295	0.4813	0.8612	0.084

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}
Co(1)	1*h*	½	½	½	0.0322(3)	0.0198(3)	0.0311(3)	–0.0058(2)	0.0051(2)	–0.0159(2)
O(1)	2*i*	0.4433(3)	0.7646(3)	0.3243(2)	0.047(1)	0.0260(9)	0.0329(9)	–0.0090(8)	0.0102(8)	–0.0160(8)
O(2)	2*i*	0.3291(4)	1.0441(3)	0.2840(2)	0.069(2)	0.024(1)	0.038(1)	–0.014(1)	0.013(1)	–0.0124(9)
O(3)	2*i*	0.1808(4)	1.2111(3)	0.4407(3)	0.055(1)	0.023(1)	0.050(1)	–0.0100(9)	0.008(1)	–0.0207(9)
O(4)	2*i*	0.0659(3)	1.1634(3)	0.6730(3)	0.048(1)	0.029(1)	0.053(1)	–0.0031(9)	0.0057(9)	–0.028(1)
O(1W)	2*i*	0.2241(3)	0.5161(3)	0.4214(3)	0.034(1)	0.028(1)	0.077(2)	–0.0051(8)	–0.004(1)	–0.031(1)
O(2W)	2*i*	0.1677(5)	0.8362(5)	0.0458(4)	0.067(2)	0.099(2)	0.058(2)	–0.014(2)	0.012(1)	–0.053(2)
N(1)	2*i*	0.3634(3)	0.6508(3)	0.6260(2)	0.030(1)	0.021(1)	0.031(1)	–0.0057(8)	0.0044(8)	–0.0145(9)
N(2)	2*i*	0.2257(3)	0.7970(3)	0.7653(3)	0.035(1)	0.028(1)	0.033(1)	–0.0076(9)	0.0056(9)	–0.0198(9)
C(1)	2*i*	0.3671(4)	0.8809(3)	0.3714(3)	0.033(1)	0.025(1)	0.033(1)	–0.008(1)	0.005(1)	–0.016(1)
C(2)	2*i*	0.3195(4)	0.8266(3)	0.5353(3)	0.029(1)	0.022(1)	0.032(1)	–0.0078(9)	0.0041(9)	–0.015(1)
C(3)	2*i*	0.2333(4)	0.9198(3)	0.6204(3)	0.029(1)	0.023(1)	0.036(1)	–0.0055(9)	0.0018(9)	–0.017(1)
C(4)	2*i*	0.1534(4)	1.1115(3)	0.5779(3)	0.032(1)	0.023(1)	0.044(1)	–0.005(1)	–0.000(1)	–0.020(1)
C(5)	2*i*	0.3056(4)	0.6366(3)	0.7657(3)	0.031(1)	0.025(1)	0.033(1)	–0.0058(9)	0.0029(9)	–0.017(1)
C(6)	2*i*	0.3148(5)	0.4699(4)	0.9034(3)	0.044(2)	0.031(1)	0.032(1)	–0.010(1)	0.004(1)	–0.014(1)
C(7)	2*i*	0.1608(6)	0.3968(5)	0.8769(4)	0.071(2)	0.055(2)	0.048(2)	–0.038(2)	0.007(2)	–0.015(2)

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