Crystal structure of diaquabis(2-ethyl-1*H*-imidazole-4,5-dicarboxylate)nickel(II) trihydrate, $[Ni(H_2O)_2(C_7H_7N_2O_4)_2] \cdot 3H_2O$

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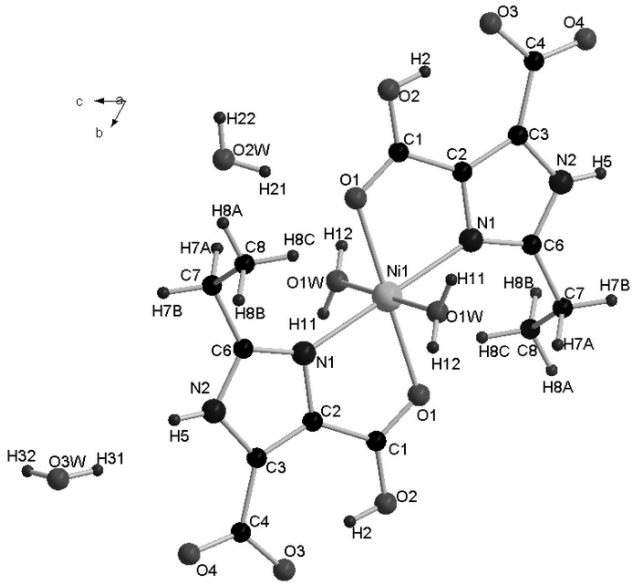

Abstract

$C_{14}H_{24}N_4NiO_{13}$, triclinic, $P\bar{1}$ (no. 2), a = 7.1905(7) Å, b = 8.8488(8) Å, c = 9.3266(9) Å, α = 66.220(1)°, β = 89.155(1)°, γ = 70.513(1)°, V = 507.0 Å^3, Z = 1, $R_{gt}(F)$ = 0.034, $wR_{ref}(F^2)$ = 0.107, T = 293 K.

Source of material

Nickel(II) acetate dihydrate (0.113 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 adding 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 triethyleneamine, and the mixture was placed in 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, blue crystals were obtained (yield 0.014 g; 51 %).

Elemental analysis — found: C, 31.92 %; H, 4.18 %; N, 11.17 %; calculated for $C_{14}H_{24}N_4NiO_{13}$: C, 32.65 %; H, 4.69 %; N; 10.88 %. 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 with a distance restraint of d(O—H) = 0.85 Å. All U_{iso} values were restrained on U_{eq} values of the parent atoms. O3W from the free water was restrained to an occupation of 0.5 in order to obtain reasonable thermal parameters.

Discussion

The design and construction of coordination polymers has attracted much attention due to their intriguing topologies [1] and potential applications as functional materials [2]. In recent years, 4,5-imidazoledicarboxylic acid, known as a rigid *N*-heterocyclic carboxylic ligand, owns great potential for coordination interactions, has been used in constructing coordination polymers with transition metals due to great potential for coordination interactions and hydrogen bonding. It can generate large diversity of supramolecular architectures due to its quality of being deprotonated into different species with different proton numbers. Up to date, it has been found that imidazoledicarboxylate complexes exhibit useful properties [3]. In order to further study the coordination behavior and role of the late transition cation in the self-assembly processes at presence of nitrogen-heterocyclic dicarboxylate, a new complex has been synthesized and characterized.

The crystal structure reveals four discrete moieties, the symmetric coordination unit and three free water molecules. The complex contains one nickel(II) cation, two 2-ethyl-1*H*-imidazole-4,5-dicarboxy- late ligands, and two coordinated water molecules, among which the singly deprotonated 2-ethyl-imidazole-4,5-dicarboxylate acts as bridging ligand, while the sodium dicyanamide does not present in the final product. In the complex unit, the Ni(II) cation is six-coordinated with a N_2O_4 donor set, with two chelating rings from *N*,*O*-bidentate 2-ethyl-1*H*-imidazole-4,5-dicarboxylate anions, and two coordinated water molecules, generating a slightly distorted octahedron coordination. The equatorial plane of the octahedron is occupied by the two nitrogen atoms of the imidazole rings, and two oxygen atoms from the two carboxylate groups of 2-ethyl-1*H*-imidazole-4,5-dicarboxylate ligands. The distances are d(Ni1—N1) = 2.075(2) Å, and d(Ni1—O) = 2.064(2) - 2.099(2) Å. Interestingly, the apical Ni1—OW distance is shorter than the equatorial ones. The slight distortion from the octahedral environment is verified by the angles of ∠O1W–Ni1–O1, ∠N1–Ni1–O1, which are 91.66(8)°, 88.34(8)°, 80.37(7)°, and 99.63(7)°, 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 0.100 Å.

The configuration of the title complex is neither comparable to that of complex $[Fe(H_2IDC)_2]_n$ [4], in which there are no water molecules in the sphere of the central ion, and the imidazole-4,5-dicarboxylic acid adopted two different coordination modes, nor similar to that of the $4d^{10}$ metal Cd complex containing the analogous ligand 2-propyl-1*H*-imidazole-4,5-dicarboxylate [5]. In

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addition, a series of hydrogen bond interactions between the oxygen atoms of the carboxylate groups, lattice and the coordinated water molecules are found. All the hydrogen atoms of coordinated water participate in the hydrogen bond, contributing to packing stability. The above mentioned complex units were connected by hydrogen bond interactions, resulting in an infinite three-dimensional supramolecular architecture.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.17 × 0.12 × 0.11 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.32 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	49.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2556, 1765
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1686
$N(param)_{refined}$:	160
Programs:	SHELXS-97, SHELXL-97 [8]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	2*i*		0.713(7)	–0.084(6)	0.654(5)	0.090
H(11)	2*i*		0.201(4)	0.433(2)	0.422(4)	0.050
H(12)	2*i*		0.124(3)	0.608(2)	0.392(4)	0.046
H(21)	2*i*		0.7989	0.1923	0.8630	0.116
H(22)	2*i*		0.8561	0.0550	1.0118	0.116
H(31)	2*i*	0.50	0.4918	0.9705	0.9070	0.273
H(32)	2*i*	0.50	0.5445	0.9788	1.0451	0.273
H(5)	2*i*		0.8199	0.1863	0.1584	0.040
H(7A)	2*i*		0.5527	0.6254	0.0829	0.049
H(7B)	2*i*		0.6981	0.5148	0.0045	0.049
H(8A)	2*i*		0.8295	0.7113	0.0330	0.096
H(8B)	2*i*		0.9716	0.5167	0.1371	0.096
H(8C)	2*i*		0.8266	0.6267	0.2162	0.096

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	1*h*		½	½	½	0.0335(3)	0.0206(3)	0.0325(3)	–0.0063(2)	0.0042(2)	–0.0162(2)
O(1)	2*i*		0.5495(3)	0.2433(2)	0.6726(2)	0.052(1)	0.029(1)	0.035(1)	–0.0113(8)	0.0112(8)	–0.0177(8)
O(2)	2*i*		0.6627(4)	–0.0380(3)	0.7142(2)	0.073(1)	0.027(1)	0.041(1)	–0.015(1)	0.014(1)	–0.0146(9)
O(3)	2*i*		0.8152(3)	–0.2078(2)	0.5598(3)	0.057(1)	0.0241(9)	0.055(1)	–0.0104(9)	0.004(1)	–0.0196(9)
O(4)	2*i*		0.9310(3)	–0.1619(3)	0.3298(3)	0.052(1)	0.034(1)	0.059(1)	–0.0039(9)	0.006(1)	–0.032(1)
O(1W)	2*i*		0.2272(3)	0.5211(3)	0.4103(3)	0.035(1)	0.030(1)	0.084(2)	–0.0046(9)	–0.006(1)	–0.033(1)
O(2W)	2*i*		0.8337(4)	0.1637(4)	0.9587(3)	0.076(2)	0.100(2)	0.059(2)	–0.013(2)	0.010(1)	–0.051(2)
O(3W)	2*i*	0.50	0.4499(4)	0.9927(4)	0.9835(3)	0.20(1)	0.179(8)	0.151(7)	–0.064(7)	0.044(7)	–0.061(6)
N(1)	2*i*		0.6356(3)	0.3557(3)	0.3740(2)	0.034(1)	0.021(1)	0.033(1)	–0.0069(8)	0.0034(9)	–0.0138(9)
C(1)	2*i*		0.6277(4)	0.1248(3)	0.6268(3)	0.036(1)	0.026(1)	0.038(1)	–0.010(1)	0.003(1)	–0.016(1)
C(2)	2*i*		0.6781(3)	0.1780(3)	0.4657(3)	0.031(1)	0.022(1)	0.035(1)	–0.0069(9)	0.002(1)	–0.015(1)
C(3)	2*i*		0.7644(4)	0.0849(3)	0.3805(3)	0.031(1)	0.026(1)	0.039(1)	–0.007(1)	0.001(1)	–0.019(1)
C(4)	2*i*		0.8436(4)	–0.1078(3)	0.4228(3)	0.033(1)	0.026(1)	0.048(2)	–0.006(1)	–0.003(1)	–0.021(1)
N(2)	2*i*		0.7724(3)	0.2081(3)	0.2361(3)	0.036(1)	0.032(1)	0.037(1)	–0.0073(9)	0.0056(9)	–0.0225(9)
C(6)	2*i*		0.6936(4)	0.3697(3)	0.2355(3)	0.033(1)	0.029(1)	0.035(1)	–0.008(1)	0.004(1)	–0.018(1)
C(7)	2*i*		0.6829(4)	0.5357(4)	0.0991(3)	0.049(2)	0.036(1)	0.035(1)	–0.013(1)	0.005(1)	–0.016(1)
C(8)	2*i*		0.8424(6)	0.6039(5)	0.1236(4)	0.081(2)	0.062(2)	0.055(2)	–0.042(2)	0.005(2)	–0.017(2)

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