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Crystal structure of diaqua[5,5'-dicarboxy-2,2'-(propane-1,3-diyl)bis(1H-imidazole-4-carboxylato- κ^4 O,O',N,N'))]zinc(II) dihydrate, $C_{13}H_{18}N_4O_{12}Zn$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.21 × 0.18 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.45 mm ⁻¹
Diffractometer, scan mode:	Bruker D8, φ and ω
$\theta_{\max}$, completeness:	27.6°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	38319, 4132, 0.028
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3750
$N(\text{param})_{\text{refined}}$:	301
Programs:	SHELX [1, 2], Bruker [3, 4]

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Abstract

$C_{13}H_{18}N_4O_{12}Zn$, triclinic, $P\bar{1}$ (no. 2), $a = 9.0311(3)$ Å, $b = 9.4464(3)$ Å, $c = 12.6951(5)$ Å, $\alpha = 109.2790(11)^\circ$, $\beta = 92.6348(12)^\circ$, $\gamma = 116.2514(10)^\circ$, $V = 892.97(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0263$, $wR_{\text{ref}}(F^2) = 0.0712$, $T = 293(2)$ K.

CCDC no.: 1937016

The molecular structure is shown in the figure (Uncoordinated water molecule and the disorder of the propenyl moiety are omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The reagents and solvents used in this work were purchased from commercial sources and used without further purification. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.05 mmol), 2,2'-(propane-1,3-diyl)bis(1H-imidazole-4,5-dicarboxylic acid (H_6 pbidc, 0.05 mmol), methanol (1 mL) and distilled water (4 mL) was sealed in a 25 mL Teflon-lined stainless steel container and heated at 393 K for 72 hours. After the mixture was cooled to room temperature at a rate of 5 K h⁻¹, colourless

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.57628(2)	0.90902(2)	0.72601(2)	0.02455(7)
N1	0.31469(16)	0.74953(16)	0.69129(11)	0.0203(3)
N2	0.04000(16)	0.58174(17)	0.65381(11)	0.0217(3)
H2A	−0.048496	0.501368	0.652992	0.026*
N3	0.70782(17)	0.81796(18)	0.79339(12)	0.0252(3)
N4	0.82540(18)	0.69593(19)	0.85872(13)	0.0296(3)
H4A	0.838009	0.627546	0.879313	0.036*
O1	0.49758(14)	1.03639(15)	0.65041(11)	0.0297(3)
O2	0.26620(15)	1.02266(17)	0.56788(12)	0.0349(3)
O3	−0.04767(16)	0.83827(19)	0.52744(14)	0.0422(3)
H3	0.055341	0.897949	0.539652	0.051*
O4	−0.22682(14)	0.60709(16)	0.55212(12)	0.0334(3)
O5	0.84619(16)	1.11732(17)	0.76480(12)	0.0367(3)
O6	1.10914(17)	1.18466(19)	0.83503(15)	0.0464(4)
H6	1.156033	1.138806	0.856642	0.056*
O7	1.24592(15)	1.04756(18)	0.90890(12)	0.0357(3)
O8	1.16830(17)	0.81224(18)	0.94498(12)	0.0370(3)
O9	0.58474(15)	0.77476(16)	0.55246(10)	0.0290(3)
H9A	0.637104	0.838741	0.517914	0.035*
H9B	0.636344	0.717931	0.551354	0.035*
O10	0.56749(16)	1.07248(19)	0.88742(11)	0.0391(3)
H10A	0.479488	1.075187	0.906511	0.047*
H10B	0.640678	1.109097	0.947941	0.047*
O11	0.71989(17)	0.33836(19)	0.63106(14)	0.0479(4)
H11A	0.653311	0.244873	0.636692	0.057*
H11B	0.646131	0.330063	0.581912	0.057*
O12	0.1587(3)	0.5603(2)	0.08474(18)	0.0699(5)
H12A	0.244207	0.651044	0.087790	0.084*
H12B	0.105117	0.609324	0.118890	0.084*
C1	0.3401(2)	0.9675(2)	0.61680(14)	0.0234(3)
C2	0.23509(19)	0.8101(2)	0.63776(13)	0.0202(3)
C3	0.06323(19)	0.7072(2)	0.61392(13)	0.0208(3)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C4	−0.0814(2)	0.7137(2)	0.56176(14)	0.0255(3)
C5	0.19330(19)	0.6113(2)	0.70014(13)	0.0213(3)
C6 ^a	0.2080(9)	0.5009(9)	0.7564(6)	0.031(2)
H6A ^a	0.185989	0.393255	0.697140	0.037*
H6B ^a	0.120415	0.475038	0.799419	0.037*
C7 ^a	0.3804(3)	0.5779(3)	0.8377(2)	0.0270(7)
H7A ^a	0.362785	0.537218	0.899347	0.032*
H7B ^a	0.430337	0.701813	0.871425	0.032*
C8 ^a	0.5045(4)	0.5293(5)	0.7751(4)	0.0351(9)
H8A ^a	0.507353	0.436525	0.790595	0.042*
H8B ^a	0.465839	0.490086	0.693072	0.042*
C6 ^b	0.2251(18)	0.505(2)	0.7560(14)	0.043(5)
H6'A ^b	0.121810	0.396341	0.735407	0.052*
H6'B ^b	0.252321	0.564349	0.838599	0.052*
C7 ^b	0.3686(6)	0.4682(6)	0.7213(4)	0.0281(13)
H7'A ^b	0.413089	0.518393	0.666712	0.034*
H7'B ^b	0.324474	0.345288	0.684251	0.034*
C8 ^b	0.5141(8)	0.5431(12)	0.8271(7)	0.042(2)
H8'A ^b	0.482974	0.593099	0.896325	0.051*
H8'B ^b	0.532239	0.452001	0.833208	0.051*
C9	0.6787(2)	0.6814(2)	0.81480(17)	0.0322(4)
C10	0.9474(2)	1.0842(2)	0.80588(16)	0.0288(4)
C11	0.88010(19)	0.9217(2)	0.82321(13)	0.0227(3)
C12	0.9556(2)	0.8476(2)	0.86483(13)	0.0230(3)
C13	1.1368(2)	0.9047(2)	0.91013(14)	0.0263(3)

^aOccupancy: 0.655(5), ^bOccupancy: 0.345(5).

crystals of [Zn(H₄pbidc)(H₂O)₂]·2H₂O were obtained (yield 57%, based on Zn).

Experimental details

The propyl group was modelled by splitting it into two parts (C6–C8 and C6'–C8'), the site-occupation factors of which refined in a ratio of 0.655(5):0.345(5). Hydrogen atoms on carbon and nitrogen atoms were positioned geometrically and refined as riding atoms, with C–H = 0.97 Å and N–H = 0.82 Å. H atoms of the nondeprotonated carboxylic acid groups of H₄pbidc^{2−} were refined as riding atoms, with O–H = 0.82 Å. The H atoms of the water molecules were located in a difference Fourier map and the O–H distance was constrained to 0.85 Å. All H atoms were refined with *U*_{iso}(H) = 1.2 *U*_{eq}(C, N, O).

Comment

Careful choice of the organic ligands is one of the most important parameters in the rational design and synthesis of complexes [5]. Imidazole-4,5-dicarboxylic acid (H₂idc) and its derivatives have been used widely as ligands for the construction of complexes since they contain N-donors as well as O-donors and can exhibit various coordination modes and high binding capacity with almost all soft and hard metal ions [6–8]. To the best of our knowledge, most of the imidazole-4,5-dicarboxylates used in the construction of complexes only

contain one imidazole-ligand. Only a few *N*-heterocyclic carboxylate ligands containing two imidazole-4,5-dicarboxylic acid motifs has been used in the preparation of complexes [9–12].

The asymmetric unit of the title structure contains one Zn(II) ion, one 5,5'-dicarboxy-2,2'-(propane-1,3-diyl)bis (1*H*-imidazole-4-carboxylate anion, two coordination water molecules and two uncoordination water molecules. The Zn1 ion is six-coordinated by two N atoms and two O atoms from the tetradentate anion in equatorial positions and by two water O atoms in axial positions, leading to a distorted octahedral environment. The Zn–N bond lengths are 2.0443(13) and 2.0886(13) Å, while the Zn–O bond lengths are in the range of 2.0810(11)–2.2501(13) Å, all of which are in the normal range of those observed in the reported Zn(II) complexes [13, 14]. The two imidazole rings are nearly co-planar, with a dihedral angle between the two least-square planes N1, N2, C2, C3, C5 and N3, N4, C9, C11, C12 of 8.2(1)°. Intramolecular O–H···O hydrogen bonds between carboxyl and carboxylate groups stabilize the molecular configuration. In addition, there are two N–H···O hydrogen bonds and eight O–H···O hydrogen bonds involving imidazoles, coordinated water molecules, uncoordinated water molecules and carboxylate/carboxylic groups of adjacent molecules. In the crystal, adjacent molecules are linked through the above hydrogen-bonding interactions into a three-dimensional supramolecular architecture, which is very similar to a literature known one [15].

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