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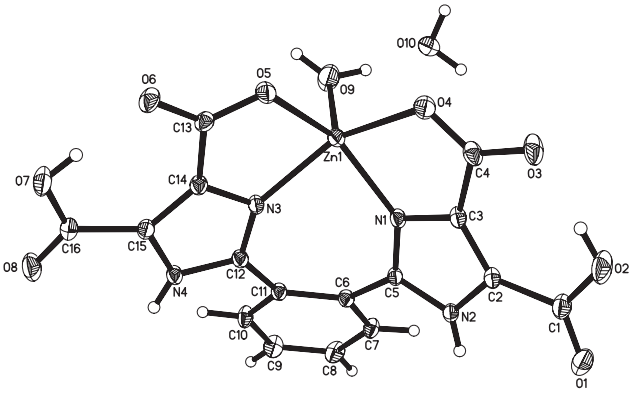
# Crystal structure of [aqua[2,2′-(1,2-phenylene)bis(1*H*-imidazole-4-carboxylato-5-carboxy)-κ$^4$*N*$^3$,*N*$^{3'}$,*O*$^4$,*O*$^{4'}$] zinc(II)] monohydrate, $C_{16}H_{10}N_4O_9Zn{\cdot}H_2O$

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## Abstract

$C_{16}H_{12}N_4O_{10}Zn$, monoclinic, *C*2/*c* (no. 15), $a = 18.6618(10)$ Å, $b = 13.5466(6)$ Å, $c = 14.7722(8)$ Å, $\beta = 108.481(2)°$, $V = 3541.9(3)$ Å$^3$, $Z = 8$, $R_{gt}(F) = 0.0392$, $wR_{ref}(F^2) = 0.1061$, $T = 293(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## Source of material

All reagents were purchased from commercial sources and used without further purification. A methanol solution (2 mL)

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**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Yellow block |
| Size: | 0.12 × 0.11 × 0.11 mm |
| Wavelength: | Mo *Kα* radiation (0.71073 Å) |
| $\mu$: | 1.46 mm$^{-1}$ |
| Diffractometer, scan mode: | Bruker D8, $\varphi$ and $\omega$ |
| $\theta_{max}$, completeness: | 27.6°, >99% |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 42976, 4093, 0.042 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 3574 |
| $N(param)_{refined}$: | 282 |
| Programs: | SHELX [1, 2], Bruker [3, 4] |

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$).

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.26353(2) | 0.40295(2) | 0.61820(2) | 0.02618(11) |
| N1 | 0.17752(12) | 0.49997(16) | 0.61009(16) | 0.0229(5) |
| N2 | 0.09564(12) | 0.60807(16) | 0.62725(17) | 0.0236(5) |
| H2A | 0.0755 | 0.6636 | 0.6338 | 0.028* |
| N3 | 0.33460(12) | 0.50341(16) | 0.70891(16) | 0.0229(5) |
| N4 | 0.40837(13) | 0.61456(16) | 0.80055(17) | 0.0254(5) |
| H4A | 0.4256 | 0.6708 | 0.8248 | 0.030* |
| O1 | −0.05281(14) | 0.5780(2) | 0.6315(2) | 0.0538(7) |
| O2 | −0.04201(13) | 0.41642(19) | 0.6188(2) | 0.0504(7) |
| H2 | −0.0110 | 0.3780 | 0.6096 | 0.076* |
| O3 | 0.05557(12) | 0.29507(16) | 0.60126(19) | 0.0418(6) |
| O4 | 0.17496(12) | 0.30331(15) | 0.60113(18) | 0.0386(5) |
| O5 | 0.34051(12) | 0.30747(14) | 0.70750(16) | 0.0330(5) |
| O6 | 0.44839(11) | 0.30101(15) | 0.82917(16) | 0.0323(5) |
| O7 | 0.54398(12) | 0.42806(17) | 0.92638(18) | 0.0396(5) |
| H7 | 0.5140 | 0.3875 | 0.8942 | 0.059* |
| O8 | 0.55500(14) | 0.59070(18) | 0.9314(2) | 0.0494(7) |
| O9 | 0.29424(14) | 0.3982(2) | 0.50384(18) | 0.0493(7) |
| H1W | 0.2557 | 0.3943 | 0.4543 | 0.074* |
| H2W | 0.3376 | 0.3832 | 0.5007 | 0.074* |
| O10 | 0.19090(13) | 0.38664(16) | 0.34254(17) | 0.0386(5) |
| H3W | 0.1818 | 0.3277 | 0.3223 | 0.058* |
| H4W | 0.1471 | 0.4031 | 0.3431 | 0.058* |
| C1 | −0.01589(17) | 0.5065(2) | 0.6241(2) | 0.0340(7) |
| C2 | 0.06170(15) | 0.5178(2) | 0.6197(2) | 0.0242(5) |
| C3 | 0.11336(15) | 0.4515(2) | 0.6089(2) | 0.0241(5) |
| C4 | 0.11433(16) | 0.3419(2) | 0.6020(2) | 0.0301(6) |
| C5 | 0.16644(14) | 0.59517(19) | 0.62259(19) | 0.0209(5) |
| C6 | 0.21735(14) | 0.67894(19) | 0.62585(19) | 0.0217(5) |
| C7 | 0.18184(15) | 0.7633(2) | 0.5775(2) | 0.0262(6) |

**Table 2** (continued)

| Atom | x | y | z | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| H7A | 0.1306 | 0.7608 | 0.5435 | 0.031* |
| C8 | 0.22075(17) | 0.8503(2) | 0.5790(2) | 0.0326(7) |
| H8A | 0.1956 | 0.9062 | 0.5484 | 0.039* |
| C9 | 0.29751(18) | 0.8530(2) | 0.6264(2) | 0.0341(7) |
| H9A | 0.3244 | 0.9111 | 0.6279 | 0.041* |
| C10 | 0.33424(16) | 0.7697(2) | 0.6714(2) | 0.0291(6) |
| H10A | 0.3862 | 0.7723 | 0.7011 | 0.035* |
| C11 | 0.29624(14) | 0.68111(19) | 0.67434(19) | 0.0217(5) |
| C12 | 0.34270(15) | 0.59950(19) | 0.72693(19) | 0.0225(5) |
| C13 | 0.39594(15) | 0.3471(2) | 0.7698(2) | 0.0250(6) |
| C14 | 0.39483(15) | 0.45662(19) | 0.77235(19) | 0.0231(5) |
| C15 | 0.44198(15) | 0.5250(2) | 0.8289(2) | 0.0242(5) |
| C16 | 0.51822(16) | 0.5181(2) | 0.9007(2) | 0.0293(6) |

of 2,2′-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylic acid) ($H_6$Phbidc, 0.05 mmol) was added dropwise to an aqueous solution (5 mL) of $Zn(NO_3)_2{\cdot}6H_2O$ (0.05 mmol), resulting in a clear solution. The mixture was then placed in a 25 mL Teflon-lined stainless steel reactor, which was sealed and heated to 393 K for 72 h. After the mixture was cooled to room temperature at a rate of 5 K $h^{-1}$, pale yellow crystals of the title compound were obtained (yield 58%, based on Zn).

## Experimental details

Hydrogen atoms bound to C and N atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and N—H = 0.86 Å. H atoms of the nondeprotonated carboxylic acid groups were refined in a similar manner, with O—H = 0.82 Å. Water H atoms were found according to the residual electron-density peaks around each water O atom and the directions of hydrogen bonds, and were then locked in position with O—H = 0.85 Å and included in the refinement with the SHELXL AFIX 3 command. All H atoms were refined with $U_{iso}$(H) = 1.2 $U_{eq}$(C, N) and 1.5 $U_{eq}$O.

## Comment

Imidazole-4,5-dicarboxylic acid ($H_3$idc) and its derivatives are widely used in the preparation of new coordination complexes since they contain *N*-atom donors, as well as *O*-atom donors, and have a rich variety of coordination modes which can lead to complexes with intriguing structures and interesting properties [5–7]. Among these ligands, 2,2′-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylic acid) ($H_6$Phbidc) is a good linker since it has twelve potential donors and can coordinate to almost all soft and hard metal ions with various coordination modes, resulting in final products with diverse structures. To the best of our knowledge, only two complexes based on $H_6$Phbidc ligand have been reported [8, 9]. In order to further enrich the categories and numbers of complexes based on this ligand, we investigated the use of $H_6$Phbidc as ligand to self-assemble with $Zn(NO_3)_2{\cdot}6H_2O$ and obtained a new complex $[Zn(H_4Phbidc)(H_2O)]{\cdot}H_2O$.

The asymmetrical unit of the title structure contains one Zn(II) ion, one 2,2′-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylate anion ($H_4Phbidc^{2-}$), one coordination water molecule and one solvent water molecule. The coordination sites of Zn(II) are occupied by two nitrogen atoms and three oxygen atoms from $H_4Phbidc^{2-}$ ligand and water molecule. The Addison parameter value of 0.021 reveals that the geometry around the Zn(II) atom can be described as slightly distorted square pyramidal [10, 11]. The Zn—O distances range from 1.949(3) to 2.087(2) Å and the Zn—N bond lengths are 2.048(2) and 2.069(2) Å, respectively; these values are comparable to distances reported in the literature for comparable Zn(II) complexes [10, 12]. In addition, there are O—H···O intramolecular hydrogen bonds between carboxyl and carboxylate groups, two N—H···O intermolecular hydrogen bonds between imidazole units and carboxylate groups, and four O—H···O intermolecular hydrogen bonds involving carboxyl groups, carboxylate groups, coordination water molecules and solvent water molecules. $[Zn(H_4Phbidc)(H_2O)]$ molecules are linked by the intermolecular hydrogen bonds mentioned above, resulting in a three-dimensional supramolecular architecture in the solid state.

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