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The crystal structure of *catena*-poly[(μ_2 -2*H*-1,2,3-triazole-4,5-dicarboxylato- κ^2 O, O')-(μ_2 -1,3-bis((1*H*-imidazol-1-yl)methyl)benzene- κ^2 N,N')) zinc(II)], C₁₈H₁₅N₇O₄Zn

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Abstract

C₁₈H₁₅N₇O₄Zn, triclinic, $P\bar{1}$ (no. 2), $a = 9.1100(8)$ Å, $b = 10.6451(7)$ Å, $c = 12.0479(8)$ Å, $\alpha = 95.238(5)^\circ$, $\beta = 112.154(7)^\circ$, $\gamma = 112.971(7)^\circ$, $V = 956.56(13)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0264$, $wR_{ref}(F^2) = 0.0731$, $T = 298$ K.

CCDC no.: 2280781

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.28 × 0.20 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.33 mm ⁻¹
Diffractometer, scan mode:	XtaLAB mini (ROW), ω
θ_{max} , completeness:	25.1°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	5299, 3397, 0.022
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3113
$N(param)_{refined}$:	272
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4], PLATON [5]

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1 Source of materials

All chemicals were purchased from commercial sources and used as received. A mixture of Zn(CH₃COO)₂·2H₂O (0.1 mmol), 2*H*-1,2,3 triazole-4,5-dicarboxylic acid (H₃tda, 0.1 mmol), 1,3-bis((1*H*-imidazol-1-yl)methyl)benzene (1,3-bib, 0.1 mmol), NaOH (0.2 mmol) and aqueous ethanol (10 mL/5 mL) was added to a 25 mL Teflon-lined stainless steel reactor and heated at 413 K for 3 days. After cooling to room temperature at a rate of 283 K h⁻¹, colorless block crystals of the title compound were obtained. Yield: 20 mg (44 %, based on ligand H₃tda). **Anal. Calcd.** for C₁₈H₁₅N₇O₄Zn (%): C, 47.08; H, 3.27; N, 21.36. Found: C, 47.10; H, 3.26; N, 21.39. (CCDC number 2280781).

2 Experimental details

Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Using OLEX2 [2], the structure was solved with the SHELXT [3] structure solution program and refined with the SHELXL [4] refinement package. Carbon-bound hydrogen atoms were placed in calculated positions ($d = 0.93$ Å for CH and $d = 0.97$ Å for CH₂) and were included in the refinement in the riding (CH) or rotating (CH₂) model approximation, with $U_{iso}(H)$ set to $1.2U_{eq}(C)$ for –CH and for –CH₂. The H atoms of phenolic hydroxyl groups in 1 were refined as rotating groups, with $d_{O-H} = 0.82$ Å and $U_{iso}(H) = 1.5U_{eq}(O)$.

3 Comment

The coordination polymers (CPs) or metal-organic frameworks (MOFs) as an important type of crystalline materials have undergone tremendous development attributable to their potential applications as functional materials, which include luminescence [5], gas sorption [6], catalysis [7], and magnetism [8]. 1*H*-1,2,3-triazole-4,5-dicarboxylic acid (H₃tda), as an excellent N- and O-donor, is soluble in water and can be partially or fully deprotonated allowing for the generation of

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
Zn1	0.87434 (3)	0.82194 (2)	0.05284 (2)	0.02718 (10)
O1	0.57230 (19)	0.71680 (17)	−0.00756 (15)	0.0419 (4)
O2	0.3328 (2)	0.7499 (2)	−0.10723 (18)	0.0548 (5)
N1	0.7839 (2)	0.94259 (16)	−0.05066 (15)	0.0258 (3)
O3	0.2637 (2)	0.9101 (2)	−0.2384 (2)	0.0597 (5)
H3	0.291753	0.868132	−0.186709	0.089*
N7	0.8489 (2)	0.64430 (17)	0.95727 (15)	0.0293 (4)
N2	0.8549 (2)	1.05215 (17)	−0.09257 (16)	0.0295 (4)
N6	0.8794 (2)	0.50027(18)	0.83539 (16)	0.0320 (4)
N3	0.7315 (2)	1.08518 (18)	−0.16350 (17)	0.0316 (4)
O4	0.4019 (2)	1.07885 (19)	−0.30825 (19)	0.0579 (5)
N4	0.9107 (2)	0.82373 (18)	0.22759 (15)	0.0309 (4)
N5	0.8448 (3)	0.7734 (2)	0.38047 (17)	0.0407 (5)
C2	0.5761 (2)	0.9945 (2)	−0.16769 (18)	0.0276 (4)
C1	0.6087 (2)	0.9048 (2)	−0.09637 (18)	0.0257 (4)
C18	0.7270 (3)	0.5061 (2)	0.9364 (2)	0.0361 (5)
H18	0.645613	0.478529	0.969200	0.043*
C3	0.4070 (3)	0.9992 (2)	−0.2444 (2)	0.0393 (5)
C16	0.9385 (3)	0.6350 (2)	0.89491 (19)	0.0324 (5)
H16	1.030667	0.712461	0.892832	0.039*
C4	0.4958 (3)	0.7804 (2)	−0.0673 (2)	0.0340 (5)
C6	1.0643 (3)	0.8929 (3)	0.3392 (2)	0.0405 (5)
H6	1.177359	0.951246	0.347882	0.049*
C15	0.9313 (3)	0.4518 (3)	0.7447 (2)	0.0412 (5)
H15A	0.919124	0.357188	0.745122	0.049*
H15B	1.055389	0.514977	0.768145	0.049*
C13	0.8149 (3)	0.4496 (2)	0.6151 (2)	0.0382 (5)
C17	0.7447 (3)	0.4177 (2)	0.8612 (2)	0.0397 (5)
H17	0.678055	0.319325	0.832184	0.048*
C5	0.7829 (3)	0.7542 (2)	0.2580 (2)	0.0366 (5)
H5	0.663746	0.698487	0.200632	0.044*
C14	0.8345 (3)	0.5765 (2)	0.5851 (2)	0.0389 (5)
H14	0.926337	0.661864	0.643305	0.047*
C7	1.0242 (3)	0.8621 (3)	0.4340 (2)	0.0469 (6)
H7	1.103066	0.894850	0.518622	0.056*
C9	0.7208 (4)	0.5793 (3)	0.4708 (2)	0.0445 (6)
C12	0.6794 (4)	0.3235 (3)	0.5264 (2)	0.0508 (6)
H12	0.664164	0.237358	0.544294	0.061*
C8	0.7354 (4)	0.7187 (3)	0.4458 (3)	0.0540 (7)
H8A	0.616362	0.706903	0.395952	0.065*
H8B	0.786585	0.788705	0.524613	0.065*
C10	0.5860 (4)	0.4508 (3)	0.3834 (2)	0.0591 (7)
H10	0.509172	0.450408	0.305874	0.071*
C11	0.5661 (4)	0.3246 (3)	0.4113 (3)	0.0647 (8)
H11	0.475905	0.239172	0.352403	0.078*

abundant coordination modes such as μ_3 , μ_4 , μ_5 and μ_6 -bridging modes in monodentate, chelating-bidentate and bridging-bidentate fashions linking metal centers. On the other hand, the aromatic triazole ring of H_3tda may take part in the formation of π - π and $C-H\cdots\pi$ interactions whilst the oxygen and nitrogen atoms may act as the acceptors or donors to form intermolecular and intramolecular hydrogen bonds ($O/N-H\cdots O/N$, $C-H\cdots O/N$). To date, some complexes based on the H_3tda ligand and different metal ions have been reported [9–11]. In addition, the introduction of appropriate secondary ligands has been demonstrated to be a very effective approach for constructing diverse coordination frameworks. The two-ligand assembly system, consisting of two spacers and capable of providing more variability to build much more complicated structures [12, 13]. Taking into the mentioned above, we selected H_3tda as ligand and luminescent d^{10} ions (Zn^{II}) as metal center in the presence of N-containing secondary ligands to construct the new CPs.

The single-crystal X-ray diffraction structural analysis has revealed that I is an one dimensional coordination polymer, whose asymmetric unit is comprised of one Zn^{2+} , one partly deprotonated ligand $Htda^{2-}$ and a neutral auxiliary N-containing ligand 1,3-bib (Figure 1). The metal ion Zn^{2+} is five-coordinated with N1, N2ⁱⁱ, N4, N7ⁱ and O1 (symmetry codes: i x, y, z−1; ii −x, 2−y, −z) atoms from two symmetry-related $Htda^{2-}$ and 1,3-bib ligands, resulting in a slightly distorted trigonal bipyramid $\{ZnN_4O\}$ configuration. The Zn–O bond distance is 2.3002(15) Å, and those of Zn–N distances are 2.0012(16) to 2.1261(16) Å, within the normal range [14]. The N(O)–Zn–O(N) angles fall in the 75.36(6)°–169.37(6)° range. It is interesting to note that the deprotonated carboxylate group of the $Htda^{2-}$ anion coordinate $Zn(II)$ in a monodentate bridging mode ($\eta^1: \eta^0$) and the non-deprotonated carboxylate group features formation a intramolecular hydrogen bond ($O3-H3\cdots O2$) with the adjacent deprotonated uncoordinated carboxylate O2. Two symmetry-related $Htda^{2-}$ ligands bond to two Zn^{2+} cations by the upside-down fashion through their deprotonated carboxylate O-atoms (O1, O1ⁱⁱⁱ) and triazole N-atoms (N1, N2, N1ⁱⁱⁱ, N2ⁱⁱⁱ; symmetry codes: iii 2−x, 2−y, −z), resulting in substructural blocks $\{[Zn(Htda)]^2\}$. These neighboring $\{[Zn(Htda)]^2\}$ are further interconnected through two μ_2 1,3-bib bridges to generate an one dimensional zigzag infinite chain framework with a Zn $\cdots$ Zn separation of 12.04(8)°.

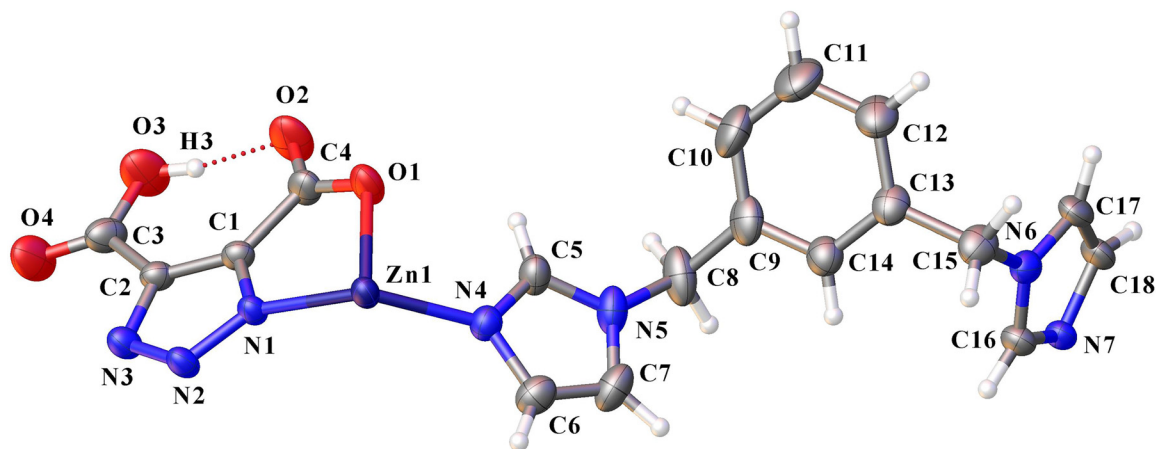


Figure 1: The asymmetric unit structure of I, showing the atom numbering scheme. Displacement ellipsoids are shown at the 30 % probability level. The dashed line shows the intra-molecular O–H...O hydrogen bond.

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