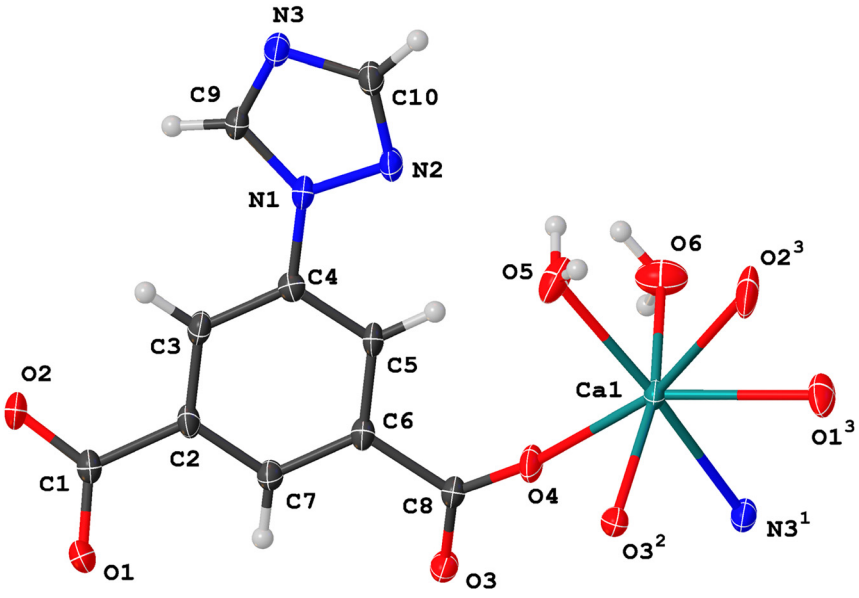
Xing-Ling Zhao*, Qi-Hang Zhang, Jian-Feng Yang and Xue-Yuan Wu

Crystal structure of poly[diaqua- (μ_4-5-(1*H*-1,2,4-triazol-1-yl)benzene-1,3-dicarboxylato-κ^5N:*O,O':O'':O'''*)calcium(II), $C_{10}H_9CaN_3O_6$



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Abstract

$C_{10}H_9CaN_3O_6$, monoclinic, $P2_1/n$, a = 9.3441(2) Å, b = 6.6142(2) Å, c = 18.6509(4) Å, β = 92.001(2)°, V = 1151.99(5) Å^3, Z = 4, $R_{gt}(F)$ = 0.0398, wR_{ref} (F^2) = 0.1101, T = 298 K.

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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:	0.25 × 0.24 × 0.22 mm
Wavelength:	CuKα radiation (1.54184 Å)
μ:	5.05 mm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD 6000, φ and ω
θ_{max}, completeness:	68.2°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5318, 2094, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 1897
$N(param)_{refined}$:	183
Programs:	Bruker [1], Olex2 [2], Shelx [3, 4]

1 Source of materials

The 5-(*1H*-1,2,4-triazol-1-yl)-1,3-benzenedicarboxylic acid (H_2L) was purchased from Yanshen Technology Co., Ltd. Other reagents were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. $Ca(NO_3)_2{\cdot}4H_2O$ (0.012 g, 0.1 mmol) and H_2L (0.008 g, 0.0343 mmol) were dissolved in a mixture of 4 mL *N*,*N*-dimethylformamide (DMF), 4 mL ethylene glycol and 2 mL deionized water. The mixture was sealed in a 20 mL capped vial, heated to 92 °C for 48 h and cooled to room

***Corresponding author: Xing-Ling Zhao**, College of Chemistry and Chemical Engineering, Weifang University, Weifang, Shandong 261061, P.R. China, E-mail: zhaoxinglingChem@outlook.com. https://orcid.org/0009-0003-4536-1790
Qi-Hang Zhang, Jian-Feng Yang and Xue-Yuan Wu, College of Chemistry and Chemical Engineering, Weifang University, Weifang, Shandong 261061, P.R. China

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ca1	0.70218 (4)	0.69313 (8)	0.10667 (2)	0.01828 (18)
O1	0.34732 (19)	0.7403 (3)	0.50637 (9)	0.0305 (5)
O2	0.13157 (19)	0.6297 (4)	0.47653 (10)	0.0383 (5)
O3	0.74521 (16)	0.5110 (3)	0.34057 (8)	0.0206 (4)
O4	0.68925 (17)	0.5865 (3)	0.22629 (9)	0.0257 (4)
O5	0.45674 (18)	0.7645 (3)	0.08915 (10)	0.0317 (5)
H5A	0.412685	0.659891	0.072319	0.048*
H5B	0.445446	0.862550	0.059316	0.048*
O6	0.6350 (2)	0.3498 (3)	0.08111 (11)	0.0366 (5)
H6A	0.542991	0.338160	0.079399	0.055*
H6B	0.669718	0.270910	0.114211	0.055*
N1	0.1516 (2)	0.5706 (3)	0.20431 (10)	0.0193 (4)
N2	0.1935 (2)	0.6058 (3)	0.13548 (10)	0.0210 (5)
N3	−0.0464 (2)	0.5774 (3)	0.13869 (10)	0.0206 (4)
C1	0.2604 (2)	0.6662 (4)	0.46223 (12)	0.0206 (5)
C2	0.3091 (2)	0.6206 (4)	0.38786 (12)	0.0190 (5)
C3	0.2088 (2)	0.6096 (4)	0.33160 (12)	0.0192 (5)
H3	0.112031	0.626366	0.339985	0.023*
C4	0.2537 (2)	0.5736 (4)	0.26259 (12)	0.0175 (5)
C5	0.3984 (2)	0.5503 (4)	0.24943 (12)	0.0183 (5)
H5	0.427512	0.526191	0.203035	0.022*
C6	0.4992 (2)	0.5632 (4)	0.30578 (12)	0.0178 (5)
C7	0.4547 (2)	0.5975 (4)	0.37554 (12)	0.0187 (5)
H7	0.521675	0.604946	0.413510	0.022*
C8	0.6570 (2)	0.5516 (4)	0.28953 (12)	0.0190 (5)
C9	0.0088 (2)	0.5543 (4)	0.20439 (12)	0.0191 (5)
H9	−0.043970	0.530314	0.244887	0.023*
C10	0.0711 (2)	0.6083 (4)	0.09882 (12)	0.0207 (5)
H10	0.064985	0.629550	0.049517	0.025*

temperature at a rate of 10 °C/h. Colorless needle crystals of the title complex were obtained, yielding 37 % (based on the organic ligand).

2 Experimental details

The crystal structure of the complex was solved using the SHELXT program and refined with the SHELXL program. All non-hydrogen atoms (Ca-, C-, N- and O-atom) were refined with anisotropic displacement parameters, while the hydrogen atoms were placed in idealized positions with isotropic thermal parameters.

3 Comment

As a semi-rigid triazole-carboxylic ligand, containing both monodentate 1,2,4-triazol group and monodentate or bidentate carboxylate group, 5-(1H-1,2,4-triazol-1-yl)-1,3-benzenedicarboxylic acid (H_2L) has been used to build metal complexes. The metal ions in the reported complexes are transition metals and rare earth metals [5–8], but the alkaline earth metals containing complexes have not been exploited. Hence, to extend the family of the metal complexes based on H_2L, the title 3D Ca(II)-complex was synthesized under hydrothermal condition.

The asymmetric unit contains one calcium(II) ion, one deprotonated L ligand and two coordinated water molecules. The Ca(II) cation is hepta-coordinated, bonded with one N-atom ($N3^{1+x,y,z}$) derived from one L ligand, four O-atoms ($O1^{1/2+x,3/2-y,-1/2+z}$, $O2^{1/2+x,3/2-y,-1/2+z}$, $O3^{1/2+x,3/2-y,-1/2+z}$, O4) derived from another three different L ligands and two O-atoms (O5, O6) derived from two different coordinated water molecules. The distances of Ca–O are in the range of 2.3468(16)–2.7548(19) Å and 2.5223(19), respectively. These bond lengths are analogous to the reported L-based crystal structures [9–12]. The dihedral angle between the triazole heterocyclic ring and benzene ring is 157.2°. For the L ligand, each ligand coordinated with four calcium(II) ions, and the two carboxyl groups display two different coordination modes ($\mu_2 - \eta^1{:}\eta^1$, η^2). It is worth noting that in the crystal exist p-p stacking interactions (between the triazole and benzene rings, centroid-centroid distance: 3.3841(1)–3.4166(1) Å, shift distance 0.904–1.037 Å) and O–H···O hydrogen bonding interactions (O5–H5A···$N2^{1/2+x,1/2-y,-1/2+z}$, O5–H5B···$O2^{1-x,-y,-z}$, O6–H6B···$O3^{-x,1-y,-z}$). Finally, the calcium(II) ions and deprotonated L ligands are connected to each other and result in a 3D supermolecular network.

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