



# Synthesis, crystal structure and Hirshfeld surface analysis of a new copper(II) complex based on diethyl 2,2'-(4*H*-1,2,4-triazole-3,5-diyl)diacetate

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**Keywords:** copper; copper(II) complex; crystal structure; 1,2,4-triazole; Hirshfeld surface analysis.

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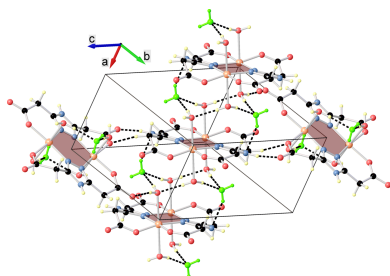
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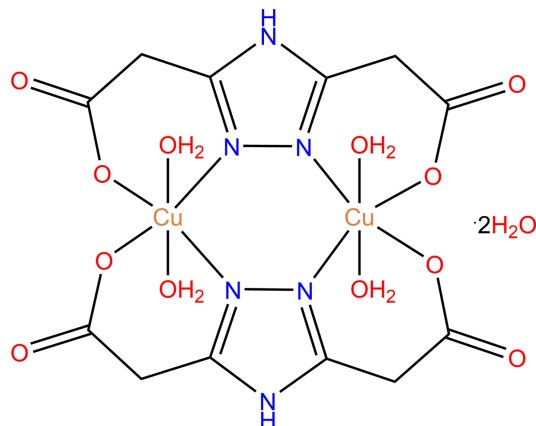
The title compound, bis[ $\mu$ -2,2'-(4*H*-1,2,4-triazole-3,5-diyl)diacetato]bis[diaqua-copper(II)] dihydrate, [Cu<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>].2H<sub>2</sub>O, is a dinuclear octahedral Cu<sup>II</sup> triazole-based complex. The central copper atoms are hexacoordinated by two nitrogen atoms in the equatorial positions, two equatorial oxygen atoms of two carboxylate substituents in position 3 and 5 of the 1,2,4-triazole ring, and two axial oxygen atoms of two water molecules. Two additional solvent water molecules are linked to the title molecule by O—H···N and O···H—O hydrogen bonds. The crystal structure is built up from the parallel packing of discrete supramolecular chains running along the *a*-axis direction. Hirshfeld surface analysis suggests that the most important contributions to the surface contacts are from H···O/O···H (53.5%), H···H (28.1%), O···O (6.3%) and H···C/C···H (6.2%) interactions. The crystal studied was twinned by a twofold rotation around [100].

## 1. Chemical context

1,2,4-Triazole-based organic compounds have been widely used as ligands for the synthesis of transition-metal complexes (Haasnoot, 2000; Aromí *et al.*, 2011; Farooq, 2021). Depending on the substituents on the azole core, the title ligands can coordinate not only in a monodentate manner (Cudzilo *et al.*, 2011; Zaleski *et al.*, 2005), but also as a linker binding two metal ions (Drabent *et al.*, 2001; Zhang *et al.*, 2005) and thus play an important role in the design of new polynuclear coordination compounds. In particular, copper(II) coordination compounds based on 1,2,4-triazoles have attracted the interest of chemists due to their magnetic properties (Petrenko *et al.*, 2020; Kaase *et al.*, 2014), bioactivity (Hernández-Gil *et al.*, 2013; Ferrer *et al.*, 2004) and catalysis (Thorseth *et al.*, 2013; Li *et al.*, 2015). Dinuclear copper(II) complexes can promote single- and double-strand DNA cleavage in both aerobic and anaerobic conditions (Li *et al.*, 2010). Being much cheaper than most metals, copper(II) coordination compounds are promising substances for exploration as catalysts. Previously we reported that a dinuclear Cu<sup>II</sup> complex based on 5-methyl-3-(2-pyridyl)-1,2,4-triazole as a ligand can selectively catalyse the oxidation of styrene towards benzaldehyde and of cyclohexane to KA oil (a mixture of cyclohexanol and cyclohexanone; Petrenko *et al.*, 2021). Finally, Cu<sup>II</sup> complexes can exhibit urease inhibitory activities (Xu *et al.*, 2015). Since dinuclear copper(II) complexes with triazole bridges can exhibit catalytic proper-

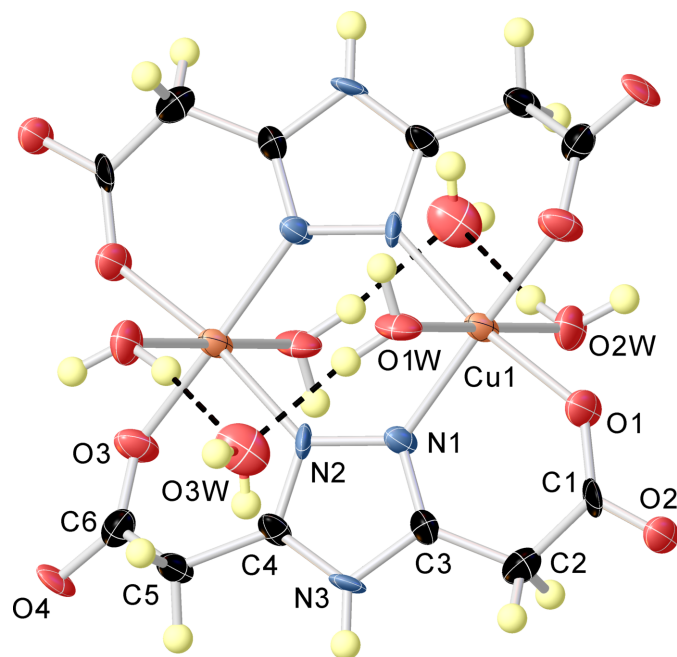


ties, we decided to continue our research in this direction. Herein, we describe the synthesis, crystal structure, and results of Hirshfeld surface analysis of the title compound,  $[\text{Cu}_2(\text{C}_6\text{H}_5\text{N}_3\text{O}_4)_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ , which potentially exhibits catalytic, inhibitory, and magnetic properties.



## 2. Structural commentary

The title compound (Fig. 1), a dinuclear copper(II) 1,2,4-triazole-based complex, crystallizes in the monoclinic,  $P2_1/n$  space group. The asymmetric unit consists of one copper(II) ion, one 4*H*-1,2,4-triazole-3,5-dicarboxylate ligand, two coordinated water molecules and one solvent water molecule. The structure of the title compound can be described as a neutral complex of formula  $[\text{Cu}_2(\text{C}_6\text{H}_5\text{N}_3\text{O}_4)_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$  in which the triazole ligand is coordinated in a tetradentate way. The  $\text{Cu}^{\text{II}}$  ion has a distorted  $\text{N}_2\text{O}_4$  octahedral geometry formed by



**Figure 1**  
The molecular structure of the title compound with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

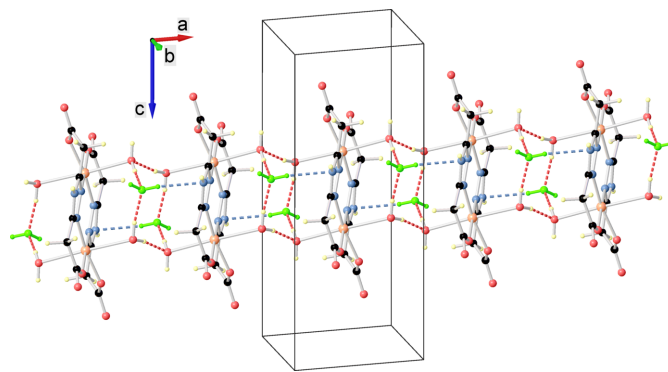
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1W}-\text{H1WA}\cdots\text{O4}^{\text{i}}$	0.87	1.91	2.762 (5)	165
$\text{O1W}-\text{H1WB}\cdots\text{O3W}$	0.87	1.94	2.797 (5)	169
$\text{O2W}-\text{H2WA}\cdots\text{O1W}^{\text{ii}}$	0.85	2.03	2.880 (4)	170
$\text{O2W}-\text{H2WB}\cdots\text{O2}^{\text{iii}}$	0.87	1.89	2.744 (4)	167
$\text{N3}-\text{H3}\cdots\text{O4}^{\text{iv}}$	0.88	1.81	2.670 (5)	165
$\text{C5}-\text{H5B}\cdots\text{O3}^{\text{iv}}$	0.99	2.32	3.257 (6)	158

Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (ii)  $x - 1, y, z$ ; (iii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (iv)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ .

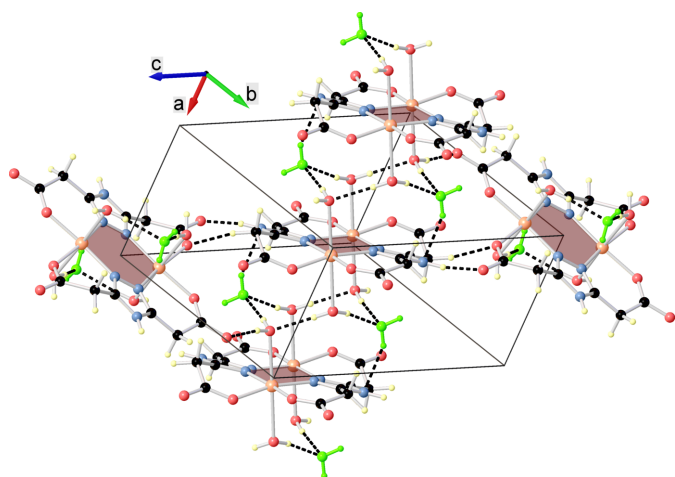
two nitrogen atoms in the equatorial positions with  $\text{Cu1}-\text{N1} = 1.982 (3) \text{\AA}$  and  $\text{Cu1}-\text{N2}^{\text{i}}$  [symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ ] =  $1.990 (4) \text{\AA}$  bond distances, two equatorial oxygen atoms of two carboxylate substituents in position 3 and 5 of the triazole ring [ $\text{Cu1}-\text{O1} = 1.962 (3) \text{\AA}$  and  $\text{Cu1}-\text{O3}^{\text{i}} = 1.974 (3) \text{\AA}$ ], and two axial oxygen atoms of two water molecules with  $\text{Cu1}-\text{O1W} = 2.497 (3) \text{\AA}$  and  $\text{Cu1}-\text{O2W} = 2.484 (3) \text{\AA}$  bond distances. The  $\text{Cu1}-\text{Cu1}^{\text{i}}$  intermetallic distance in the complex molecule is  $3.9866 (15) \text{\AA}$ . Two copper atoms bridged by two 4*H*-1,2,4-triazole-3,5-dicarboxylate ligands form a non-planar six-membered bimetallic ring. In addition, four six-membered non-planar chelate rings are formed due to the presence of carboxylate substituents at the 3 and 5 positions of the 1,2,4-triazole rings. There are medium strength intermolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds between the main compound and solvent water molecules. Intermolecular  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds between two complex molecules are also observed (Table 1).

## 3. Supramolecular features

The crystal structure is built up from the parallel packing of discrete supramolecular chains running along the *a*-axis direction with a  $\text{Cu}\cdots\text{Cu}$  separation of  $6.5248 (11) \text{\AA}$  (Fig. 2). Within the chain, the complex molecules interact through  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds, while the association with the interstitial water molecules occurs *via*  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds (Fig. 3, Table 1).



**Figure 2**  
One-dimensional supramolecular chain running parallel to the *a* axis and viewed along the *b* axis. Solvent water molecules are shown in green,  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds are shown as red and blue dotted lines, respectively.



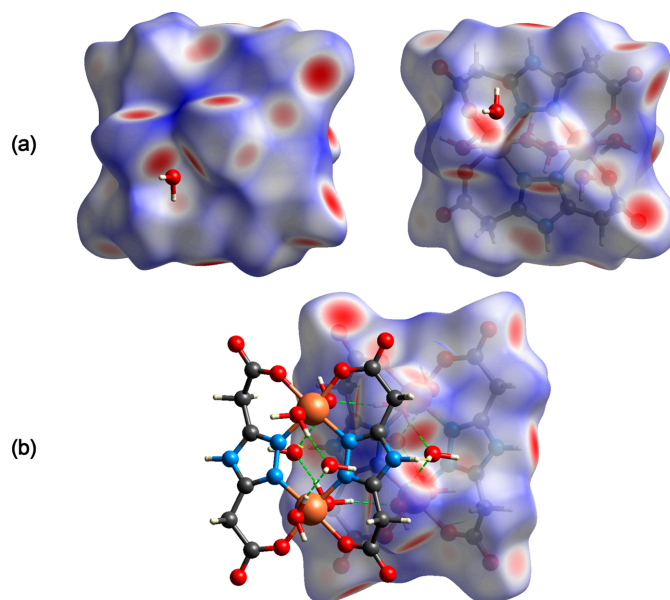
**Figure 3**  
Partial view of the crystal packing showing hydrogen-bond contacts between adjacent molecules.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD version 5.41, update of November 2021; Groom *et al.*, 2016) for the  $\text{Cu}_2(\text{C}_2\text{N}_3)_2\text{O}_4$  moiety (two 1,2,4-triazole ring skeletons connected *via* two Cu atoms; each copper atom is coordinated by two oxygen atoms) revealed 48 hits. Most similar to the title compound are dinuclear copper(II) complexes with following database refcodes: COCZAV (Ferrer *et al.*, 1999), DODRET and DODRIX (Prins *et al.*, 1985), FIVGEY (Matthews *et al.*, 2003), JOZXAX (van Koningsbruggen *et al.*, 1992) and VALZOA (Doroschuk, 2016). All coordination compounds have many common characteristics, but there are also some minor differences between them. All these dinuclear copper(II) complexes contain two 1,2,4-triazole-based ligands. The triazole derivatives have two substituents at positions 3 and 5 of the triazole ring. The substituents containing donor atoms also participate in coordination with the copper atom. These ligands exhibit bridging functions and link two copper atoms at distances in the range of 3.85 to 4.09 Å. Two six-coordinated copper atoms are involved in the formation of a six-membered ring. There are two water molecules in the axial positions of the central copper atom in the title compound and the compound JOZXAX. In other complexes, one axial position in the geometric environment of the copper atom is occupied by a water molecule, while the second axial position is typically occupied by an anion of an inorganic salt. The title compound crystallizes in the monoclinic  $P2_1/n$  space group. Five complexes crystallized in the triclinic,  $P\bar{1}$  space group, while JOZXAX crystallized in the monoclinic  $C2/c$  space group.

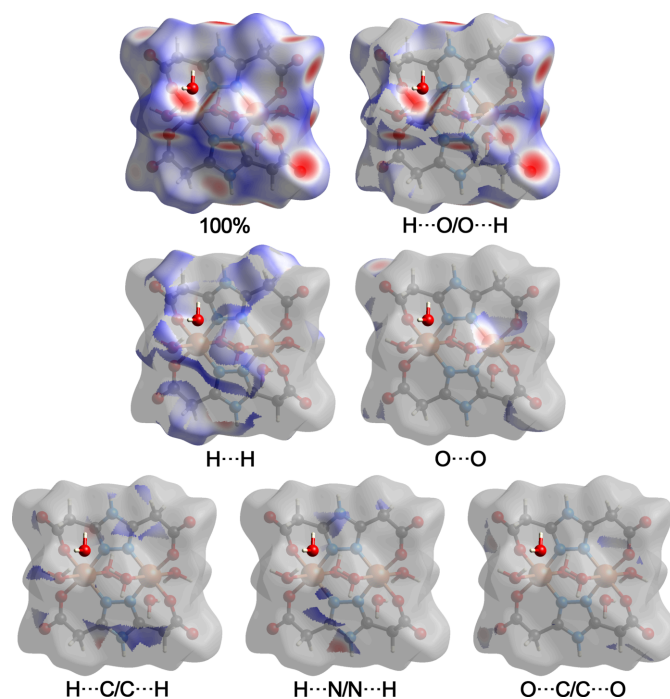
#### 5. Hirshfeld surface analysis

The Hirshfeld surface analysis was performed and the associated two-dimensional fingerprint plots were generated using *Crystal Explorer 17.5* software (Spackman *et al.*, 2021), with a standard resolution of the three-dimensional  $d_{\text{norm}}$  surfaces

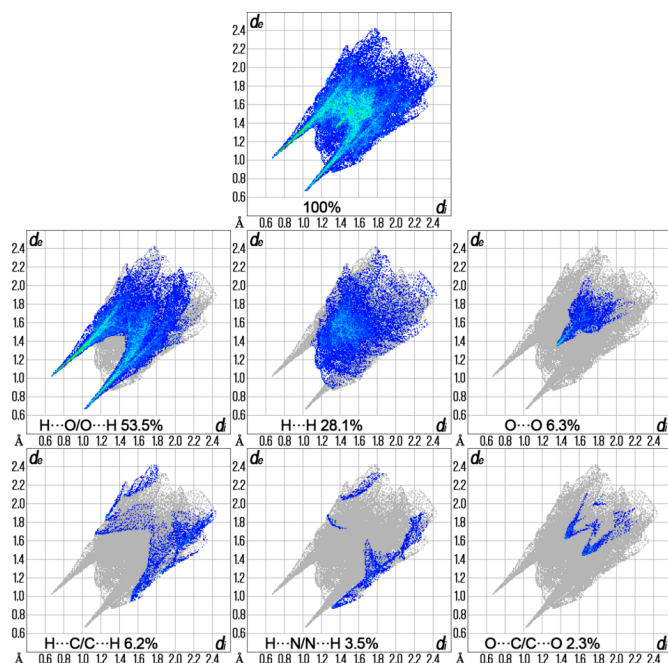


**Figure 4**  
(a) Two projections of the Hirshfeld surfaces mapped over  $d_{\text{norm}}$  showing the intermolecular interactions within the molecule and (b) an illustration of selected  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{N}$  interactions depicted by green and yellow dashed lines, respectively.

(shown in Figs. 4 and 5). The dark-red spots arise as a result of short interatomic contacts and represent negative  $d_{\text{norm}}$  values on the surface, while the other weaker intermolecular interactions appear as light-red spots. The Hirshfeld surfaces mapped over  $d_{\text{norm}}$  are shown for the  $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$ ,  $\text{H}\cdots\text{H}$ ,  $\text{O}\cdots\text{O}$ ,  $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ ,  $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$  and  $\text{O}\cdots\text{C}/\text{C}\cdots\text{O}$



**Figure 5**  
Hirshfeld surface representations with the function  $d_{\text{norm}}$  plotted onto the surface for the different interactions.



**Figure 6**  
The overall two-dimensional fingerprint plot and those delineated into specified interactions.

contacts (Fig. 6), the overall two-dimensional fingerprint plot and the decomposed two-dimensional fingerprint plots are given in Fig. 7. Two pairs of N3–H3...O4 interatomic contacts with lengths of 1.696 Å are the shortest. The most significant contributions to the overall crystal packing are from H...O/O...H (53.5%), H...H (28.1%), O...O (6.3%) and H...C/C...H (6.2%) contacts. The predominance of contributions from H...H and H...O contacts to the overall crystal packing is typical not only for the title compound and other dinuclear copper(II) complexes with triazole-containing ligands but also of copper(II) coordination compounds with azole-based ligands in general. There is a small contribution from H...N/N...H (3.5%) and O...C/C...O (2.3%) weak intermolecular contacts. The relative percentage contributions to the overall Hirshfeld surface by elements: H...all atoms = 55.4%, O...all atoms = 35.6%, C...all atoms = 6.1%, N...all atoms = 3.0% and Cu...all atoms = 0%. In addition, quantitative physical properties of the Hirshfeld surface for this compound were obtained, such as molecular volume (444.48 Å<sup>3</sup>), surface area (384.06 Å<sup>2</sup>), globularity (0.733) and asphericity (0.063). The asphericity value for the title compound at 0.063 is close to zero, indicating a near isotropic nature. The globularity value (0.733) is less than one, suggesting a modest deviation from a spherical surface and indicating that this molecular surface is more structured compared to a sphere.

## 6. Synthesis and crystallization

**[Cu<sub>2</sub>(HL)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O.** An aqueous solution (2 ml) of Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.296 g, 1 mmol) was added to 2 ml of an

**Table 2**  
Experimental details.

Crystal data	[Cu <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> N <sub>3</sub> O <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]·2H <sub>2</sub> O
Chemical formula	601.44
<i>M</i> <sub>r</sub>	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Crystal system, space group	200
Temperature (K)	6.5176 (13), 9.4854 (19), 15.967 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	93.035 (15)
β (°)	985.7 (3)
<i>V</i> (Å <sup>3</sup> )	2
<i>Z</i>	Mo <i>K</i> α
Radiation type	2.25
μ (mm <sup>-1</sup> )	0.56 × 0.37 × 0.33 × 0.22 (radius)
Crystal size (mm)	
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	For a sphere ( <i>CrysAlis PRO</i> ; Rigaku OD, 2024)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.488, 0.498
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	2569, 2569, 1969
<i>R</i> <sub>int</sub>	0.053
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.686
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.041, 0.096, 1.00
No. of reflections	2569
No. of parameters	159
No. of restraints	18
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.63, -0.53

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXS* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

aqueous solution of ethyl 2,2'-(1*H*-1,2,4-triazole-3,5-diyl)diacetate (0.241 g, 1 mmol) to give a clear blue solution. The blue crystals that precipitated after 2 days were filtered off, washed with water, and dried in air (Kiseleva *et al.*, 1990). Yield 0.247 g (82.18%). IR data (in KBr, cm<sup>-1</sup>): 3404, 3224, 1638, 1620, 1606, 1568, 1540, 1454, 1418, 1400, 1386, 1274, 1250, 1052, 956, 752, 644, 578. Analysis calculated for C<sub>12</sub>H<sub>22</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>14</sub> (601.43): C, 23.96%; H, 3.69%; N, 13.97%. Found: C, 23.88%; H, 3.72%; N, 13.88%.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal studied was twinned by a twofold rotation around [100]. The corresponding HKLF5 generated by the *CrysAlis* program was used for refinement. The O- and N-bound hydrogen atoms were identified in difference-Fourier maps and refined isotropically with positional restraints. All other H atoms were placed in calculated positions and refined using a riding model with C–H = 0.99 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C).

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## supporting information

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## Synthesis, crystal structure and Hirshfeld surface analysis of a new copper(II) complex based on diethyl 2,2'-(4*H*-1,2,4-triazole-3,5-diyl)diacetate

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### Computing details

Bis[ $\mu$ -2,2'-(4*H*-1,2,4-triazole-3,5-diyl)diacetato]bis[diaquacopper(II)] dihydrate

#### Crystal data

[Cu<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] $\cdot$ 2H<sub>2</sub>O

$M_r = 601.44$

Monoclinic,  $P2_1/n$

$a = 6.5176$  (13) Å

$b = 9.4854$  (19) Å

$c = 15.967$  (2) Å

$\beta = 93.035$  (15)°

$V = 985.7$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 612$

$D_x = 2.026$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 833 reflections

$\theta = 2.5$ – $28.3$ °

$\mu = 2.25$  mm<sup>-1</sup>

$T = 200$  K

Prism, clear intense green

$0.56 \times 0.37 \times 0.33 \times 0.22$  (radius) mm

#### Data collection

Xcalibur, Eos

diffractometer

Detector resolution: 16.1593 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: for a sphere

(CrysAlisPro; Rigaku OD, 2024)

$T_{\min} = 0.488$ ,  $T_{\max} = 0.498$

2569 measured reflections

2569 independent reflections

1969 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 29.2$ °,  $\theta_{\min} = 2.5$ °

$h = -8$ → $8$

$k = -12$ → $12$

$l = -21$ → $21$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.096$

$S = 1.00$

2569 reflections

159 parameters

18 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.63$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.53$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refined as a 2-component twin.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.48120 (9)	0.59062 (7)	0.61179 (3)	0.01441 (17)
O1	0.4081 (5)	0.7706 (4)	0.66289 (18)	0.0196 (8)
O1W	0.8274 (4)	0.6812 (4)	0.57854 (18)	0.0176 (8)
H1WA	0.849334	0.760096	0.605348	0.026*
H1WB	0.826653	0.704497	0.525777	0.026*
O2	0.3198 (5)	0.9950 (4)	0.67791 (19)	0.0167 (8)
O2W	0.1424 (5)	0.4979 (4)	0.65012 (18)	0.0220 (8)
H2WA	0.058325	0.553892	0.624170	0.033*
H2WB	0.134335	0.500812	0.704360	0.033*
O3	0.3906 (5)	0.4446 (3)	0.27539 (18)	0.0181 (8)
O3W	0.8739 (6)	0.7755 (4)	0.4147 (2)	0.0255 (9)
H3WA	0.888191	0.700243	0.386753	0.038*
H3WB	0.812698	0.836952	0.383823	0.038*
O4	0.3227 (4)	0.5597 (3)	0.15734 (18)	0.0148 (8)
N1	0.3931 (5)	0.6605 (4)	0.4985 (2)	0.0110 (9)
N2	0.4400 (5)	0.6031 (4)	0.42206 (19)	0.0104 (8)
N3	0.3370 (5)	0.8181 (4)	0.4021 (2)	0.0115 (9)
H3	0.302775	0.898014	0.377062	0.014*
C1	0.3396 (6)	0.8877 (6)	0.6350 (3)	0.0114 (11)
C2	0.2603 (7)	0.8982 (5)	0.5444 (3)	0.0190 (12)
H2A	0.108417	0.894494	0.543222	0.023*
H2B	0.298467	0.992262	0.523253	0.023*
C3	0.3309 (6)	0.7904 (6)	0.4839 (3)	0.0112 (11)
C4	0.4041 (6)	0.7029 (5)	0.3657 (3)	0.0126 (11)
C5	0.4403 (7)	0.6970 (5)	0.2737 (3)	0.0134 (11)
H5A	0.587709	0.714517	0.265692	0.016*
H5B	0.360820	0.773275	0.244772	0.016*
C6	0.3793 (6)	0.5556 (6)	0.2329 (3)	0.0145 (12)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0258 (3)	0.0090 (3)	0.0082 (2)	0.0024 (3)	-0.0025 (2)	0.0000 (3)
O1	0.0343 (19)	0.0125 (18)	0.0119 (15)	0.0043 (18)	0.0005 (15)	-0.0056 (15)
O1W	0.0274 (17)	0.013 (2)	0.0122 (15)	-0.0017 (18)	-0.0028 (13)	-0.0004 (17)
O2	0.0299 (18)	0.0093 (19)	0.0107 (16)	0.0032 (18)	0.0007 (14)	-0.0018 (15)
O2W	0.0337 (19)	0.019 (2)	0.0129 (16)	0.012 (2)	-0.0023 (14)	0.0013 (17)
O3	0.034 (2)	0.008 (2)	0.0124 (16)	-0.0008 (17)	-0.0041 (14)	0.0030 (15)

O3W	0.038 (2)	0.017 (2)	0.0212 (17)	0.000 (2)	-0.0018 (16)	-0.0045 (19)
O4	0.0280 (17)	0.010 (2)	0.0061 (15)	-0.0003 (16)	-0.0051 (12)	0.0013 (15)
N1	0.0183 (19)	0.008 (2)	0.0063 (17)	-0.0002 (19)	-0.0012 (15)	0.0007 (17)
N2	0.0103 (16)	0.015 (2)	0.0066 (14)	0.003 (2)	0.0029 (14)	-0.0029 (19)
N3	0.019 (2)	0.008 (2)	0.0077 (18)	0.0014 (19)	-0.0009 (15)	0.0053 (18)
C1	0.013 (2)	0.017 (3)	0.0041 (19)	-0.003 (2)	0.0056 (16)	0.000 (2)
C2	0.026 (3)	0.013 (3)	0.018 (2)	0.005 (3)	0.0021 (18)	-0.001 (3)
C3	0.014 (2)	0.012 (3)	0.007 (2)	0.000 (2)	-0.0001 (17)	0.004 (2)
C4	0.014 (2)	0.013 (3)	0.012 (2)	-0.003 (2)	0.0015 (18)	0.003 (2)
C5	0.019 (2)	0.010 (3)	0.011 (2)	0.001 (2)	-0.0012 (19)	-0.001 (2)
C6	0.011 (2)	0.018 (3)	0.016 (2)	0.004 (2)	0.0031 (17)	-0.001 (2)

*Geometric parameters (Å, °)*

Cu1—O1	1.962 (3)	O4—C6	1.243 (5)
Cu1—O1W	2.497 (3)	N1—N2	1.385 (4)
Cu1—O2W	2.484 (3)	N1—C3	1.314 (6)
Cu1—O3 <sup>i</sup>	1.974 (3)	N2—C4	1.319 (5)
Cu1—N1	1.982 (3)	N3—H3	0.8800
Cu1—N2 <sup>i</sup>	1.990 (4)	N3—C3	1.336 (5)
O1—C1	1.269 (5)	N3—C4	1.323 (6)
O1W—H1WA	0.8703	C1—C2	1.514 (6)
O1W—H1WB	0.8707	C2—H2A	0.9900
O2—C1	1.238 (5)	C2—H2B	0.9900
O2W—H2WA	0.8546	C2—C3	1.495 (6)
O2W—H2WB	0.8709	C4—C5	1.502 (5)
O3—C6	1.253 (5)	C5—H5A	0.9900
O3W—H3WA	0.8491	C5—H5B	0.9900
O3W—H3WB	0.8489	C5—C6	1.534 (6)
O1—Cu1—O1W	91.79 (13)	C4—N2—N1	106.2 (4)
O1—Cu1—O2W	88.11 (12)	C3—N3—H3	126.4
O1—Cu1—O3 <sup>i</sup>	82.43 (13)	C4—N3—H3	126.4
O1—Cu1—N1	91.35 (14)	C4—N3—C3	107.1 (4)
O1—Cu1—N2 <sup>i</sup>	171.18 (13)	O1—C1—C2	119.3 (4)
O2W—Cu1—O1W	177.86 (9)	O2—C1—O1	124.8 (4)
O3 <sup>i</sup> —Cu1—O1W	84.77 (12)	O2—C1—C2	115.8 (5)
O3 <sup>i</sup> —Cu1—O2W	93.10 (12)	C1—C2—H2A	107.8
O3 <sup>i</sup> —Cu1—N1	167.83 (15)	C1—C2—H2B	107.8
O3 <sup>i</sup> —Cu1—N2 <sup>i</sup>	89.34 (13)	H2A—C2—H2B	107.1
N1—Cu1—O1W	84.98 (13)	C3—C2—C1	118.1 (4)
N1—Cu1—O2W	97.16 (13)	C3—C2—H2A	107.8
N1—Cu1—N2 <sup>i</sup>	97.31 (14)	C3—C2—H2B	107.8
N2 <sup>i</sup> —Cu1—O1W	90.61 (13)	N1—C3—N3	109.5 (4)
N2 <sup>i</sup> —Cu1—O2W	89.17 (13)	N1—C3—C2	129.0 (4)
C1—O1—Cu1	134.8 (3)	N3—C3—C2	121.5 (4)
Cu1—O1W—H1WA	108.5	N2—C4—N3	110.2 (4)
Cu1—O1W—H1WB	109.5	N2—C4—C5	127.5 (4)



H1WA—O1W—H1WB	104.5	N3—C4—C5	122.2 (4)
Cu1—O2W—H2WA	102.5	C4—C5—H5A	108.9
Cu1—O2W—H2WB	109.6	C4—C5—H5B	108.9
H2WA—O2W—H2WB	113.0	C4—C5—C6	113.5 (4)
C6—O3—Cu1 <sup>i</sup>	130.3 (3)	H5A—C5—H5B	107.7
H3WA—O3W—H3WB	109.5	C6—C5—H5A	108.9
N2—N1—Cu1	127.3 (3)	C6—C5—H5B	108.9
C3—N1—Cu1	123.1 (3)	O3—C6—C5	119.8 (4)
C3—N1—N2	107.0 (4)	O4—C6—O3	123.9 (5)
N1—N2—Cu1 <sup>i</sup>	132.4 (3)	O4—C6—C5	116.2 (4)
C4—N2—Cu1 <sup>i</sup>	121.1 (3)		
Cu1—O1—C1—O2	-173.2 (3)	N2—N1—C3—N3	-0.2 (5)
Cu1—O1—C1—C2	11.6 (7)	N2—N1—C3—C2	179.4 (4)
Cu1 <sup>i</sup> —O3—C6—O4	168.2 (3)	N2—C4—C5—C6	41.1 (6)
Cu1 <sup>i</sup> —O3—C6—C5	-11.0 (6)	N3—C4—C5—C6	-142.1 (4)
Cu1—N1—N2—Cu1 <sup>i</sup>	24.3 (5)	C1—C2—C3—N1	26.4 (7)
Cu1—N1—N2—C4	-161.7 (3)	C1—C2—C3—N3	-154.0 (4)
Cu1—N1—C3—N3	162.8 (3)	C3—N1—N2—Cu1 <sup>i</sup>	-173.6 (3)
Cu1—N1—C3—C2	-17.6 (7)	C3—N1—N2—C4	0.4 (5)
Cu1 <sup>i</sup> —N2—C4—N3	174.4 (3)	C3—N3—C4—N2	0.2 (5)
Cu1 <sup>i</sup> —N2—C4—C5	-8.4 (6)	C3—N3—C4—C5	-177.1 (4)
O1—C1—C2—C3	-21.3 (6)	C4—N3—C3—N1	0.0 (5)
O2—C1—C2—C3	163.0 (4)	C4—N3—C3—C2	-179.7 (4)
N1—N2—C4—N3	-0.4 (5)	C4—C5—C6—O3	-30.0 (6)
N1—N2—C4—C5	176.8 (4)	C4—C5—C6—O4	150.8 (4)

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA $\cdots$ O4 <sup>ii</sup>	0.87	1.91	2.762 (5)	165
O1W—H1WB $\cdots$ O3W	0.87	1.94	2.797 (5)	169
O2W—H2WA $\cdots$ O1W <sup>iii</sup>	0.85	2.03	2.880 (4)	170
O2W—H2WB $\cdots$ O2 <sup>iv</sup>	0.87	1.89	2.744 (4)	167
N3—H3 $\cdots$ O4 <sup>v</sup>	0.88	1.81	2.670 (5)	165
C5—H5B $\cdots$ O3 <sup>v</sup>	0.99	2.32	3.257 (6)	158

Symmetry codes: (ii)  $x+1/2, -y+3/2, z+1/2$ ; (iii)  $x-1, y, z$ ; (iv)  $-x+1/2, y-1/2, -z+3/2$ ; (v)  $-x+1/2, y+1/2, -z+1/2$ .