



Crystal structure and Hirshfeld-surface analysis of diaquabis(5-methyl-1*H*-1,2,4-triazole-3-carboxylato)copper(II)

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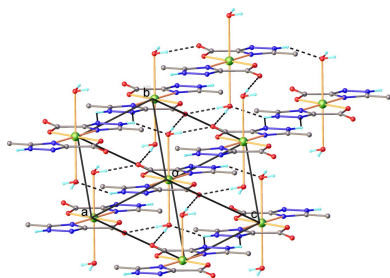
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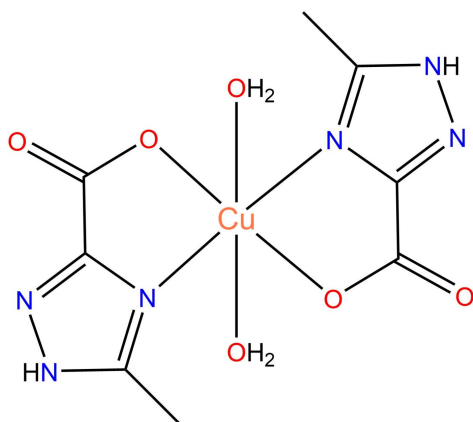
The title compound, [Cu(HL)₂(H₂O)₂] or [Cu(C₄H₄N₃O₂)₂(H₂O)₂], is a mononuclear octahedral Cu^{II} complex based on 5-methyl-1*H*-1,2,4-triazole-3-carboxylic acid (H₂L). [Cu(HL)₂(H₂O)₂] was synthesized by reaction of H₂L with copper(II) nitrate hexahydrate (2:1 stoichiometric ratio) in water under ambient conditions to produce clear light-blue crystals. The central Cu atom exhibits an N₂O₄ coordination environment in an elongated octahedral geometry provided by two bidentate HL[−] anions in the equatorial plane and two water molecules in the axial positions. Hirshfeld surface analysis revealed that the most important contributions to the surface contacts are from H⋯O/O⋯H (33.1%), H⋯H (29.5%) and H⋯N/N⋯H (19.3%) interactions.

1. Chemical context

A few decades ago, 1,2,4-triazole-containing compounds became a focal point for both organic and inorganic chemists. It turned out that 1,2,4-triazoles are substances that show promising results as antibacterial, anticancer, antifungal, anti-inflammatory, and antiviral agents and have miscellaneous biological activities (Opsomer & Dehaen, 2022; Strzelecka & Świątek, 2021; Karczmarzyk *et al.*, 2020). The presence of three nitrogen atoms and the possibility of being involved in metal bonding, both in their acid and deprotonated forms, resulted in the synthesis and investigation of numerous coordination compounds based on 1,2,4-triazole derivatives (Haasnoot, 2000). As a result of the presence of the N–N bridging function in the triazole ring, these ligands can form polynuclear complexes with specific magnetic properties (Aromí *et al.*, 2011; Kitchen & Brooker, 2008; Klingele & Brooker, 2003; Petrenko *et al.*, 2020; 2021). Meanwhile, 1,2,4-triazole used as linker in ligands for MOF construction, is not usually involved in the formation of coordination bonds (Du *et al.*, 2005). The most widely used ligands of such type are 3-(2-pyridyl)-1,2,4-triazole derivatives, which readily form extremely stable planar coordination compounds with platinum (Chang *et al.*, 2006; Chen *et al.*, 2013) and palladium (Zakharchenko *et al.*, 2017; 2019; 2021), showing promising photoelectronic and catalytic properties, respectively. A carboxylic acid group connected directly to the 1,2,4-triazole ring could potentially play the same role as a 2-pyridyl moiety, forcing the formation of chelates. In addition, it should be noted that the presence of both carboxylic and 1,2,4-triazole groups as parts of one molecule provides interesting theoretical insights into the structural peculiarities of these molecules.



This is mainly due to the possibility of 1,2,4-triazole existing in three tautomeric forms (Pagacz-Kostrzewa *et al.*, 2019, 2020). Generally, compounds containing a carboxylic function are probably the most important materials for high-throughput synthesis and 1,2,4-triazoles are not an exception. Recently, as part of our efforts to prepare new synthesis building blocks, we obtained a series of carboxylic acids and their derivatives (Khomenko *et al.*, 2022). One of those compounds was used to synthesize a copper complex.



2. Structural commentary

The molecular structure of the title compound consists of a neutral complex unit $[\text{Cu}(\text{HL})_2(\text{H}_2\text{O})_2]$ (Fig. 1), where HL is the deprotonated 5-methyl-1H-1,2,4-triazole-3-carboxylate ligand. The Cu^{II} atom occupies a special position (inversion centre), thus imposing crystallographic inversion symmetry on the complex. The central atom exhibits an N_2O_4 coordination environment in an elongated octahedral geometry provided by two bidentate L^- anions in the equatorial plane [$\text{Cu1}-\text{O1} = 1.9987(12) \text{ \AA}$, $\text{Cu1}-\text{N1} = 1.9603(15) \text{ \AA}$] and two water molecules in the axial positions [$\text{Cu1}-\text{O1W} = 2.5405(15) \text{ \AA}$]. It is worth noting that the structure of the title compound closely resembles those of earlier published analogous compounds with unsubstituted 1H-1,2,4-triazole-3-carboxylate anions (Liu, 2007; Zhu *et al.*, 2007).

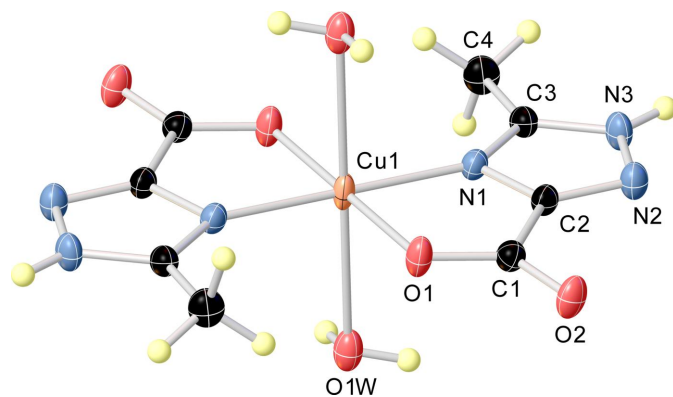


Figure 1

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 (\AA , $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N3}-\text{H3}\cdots\text{O1W}^{\text{i}}$	0.86	2.06	2.822 (2)	147
$\text{N3}-\text{H3}\cdots\text{N2}^{\text{ii}}$	0.86	2.58	3.121 (2)	122
$\text{O1W}-\text{H1WB}\cdots\text{O2}^{\text{iii}}$	0.85	1.93	2.781 (2)	175
$\text{O1W}-\text{H1WA}\cdots\text{O2}^{\text{iv}}$	0.85	1.92	2.737 (2)	160

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

3. Supramolecular features

In the crystal, the complex molecules $[\text{Cu}(\text{HL})_2(\text{H}_2\text{O})_2]$ interact *via* numerous intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 1). Each NH group of the carboxylate ligands is involved as the donor of a proton in bifurcated hydrogen bonding towards atom N2 and the coordinated water molecule of the adjacent molecule, while each O1W molecule acts as donor in two hydrogen bonds with two O2 atoms of the symmetry-related complexes. Thus, all the potential hydrogen bonds are completely realized in the crystal, which results in the formation of a three-dimensional supramolecular network, as shown in Fig. 2.

4. Hirshfeld surface analysis

A Hirshfeld surface analysis was performed and the associated two-dimensional fingerprint plots were generated using *CrystalExplorer 17.5* software (Spackman *et al.*, 2021), with a standard resolution of the three-dimensional d_{norm} surfaces. There are 20 red spots on the d_{norm} surface (Fig. 3). The dark-red spots arise as a result of short interatomic contacts and represent contacts shorter than the sum of van der Waals radii, while the other weaker intermolecular interactions appear as light-red spots. The Hirshfeld surfaces mapped over d_{norm} are shown for the $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, $\text{H}\cdots\text{H}$ and $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$ contacts, and the decomposed two-dimensional fingerprint plots of different types of interactions are given in Fig. 4. All short interatomic contacts are in the range of 1.797–2.505 \AA .

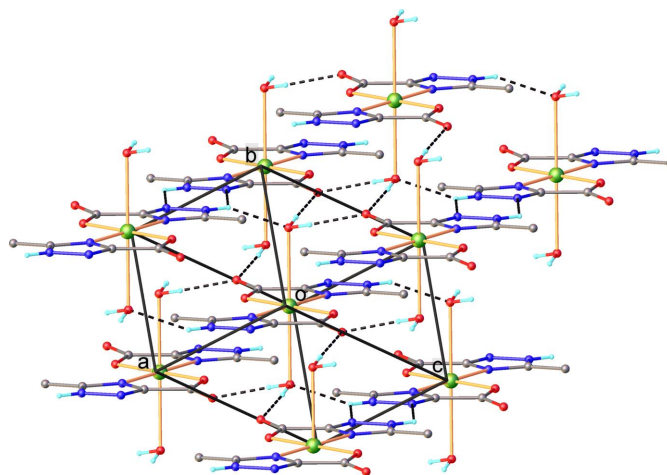


Figure 2

Partial view of the crystal packing showing the formation of the three-dimensional supramolecular architecture.

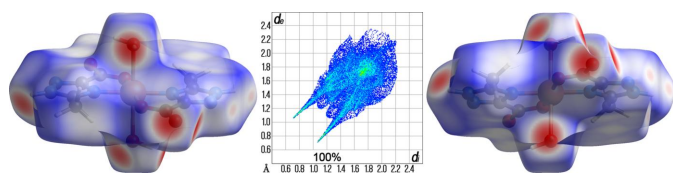


Figure 3
Two projections of the Hirshfeld surfaces mapped over d_{norm} showing the intermolecular interactions within the molecule and the full two-dimensional fingerprint plot for the title compound.

The shortest contacts are $\text{OH}\cdots\text{O}$ and the longest contacts are $\text{NH}\cdots\text{N}$. The most abundant contributions to the overall crystal packing are from $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$ (33.1%), $\text{H}\cdots\text{H}$ (29.5%) and $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$ (19.3%). There is a small contribution by other weak intermolecular contacts: $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ (4.6%), $\text{O}\cdots\text{N}/\text{N}\cdots\text{O}$ (4.2%), $\text{O}\cdots\text{C}/\text{C}\cdots\text{O}$ (3.3%), $\text{C}\cdots\text{C}$ (2.2%), $\text{O}\cdots\text{O}$ (1.8%), $\text{N}\cdots\text{C}/\text{C}\cdots\text{N}$ (1.4%) and $\text{N}\cdots\text{N}$ (0.5%). In addition, quantitative physical properties of the Hirshfeld surface for this compound were obtained, such as molecular volume (303.40 \AA^3), surface area (289.05 \AA^2), globularity (0.755), as well as asphericity (0.087).

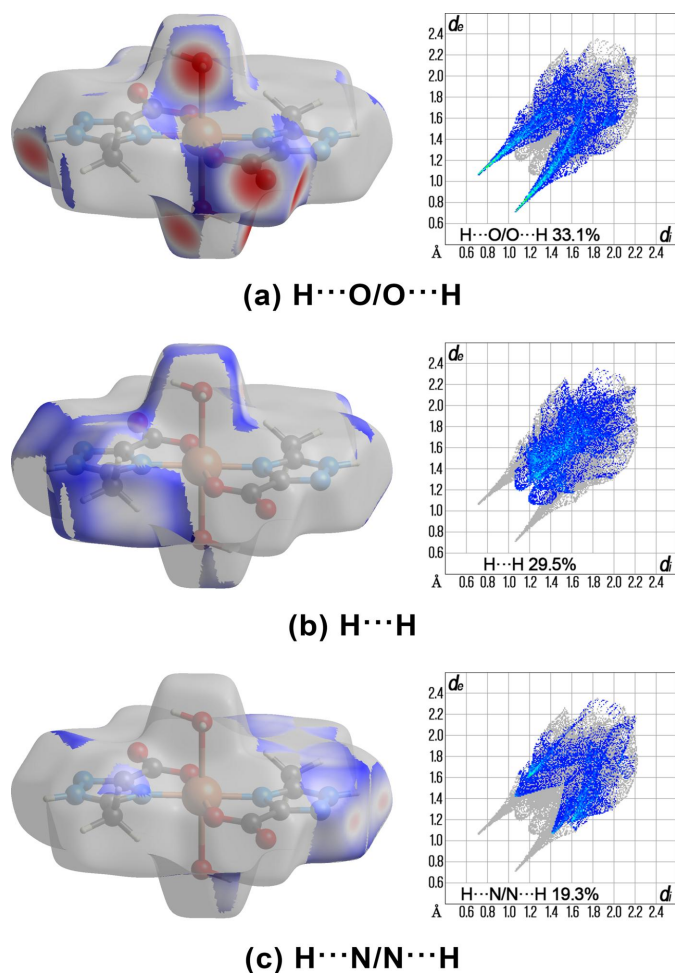


Figure 4
Hirshfeld surface representations with the function d_{norm} plotted onto the surface and the decomposed two-dimensional fingerprint plots for selected interactions.

5. Database survey

A search of the Cambridge Structural Database (CSD version 5.43, November 2021; Groom *et al.*, 2016) for the moiety including a transition metal coordinated by the N and O atoms of the 1*H*-1,2,4-triazole-3-carboxylate anion in a bidentate way revealed 22 hits. Most similar to the title compound are mononuclear complexes with two unsubstituted 1*H*-1,2,4-triazole-3-carboxylate anions and two water molecules in axial positions: Mn^{II} [GEVKAW (Yan *et al.*, 2018)]; Zn^{II} [RIRVIY (Liu, 2007)]; Cd^{II} [XIRZOO (Zhu *et al.*, 2008)]; Cu^{II} [YIQROG (Zhu *et al.*, 2007) and YIQROG01 (Liu, 2007)]. Other compounds with a close relation to the title complex are mononuclear complexes with 5-substituted 1*H*-1,2,4-triazole-3-carboxylate anions. In all cases, the substituent was the NH_2 group: Mn^{II} [HEDWIZ (Yang *et al.*, 2019)], Mn^{II} dihydrate [OPOMAJ (Liu *et al.*, 2015)], Cd^{II} [ISACEL (Wang *et al.*, 2011)], Co^{II} dihydrate [ONILIJ (Li *et al.*, 2021)], Zn^{II} based on 5-amino-1*H*-1,2,4-triazole-3-carboxylate anion and with only one coordinated water molecule [OPOLUC (Liu *et al.*, 2015)].

6. Synthesis and crystallization

H_2L : LiHL (Khomenko *et al.*, 2022) (1.33 g, 10 mmol) was dissolved in H_2O (10 ml). The obtained solution was cooled and slowly acidified with concentrated HCl (1 ml), maintaining the temperature between 273 and 278 K. The precipitation of colourless crystals occurred after addition of all the HCl. The reaction mixture was additionally stirred for 15 min at low temperature. Then, the precipitate was filtered off, washed with cold water and dried *in vacuo*. Yield 0.76 g (60%). ^1H NMR (400 MHz, D_2O): δ 2.61 (s, 3H) ppm. IR data (in KBr, cm^{-1}): 3330, 1648, 1567, 1509, 1418, 1313, 1103, 835. Elemental analysis: analysis calculated for $\text{C}_4\text{H}_5\text{N}_3\text{O}_2$ (127.10): C, 37.80%; H, 3.97%; N, 33.06%. Found: C, 37.41%; H, 3.65%; N, 32.71%.

$[\text{Cu}(\text{HL})_2(\text{H}_2\text{O})_2]$: A solution of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.148 g, 0.5 mmol) in H_2O (5 ml) was added to an aqueous solution of H_2L (0.127 g, 13 ml, 1 mmol) to give a clear blue solution. The blue crystals obtained after 2 days were filtered off, washed with water and dried in air. Yield 0.140 g (80%). IR data (in KBr, cm^{-1}): 3330, 1648, 1557, 1509, 1418, 1304, 1113, 835. Elemental analysis: analysis calculated for $\text{C}_8\text{H}_{12}\text{CuN}_6\text{O}_6$ (351.77): C, 27.32%; H, 3.44%; N, 23.89%. Found: C, 27.30%; H, 3.45%; N, 23.82%.

IR and ^1H NMR spectra of 5-methyl-1*H*-1,2,4-triazole-3-carboxylic acid are given in the supporting information for this article.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were found in difference-Fourier maps, but subsequently included in the refinement using riding models, with constrained distances set to 0.96 Å (RCH_3), 0.86 Å ($\text{Nsp}^2\text{-H}$), and 0.85 Å (OH_2). $U_{\text{iso}}(\text{H})$ parameters were set to values of either $1.2U_{\text{eq}}$ or $1.5U_{\text{eq}}$ (RCH_3 , OH_2) of the attached atom.

Table 2

Experimental details.

Crystal data	
Chemical formula	[Cu(C ₄ H ₄ N ₃ O ₂) ₂ (H ₂ O) ₂]
<i>M_r</i>	351.78
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.8465 (4), 7.1097 (7), 7.2090 (5)
α , β , γ (°)	79.267 (7), 83.193 (6), 64.076 (8)
<i>V</i> (Å ³)	309.80 (5)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.81
Crystal size (mm)	0.45 × 0.1 × 0.1
Data collection	
Diffractionmeter	Xcalibur, Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2012)
<i>T_{min}</i> , <i>T_{max}</i>	0.774, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	2216, 1397, 1381
<i>R_{int}</i>	0.016
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.681
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.024, 0.062, 1.11
No. of reflections	1397
No. of parameters	101
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.35, -0.38

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov et al., 2009).

Funding information

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References

- Agilent (2012). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, England.
- Aromí, G., Barrios, L. A., Roubeau, O. & Gamez, P. (2011). *Coord. Chem. Rev.* **255**, 485–546.
- Chang, S.-Y., Kavitha, J., Li, S.-W., Hsu, C.-S., Chi, Y., Yeh, Y.-S., Chou, P.-T., Lee, G.-H., Carty, A. J., Tao, Y.-T. & Chien, C.-H. (2006). *Inorg. Chem.* **45**, 137–146.
- Chen, J.-L., Chen, X.-X., Tan, X.-Z., Wang, J.-Y., Fu, X.-F., He, L.-H., Li, Y., Zhong, G.-Q. & Wen, H.-R. (2013). *Inorg. Chem. Commun.* **35**, 96–99.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Du, M., Chen, S.-T., Guo, Y.-M., Bu, X.-H. & Ribas, J. (2005). *J. Mol. Struct.* **737**, 17–21.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst. B* **72**, 171–179.
- Haasnoot, J. G. (2000). *Coord. Chem. Rev.* **200–202**, 131–185.
- Karczmarzyk, Z., Swatko-Ossor, M., Wysocki, W., Drozd, M., Ginalska, G., Pachuta-Stec, A. & Pitucha, M. (2020). *Molecules*, **25**, 6033.
- Khomenko, D. M., Doroshchuk, R. O., Ohorodnik, Y. M., Ivanova, H. V., Zakharchenko, B. V., Raspertova, I. V., Vaschenko, O. V., Dobrydnev, A. V., Grygorenko, O. O. & Lampeka, R. D. (2022). *Chem. Heterocycl. Compd.* **58**, 116–128.
- Kitchen, J. A. & Brooker, S. (2008). *Coord. Chem. Rev.* **252**, 2072–2092.
- Klinge, M. H. & Brooker, S. (2003). *Coord. Chem. Rev.* **241**, 119–132.
- Li, B., Song, H., Wu, H., Wang, J., Tian, X. & Ma, X. (2021). *J. Coord. Chem.* **74**, 1159–1167.
- Liu, B., Fernandes, J., Tomé, J., Paz, F. & Cunha-Silva, L. (2015). *Molecules*, **20**, 12341–12363.
- Liu, Y.-Y. (2007). *J. Coord. Chem.* **60**, 2597–2605.
- Opsomer, T. & Dehaen, W. (2022). *Triazoles*. In *Comprehensive Heterocyclic Chemistry IV*, edited by D. S. Black, J. Cossy & C. V. Stevens, pp. 78–121. Oxford: Elsevier.
- Pagacz-Kostrzewska, M., Krupa, J., Gul, W. & Wierzejewska, M. (2020). *J. Mol. Struct.* **1209**, 127938.
- Pagacz-Kostrzewska, M., Sałdyka, M., Bil, A., Gul, W., Wierzejewska, M., Khomenko, D. M. & Doroshchuk, R. O. (2019). *J. Phys. Chem. A*, **123**, 841–850.
- Petrenko, Y. P., Khomenko, D. M., Doroshchuk, R. O., Shova, S., Novitchi, G., Piasta, K., Gumienna-Kontecka, E. & Lampeka, R. D. (2020). *Inorg. Chim. Acta*, **500**, 119216.
- Petrenko, Y. P., Piasta, K., Khomenko, D. M., Doroshchuk, R. O., Shova, S., Novitchi, G., Toporivska, Y., Gumienna-Kontecka, E., Martins, L. M. D. R. S. & Lampeka, R. D. (2021). *RSC Adv.* **11**, 23442–23449.
- Sheldrick, G. M. (2015a). *Acta Cryst. A* **71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst. C* **71**, 3–8.
- Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.
- Strzelecka, M. & Świątek, P. (2021). *Pharmaceuticals*, **14**, 224.
- Wang, J., Li, W.-Z., Wang, J.-G. & Xiao, H.-P. (2011). *Z. Krist. New Cryst. Struct.* **226**, 163–164.
- Yan, J., Lu, L., Zhu, M. & Feng, S. (2018). *J. Solid State Chem.* **262**, 351–359.
- Yang, K., Tan, Y.-H., Wang, B., Zhou, H.-T., Li, C., Yang, C.-S., Liu, Y., Gao, J.-X. & Tang, Y.-Z. (2019). *Wuji Huaxue*, **35**, 703.
- Zakharchenko, B. V., Khomenko, D. M., Doroshchuk, R. O., Raspertova, I. V., Fesych, I. V., Starova, V. S., Rusakova, N. V., Smola, S. S., Shova, S. & Lampeka, R. D. (2021). *Theor. Exp. Chem.* **57**, 358–365.
- Zakharchenko, B. V., Khomenko, D. M., Doroshchuk, R. O., Raspertova, I. V., Starova, V. S., Trachevsky, V. V., Shova, S., Severynovska, O. V., Martins, L. M. D. R. S., Pombeiro, A. J. L., Arion, V. B. & Lampeka, R. D. (2019). *New J. Chem.* **43**, 10973–10984.
- Zakharchenko, B. V., Khomenko, D. M., Doroshchuk, R. O., Severynovska, O. V., Raspertova, I. V., Starova, V. S. & Lampeka, R. D. (2017). *Chem. Pap.* **71**, 2003–2009.
- Zhu, J., Yin, X.-H., Feng, Y., Hu, F.-L., Zhuang, Y. & Lin, C.-W. (2008). *Acta Cryst. E* **64**, m119.
- Zhu, J., Yin, X.-H., Feng, Y., Su, Z.-X. & Lin, C.-W. (2007). *Acta Cryst. E* **63**, m3167.

supporting information

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Computing details

Diaquabis(5-methyl-1*H*-1,2,4-triazole-3-carboxylato)copper(II)

Crystal data

[Cu(C₄H₄N₃O₂)₂(H₂O)₂]

$M_r = 351.78$

Triclinic, $P\bar{1}$

$a = 6.8465$ (4) Å

$b = 7.1097$ (7) Å

$c = 7.2090$ (5) Å

$\alpha = 79.267$ (7)°

$\beta = 83.193$ (6)°

$\gamma = 64.076$ (8)°

$V = 309.80$ (5) Å³

$Z = 1$

$F(000) = 179$

$D_x = 1.886$ Mg m⁻³

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

Cell parameters from 1444 reflections

$\theta = 2.9$ – 28.9 °

$\mu = 1.81$ mm⁻¹

$T = 200$ K

Prism, clear light blue

$0.45 \times 0.1 \times 0.1$ mm

Data collection

Xcalibur, Eos

diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1593 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlisPro*; Agilent, 2012)

$T_{\min} = 0.774$, $T_{\max} = 1.000$

2216 measured reflections

1397 independent reflections

1381 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 29.0$ °, $\theta_{\min} = 2.9$ °

$h = -8$ → 9

$k = -9$ → 9

$l = -9$ → 9

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.062$

$S = 1.11$

1397 reflections

101 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 0.1883P]$

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

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

$\Delta\rho_{\max} = 0.35$ e Å⁻³

$\Delta\rho_{\min} = -0.38$ e Å⁻³

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.500000	0.500000	0.500000	0.01665 (11)
O1	0.7195 (2)	0.6171 (2)	0.41929 (19)	0.0200 (3)
O1W	0.2171 (2)	0.8296 (2)	0.31785 (19)	0.0211 (3)
H1WA	0.100833	0.815339	0.353434	0.032*
H1WB	0.208435	0.929486	0.372183	0.032*
O2	0.8357 (2)	0.8422 (2)	0.49419 (19)	0.0216 (3)
N1	0.4392 (2)	0.6629 (2)	0.7081 (2)	0.0148 (3)
N2	0.5479 (2)	0.8664 (2)	0.8331 (2)	0.0184 (3)
N3	0.3859 (2)	0.8329 (2)	0.9412 (2)	0.0187 (3)
H3	0.332405	0.882766	1.045013	0.022*
C1	0.7246 (3)	0.7403 (3)	0.5225 (3)	0.0161 (3)
C2	0.5727 (3)	0.7621 (3)	0.6937 (2)	0.0151 (3)
C3	0.3199 (3)	0.7127 (3)	0.8661 (2)	0.0160 (3)
C4	0.1414 (3)	0.6522 (3)	0.9429 (3)	0.0223 (4)
H4A	0.011749	0.743962	0.876397	0.033*
H4B	0.115402	0.664910	1.074796	0.033*
H4C	0.181446	0.508565	0.927290	0.033*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02239 (18)	0.01979 (18)	0.01580 (17)	-0.01517 (14)	0.00516 (11)	-0.00932 (12)
O1	0.0244 (7)	0.0226 (7)	0.0205 (7)	-0.0158 (6)	0.0067 (5)	-0.0108 (5)
O1W	0.0233 (7)	0.0253 (7)	0.0215 (7)	-0.0154 (6)	0.0071 (5)	-0.0113 (6)
O2	0.0219 (7)	0.0232 (7)	0.0275 (7)	-0.0161 (6)	0.0066 (5)	-0.0102 (6)
N1	0.0170 (7)	0.0143 (7)	0.0156 (7)	-0.0087 (6)	0.0009 (5)	-0.0038 (6)
N2	0.0198 (7)	0.0214 (8)	0.0188 (8)	-0.0121 (7)	0.0022 (6)	-0.0076 (6)
N3	0.0215 (8)	0.0221 (8)	0.0164 (8)	-0.0114 (7)	0.0041 (6)	-0.0098 (6)
C1	0.0168 (8)	0.0150 (8)	0.0165 (8)	-0.0067 (7)	-0.0001 (6)	-0.0034 (7)
C2	0.0162 (8)	0.0148 (8)	0.0166 (8)	-0.0085 (7)	-0.0006 (6)	-0.0033 (7)
C3	0.0180 (8)	0.0151 (8)	0.0147 (8)	-0.0063 (7)	-0.0002 (6)	-0.0041 (7)
C4	0.0216 (9)	0.0270 (10)	0.0216 (9)	-0.0140 (8)	0.0041 (7)	-0.0056 (8)

Geometric parameters (\AA , $^\circ$)

Cu1—O1	1.9987 (12)	N1—C2	1.363 (2)
Cu1—O1 ⁱ	1.9987 (12)	N1—C3	1.329 (2)
Cu1—O1W	2.5405 (15)	N2—N3	1.361 (2)
Cu1—N1	1.9603 (15)	N2—C2	1.310 (2)

Cu1—N1 ⁱ	1.9603 (15)	N3—C3	1.340 (2)
O1—C1	1.264 (2)	C1—C2	1.501 (2)
O2—C1	1.239 (2)	C3—C4	1.481 (2)
O1 ⁱ —Cu1—O1	180.0	C3—N1—C2	104.36 (14)
O1—Cu1—O1W	89.09 (5)	C2—N2—N3	101.94 (14)
O1 ⁱ —Cu1—O1W	90.91 (5)	C3—N3—N2	111.67 (15)
N1 ⁱ —Cu1—O1	97.00 (5)	O1—C1—C2	113.53 (15)
N1 ⁱ —Cu1—O1 ⁱ	83.00 (5)	O2—C1—O1	127.10 (17)
N1—Cu1—O1 ⁱ	97.00 (5)	O2—C1—C2	119.35 (16)
N1—Cu1—O1	83.00 (5)	N1—C2—C1	116.79 (15)
N1 ⁱ —Cu1—O1W	92.71 (5)	N2—C2—N1	114.35 (16)
N1—Cu1—O1W	87.29 (5)	N2—C2—C1	128.86 (16)
N1 ⁱ —Cu1—N1	180.0	N1—C3—N3	107.67 (15)
C1—O1—Cu1	115.49 (11)	N1—C3—C4	126.36 (16)
C2—N1—Cu1	111.00 (11)	N3—C3—C4	125.95 (16)
C3—N1—Cu1	144.60 (12)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3 \cdots O1W ⁱⁱ	0.86	2.06	2.822 (2)	147
N3—H3 \cdots N2 ⁱⁱⁱ	0.86	2.58	3.121 (2)	122
O1W—H1WB \cdots O2 ^{iv}	0.85	1.93	2.781 (2)	175
O1W—H1WA \cdots O2 ^v	0.85	1.92	2.737 (2)	160
C4—H4B \cdots O1W ⁱⁱ	0.96	2.59	3.367 (2)	139

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