IUCrData

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catena-Poly[[[aquacopper(II)]-μ-hydroxido-κ^2O:O-μ-[3-(4*H*-1,2,4-triazol-4-yl)benzoato]-κ^2N^1:N^2] monohydrate]

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Keywords: crystal structure; coordination polymer; triazole-carboxylate; copper complex.

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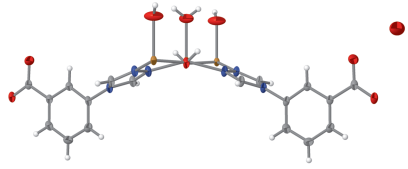
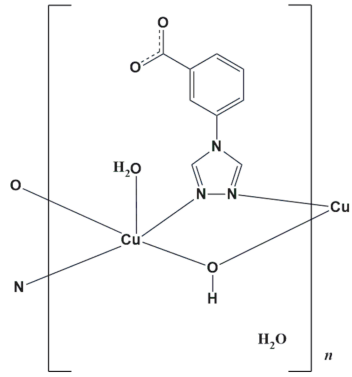
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $\{[Cu(C_9H_6N_3O_2)(OH)(H_2O)]\cdot H_2O\}_n$, the Cu^{2+} cation is situated on a twofold rotation axis and is coordinated by two triazole N atoms from two different 3-(4*H*-1,2,4-triazol-4-yl)benzoate (3-tba) ligands, by two hydroxyl O atoms and by a water O atom, forming a coordination environment intermediate between a square pyramid and a trigonal bipyramid. The Cu^{2+} ions are connected by 3-tba ligand and a hydroxy group into polymeric chains parallel to [001]. O—H···O hydrogen bonds and C—H···O interactions consolidate the crystal structure.

3D view



Chemical scheme



Structure description

Coordination polymers have attracted considerable interest because of their distinctive topologies and various potential applications (Kitagawa *et al.*, 2004; Leong & Vittal, 2011). Since organic ligands are crucial for the assembly and structural regulation of coordination polymers, they play a decisive role in the design of such compounds. In this regard, bifunctional groups are very useful, such as triazole-carboxylate ligands. For example, 4-(4*H*-1,2,4-triazol-4-yl)benzoate, 4-(1*H*-1,2,4-triazol-1-yl)benzoate, 3-(4*H*-1,2,4-triazol-4-yl)benzoate and 3-(1*H*-1,2,4-triazol-1-yl)benzoate have been used in the construction of various coordination polymers with different periodicities including dimers, chains, layers or networks (Mu *et al.*, 2014; Wang *et al.*, 2020; Yang *et al.*, 2016*a*,*b*). In this contribution, we selected 3-(4*H*-1,2,4-triazol-4-yl)benzoate (3-tba) as a triazole-carboxylate ligand, generating a new coordination polymer, $\{[Cu(C_9H_6N_3O_2)(OH)(H_2O)]\cdot H_2O\}_n$, which is reported here.

All units in the crystal structure are on special positions. The Cu^{2+} ion and the coordinating water molecule (O1*W*) are situated on a twofold rotation axis, whereas the hydroxyl group (O3), the non-coordinating water molecule (O2*W*) and the benzoate entity of the 3-tba ligand are situated on a mirror plane, which also bisects the triazole

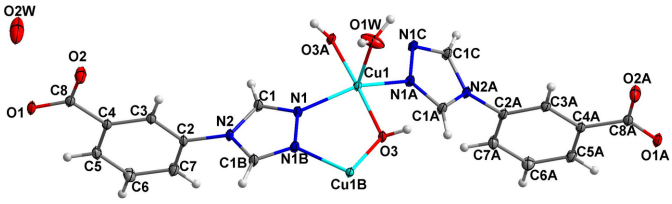


Figure 1
Parts of the crystal structure showing the coordination environment of Cu^{2+} in the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (A) $x, \frac{3}{2} - y, 1 - z$; (B) $x, y, \frac{1}{2} - z$; (C) $x, \frac{3}{2} - y, \frac{1}{2} + z$.]

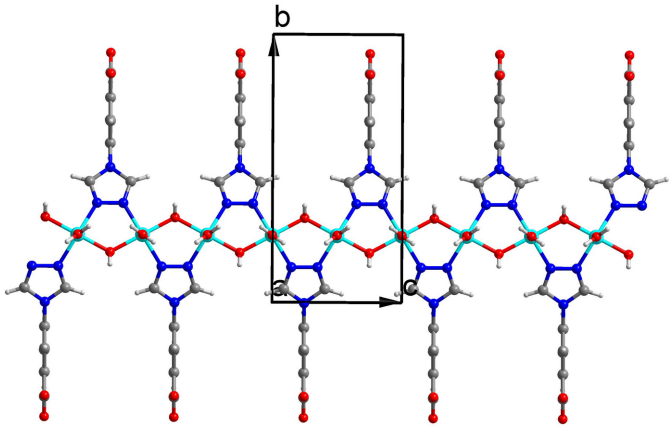


Figure 2
The formed polymeric chain in the title compound.

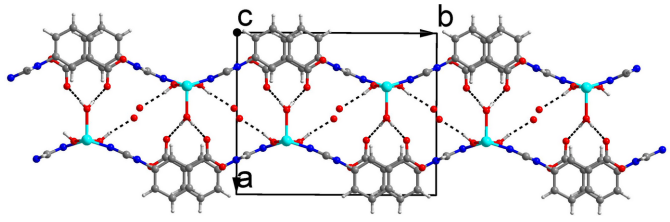


Figure 3
The double-sheet structure formed by O—H···O hydrogen-bonding interactions (black dashes lines) viewed along the *c* axis.

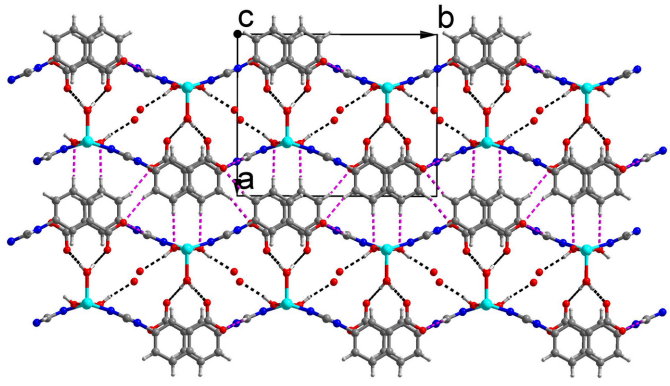


Figure 4
The crystal structure with O—H···O hydrogen bonds (black dashed lines) and C—H···O hydrogen bonds (purple dashed lines) viewed along the *c* axis.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O2^{i}	0.85	1.90	2.746 (2)	175
O3—H3*A*···O2*W*^{ii}	0.85	2.09	2.936 (4)	171
C1—H1···O1^{iii}	0.93	2.19	3.027 (2)	149
C6—H6···O3^{iv}	0.93	2.50	3.426 (3)	180
C7—H7···O1^{v}	0.93	2.38	3.270 (3)	161

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_9H_6N_3O_2)(OH)(H_2O)]\cdot H_2O$
M_r	304.75
Crystal system, space group	Orthorhombic, *Pbcm*
Temperature (K)	293
a, *b*, *c* (Å)	11.456 (2), 14.140 (3), 6.8502 (14)
V (Å^3)	1109.6 (4)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	1.99
Crystal size (mm)	0.25 × 0.22 × 0.20
Data collection	
Diffractometer	Rigaku R-AXIS SPIDER
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 2001)
T_{min}, T_{max}	0.746, 0.896
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10406, 1374, 1209
R_{int}	0.038
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.648
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.027, 0.078, 1.13
No. of reflections	1374
No. of parameters	101
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.45

Computer programs: *RAPID-AUTO* (Rigaku, 1999), *CrystalClear* (Rigaku, 2002), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 1999) and *publCIF* (Westrip, 2010).

entity. As shown in Fig. 1, the Cu^{2+} ion is coordinated by two nitrogen atoms from two different 3-tba ligands and three oxygen atoms from two different hydroxyl groups and a coordinating water molecule. The τ_5 index (Addison *et al.*, 1984) of 0.40 indicates a coordination environment between a square pyramid (SP) and a trigonal bipyramid (TP) (extreme forms: τ_5 = 0.00 for SP and 1.00 for TP). The Cu—O bond lengths are 1.9434 (9) (2× to the hydroxide O atom) and 2.186 (2) Å (to the coordinating water O atom), and the Cd—N bond length is 2.0254 (14) Å (2× to triazole N atoms). As shown in Fig. 2, the 3-tba ligand and the hydroxyl group display μ_2-bridging modes to link adjacent Cu^{2+} ions into a polymeric chain extending parallel to [001]. These chain are joined *via* intermolecular O—H···O hydrogen-bonding interactions into double sheets parallel to (100) (Table 1, Fig. 3). Since the H atoms of the non-coordinating water molecule (O2*W*) were not located, the role of this molecule as a donor group is unclear. However, the proximity to oxygen atoms O2 and O3 [2.746 (2) and 2.936 (4) Å] allows conclusions to be drawn as possible acceptor atoms for hydrogen

bonding. The cohesion of the crystal structure into a tri-periodic framework is ensured by weak C—H···O interactions (Table 1, Fig. 4).

Synthesis and crystallization

A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (12 mg, 0.05 mmol), 3-Htba (9 mg, 0.05 mmol), water (4 ml) and ammonia solution (0.05 ml, 1 mol l^{-1}) was placed in a Teflon-lined stainless steel vessel (15 ml). The vessel was sealed and heated in an oven at 393 K for 72 h, and then slowly cooled to the room temperature. Blue block-shaped crystals were harvested by filtration, washed with water and dried under ambient condition (yield 36%).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Since reliable positions of hydrogen atoms bonded to non-coordinating water molecule O2*W* could not be derived from difference-Fourier maps, they were excluded from the model but are part of the formula and other structural data.

Funding information

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full crystallographic data

IUCrData (2025). **10**, x250638 [https://doi.org/10.1107/S2414314625006388]

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Crystal data

$[Cu(C_9H_6N_3O_2)(OH)(H_2O)]\cdot H_2O$
M_r = 304.75
Orthorhombic, *Pbcm*
a = 11.456 (2) Å
b = 14.140 (3) Å
c = 6.8502 (14) Å
V = 1109.6 (4) Å^3
Z = 4
$F(000)$ = 620
D_x = 1.824 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2652 reflections
θ = 5.2–54.9°
μ = 1.99 mm^{-1}
T = 293 K
Block, blue
0.25 × 0.22 × 0.20 mm

Data collection

Rigaku R-AXIS SPIDER diffractometer
ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 2001)
T_{min} = 0.746, T_{max} = 0.896
10406 measured reflections
1374 independent reflections
1209 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 27.4°, θ_{min} = 3.4°
h = −14→14
k = −17→18
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.078
S = 1.13
1374 reflections
101 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.7023P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.33189 (3)	0.750000	0.500000	0.01519 (13)
N1	0.28663 (14)	0.63184 (10)	0.3510 (2)	0.0197 (3)
N2	0.2127 (2)	0.49830 (15)	0.250000	0.0194 (4)
C1	0.24192 (17)	0.55131 (12)	0.4081 (2)	0.0218 (4)
H1	0.231667	0.533087	0.537449	0.026*
C2	0.1535 (2)	0.40752 (18)	0.250000	0.0190 (5)
C3	0.2189 (2)	0.32508 (17)	0.250000	0.0187 (5)
H3	0.300014	0.327427	0.250000	0.022*
C4	0.1603 (2)	0.23812 (17)	0.250000	0.0182 (5)
C5	0.0387 (3)	0.23727 (18)	0.250000	0.0235 (5)
H5	−0.000599	0.179720	0.250000	0.028*
C6	−0.0245 (2)	0.3205 (2)	0.250000	0.0284 (6)
H6	−0.105621	0.318531	0.250000	0.034*
C7	0.0329 (2)	0.40733 (19)	0.250000	0.0261 (6)
H7	−0.008844	0.463720	0.250000	0.031*
C8	0.2265 (2)	0.14552 (17)	0.250000	0.0207 (5)
O1	0.16904 (17)	0.07078 (13)	0.250000	0.0247 (4)
O2	0.33717 (18)	0.14919 (15)	0.250000	0.0361 (5)
O3	0.32341 (16)	0.81461 (12)	0.250000	0.0186 (4)
H3A	0.371738	0.860229	0.250000	0.022*
O1W	0.5227 (2)	0.750000	0.500000	0.0501 (8)
H1W	0.565365	0.778680	0.582500	0.060*
O2W	0.4674 (3)	−0.0136 (2)	0.250000	0.0820 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0241 (2)	0.00965 (18)	0.01184 (18)	0.000	0.000	−0.00046 (9)
N1	0.0339 (8)	0.0132 (7)	0.0122 (7)	−0.0031 (6)	−0.0007 (6)	−0.0003 (6)
N2	0.0297 (11)	0.0099 (9)	0.0186 (10)	−0.0024 (8)	0.000	0.000
C1	0.0359 (10)	0.0133 (8)	0.0161 (8)	−0.0029 (7)	0.0003 (7)	0.0008 (6)
C2	0.0278 (13)	0.0106 (11)	0.0186 (12)	−0.0039 (9)	0.000	0.000
C3	0.0222 (12)	0.0143 (11)	0.0196 (11)	−0.0020 (9)	0.000	0.000
C4	0.0247 (13)	0.0127 (12)	0.0172 (13)	−0.0007 (9)	0.000	0.000
C5	0.0269 (13)	0.0160 (12)	0.0277 (14)	−0.0067 (10)	0.000	0.000
C6	0.0200 (13)	0.0249 (14)	0.0403 (15)	−0.0017 (11)	0.000	0.000
C7	0.0278 (14)	0.0158 (12)	0.0348 (14)	0.0037 (10)	0.000	0.000
C8	0.0296 (14)	0.0140 (12)	0.0185 (11)	0.0005 (10)	0.000	0.000
O1	0.0344 (11)	0.0109 (9)	0.0288 (10)	−0.0020 (7)	0.000	0.000
O2	0.0267 (11)	0.0192 (10)	0.0624 (15)	0.0028 (8)	0.000	0.000
O3	0.0302 (10)	0.0106 (8)	0.0151 (8)	−0.0030 (7)	0.000	0.000
O1W	0.0236 (12)	0.091 (2)	0.0357 (13)	0.000	0.000	−0.0226 (12)
O2W	0.0488 (17)	0.0304 (15)	0.167 (4)	−0.0002 (13)	0.000	0.000

Geometric parameters (Å, º)

Cu1—O3^{i}	1.9434 (9)	C3—H3	0.9300
Cu1—O3	1.9434 (9)	C4—C5	1.393 (4)
Cu1—N1^{ii}	2.0254 (14)	C4—C8	1.513 (3)
Cu1—N1	2.0254 (14)	C5—C6	1.382 (4)
Cu1—O1W	2.186 (2)	C5—H5	0.9300
N1—C1	1.309 (2)	C6—C7	1.393 (4)
N1—N1^{iii}	1.384 (3)	C6—H6	0.9300
N2—C1	1.359 (2)	C7—H7	0.9300
N2—C1^{iii}	1.359 (2)	C8—O1	1.245 (3)
N2—C2	1.452 (3)	C8—O2	1.269 (3)
C1—H1	0.9300	O3—H3A	0.8501
C2—C7	1.382 (4)	O1W—H1W	0.8500
C2—C3	1.385 (4)	O1W—H1W^{ii}	0.8499
C3—C4	1.401 (3)		
O3^{i}—Cu1—O3	174.27 (11)	C2—C3—H3	120.7
O3^{i}—Cu1—N1^{ii}	86.03 (6)	C4—C3—H3	120.7
O3—Cu1—N1^{ii}	92.49 (6)	C5—C4—C3	119.1 (2)
O3^{i}—Cu1—N1	92.50 (6)	C5—C4—C8	119.6 (2)
O3—Cu1—N1	86.04 (6)	C3—C4—C8	121.3 (2)
N1^{ii}—Cu1—N1	150.33 (9)	C6—C5—C4	121.1 (2)
O3^{i}—Cu1—O1W	92.87 (5)	C6—C5—H5	119.4
O3—Cu1—O1W	92.87 (5)	C4—C5—H5	119.4
N1^{ii}—Cu1—O1W	104.83 (5)	C5—C6—C7	120.2 (3)
N1—Cu1—O1W	104.83 (5)	C5—C6—H6	119.9
C1—N1—N1^{iii}	107.40 (10)	C7—C6—H6	119.9
C1—N1—Cu1	131.86 (12)	C2—C7—C6	118.3 (3)
N1^{iii}—N1—Cu1	120.26 (4)	C2—C7—H7	120.9
C1—N2—C1^{iii}	105.7 (2)	C6—C7—H7	120.9
C1—N2—C2	127.06 (10)	O1—C8—O2	124.3 (2)
C1^{iii}—N2—C2	127.06 (10)	O1—C8—C4	118.0 (2)
N1—C1—N2	109.75 (15)	O2—C8—C4	117.7 (2)
N1—C1—H1	125.1	Cu1^{iii}—O3—Cu1	123.58 (9)
N2—C1—H1	125.1	Cu1^{iii}—O3—H3A	108.9
C7—C2—C3	122.6 (2)	Cu1—O3—H3A	108.9
C7—C2—N2	118.0 (2)	Cu1—O1W—H1W	125.1
C3—C2—N2	119.4 (2)	Cu1—O1W—H1W^{ii}	125.078 (7)
C2—C3—C4	118.7 (2)	H1W—O1W—H1W^{ii}	109.8
N1^{iii}—N1—C1—N2	0.11 (19)	C2—C3—C4—C8	180.0
Cu1—N1—C1—N2	172.00 (15)	C3—C4—C5—C6	0.0
C1^{iii}—N2—C1—N1	−0.2 (3)	C8—C4—C5—C6	180.0
C2—N2—C1—N1	−175.4 (2)	C4—C5—C6—C7	0.0
C1—N2—C2—C7	87.1 (2)	C3—C2—C7—C6	0.0
C1^{iii}—N2—C2—C7	−87.1 (2)	N2—C2—C7—C6	180.0
C1—N2—C2—C3	−92.9 (2)	C5—C6—C7—C2	0.0

C1^{iii}—N2—C2—C3	92.9 (2)	C5—C4—C8—O1	0.0
C7—C2—C3—C4	0.0	C3—C4—C8—O1	180.0
N2—C2—C3—C4	180.0	C5—C4—C8—O2	180.0
C2—C3—C4—C5	0.0	C3—C4—C8—O2	0.0

Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) *x*, −*y*+3/2, −*z*+1; (iii) *x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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C6—H6···O3^{vii}	0.93	2.50	3.426 (3)	180
C7—H7···O1^{viii}	0.93	2.38	3.270 (3)	161

Symmetry codes: (iv) −*x*+1, −*y*+1, −*z*+1; (v) *x*, *y*+1, *z*; (vi) *x*, −*y*+1/2, *z*+1/2; (vii) −*x*, *y*−1/2, −*z*+1/2; (viii) −*x*, *y*+1/2, −*z*+1/2.