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catena-Poly[copper(II)-μ-aqua-di-μ-benzotriazole]

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Key indicators

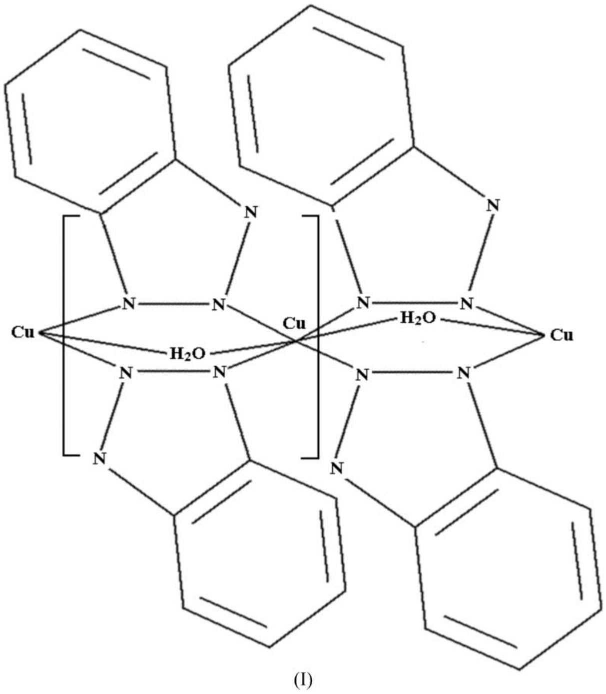
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.007 Å
R factor = 0.045
wR factor = 0.104
Data-to-parameter ratio = 12.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $[Cu(C_6H_4N_3)_2(H_2O)]_n$, the Cu^{II} atom is coordinated by four N atoms from two deprotonated benzotriazole (Bta) ligands and two O atoms from two water molecules. Each deprotonated Bta links two Cu^{II} centers *via* its two neighboring N atoms, giving a chain-like structure. Strong interchain π–π stacking interactions are observed.

Comment

In recent years, studies of the coordination chemistry of benzotriazole (Bta) and its ring-substituted derivatives have attracted increasing interest owing to their superior anti-corrosion effect when they are exposed to certain metals, especially copper and its alloys (Bakalbassis *et al.*, 1995; Boyd & Martin, 1981; Reedijk *et al.*, 1979; Skorda *et al.*, 1981; Tangoulis *et al.*, 1998; Tangoulis *et al.*, 2000; Olby *et al.*, 1990). To understand the complex surface chemistry that leads to corrosion inhibition and to create new inhibitors more efficient than Bta, primary investigations have focused on the chemical, physical and structural studies of realistic model complexes.



(I)

Despite of the extensive use of Bta and its derivatives as corrosion inhibitors for copper, zinc, silver and their alloys (Collison *et al.*, 2006; Okeefe & Steel, 2000), only a few compounds have been characterized by X-ray diffraction

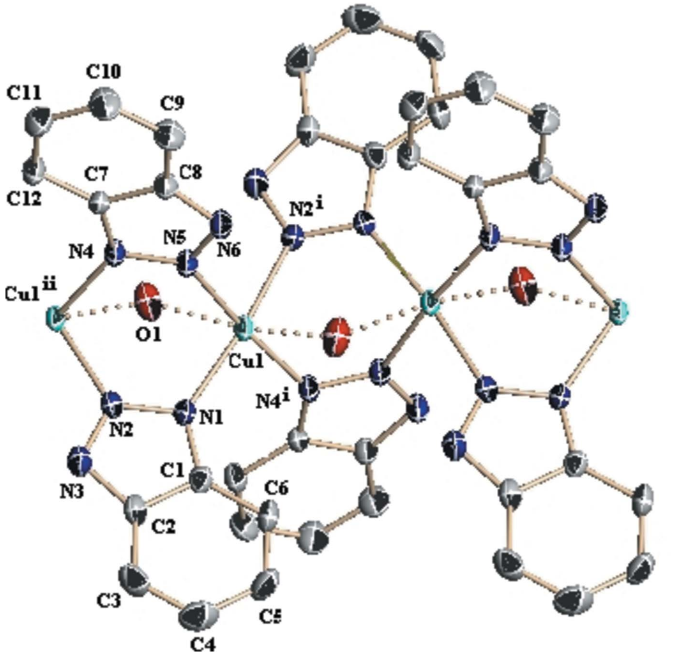


Figure 1
Part of the polymeric structure of the title complex, with the atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level. The dotted bonds indicate the longer bond length of 2.48 (7)Å. H atoms have been omitted. [Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$, (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.]

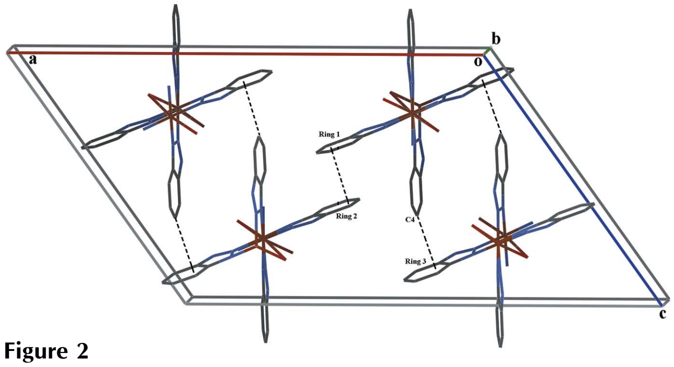


Figure 2
The π–π stacking mode of the title complex.

(Himes *et al.*, 1981; Hu *et al.*, 2005; Jones *et al.*, 2005; Li *et al.*, 2002; Rajeswarana *et al.*, 2006). Most of the structures involve inorganic anions such as $Zn(Bta)_4(H_2O)_2(ClO_4)_2$ and $Cu(Bta)_4(H_2O)_2(ClO_4)_2$ (Himes *et al.*, 1981; Jones *et al.*, 2005; Li *et al.*, 2002). In the absence of inorganic anions, water is not incorporated into the structures, as exemplified by anhydrous $Zn(Bta)_4$ and Ag(Bta)(Hu *et al.*, 2005; Rajeswarana *et al.*, 2006). Here we report the synthesis and crystal structure of a new copper–Bta complex, (I).

There are one Cu^{II}, two deprotonated Bta and one water molecule in the asymmetric unit (Fig. 1). The Cu^{II} center is six-coordinated by four N atoms from two deprotonated Bta and two O atoms from two aqua ligands in an octahedral geometry. The Cu—O bond length is 2.48 (7) Å. Each Bta links two Cu^{II} centers *via* its two neighboring N atoms with a Cu···Cu separation of 3.458 (12)Å (Fig. 1), leaving the third N atom uncoordinated. Complex (I) exhibits a chain-like structure. The uncoordinated N atom of triazole can form hydrogen bonds with the water molecules (Table 2 and Table 2).

There is a strong offset face-to-face π–π stacking interaction (Fig. 2) between benzene rings C7–C12 and $C7^{ii}$–$C12^{ii}$ [symmetry code: (ii) $1-x, 1-y, 1-z$] with a perpendicular distance of 3.44 (6)Å and a centroid–centroid distance of 3.904Å. There is also a strong edge-to-face π–π stacking interaction between C7–C12 and $C7^{iii}$–$C12^{iii}$ [symmetry code: (iii) $\frac{1}{2}-x, \frac{3}{2}-y, -z$]. The dihedral angle between rings C7–C12 and $C7^{iii}$–$C12^{iii}$ is 106.5 (8)° and the distance between atom C4 and the $C7^{iii}$–$C12^{iii}$ ring is 3.45 (7) Å. The title compound thus exhibits a three-dimensional supramolecular structure.

Experimental

A mixture of $CuSO_4\cdot5H_2O$ (0.5 mmol, 0.125 g), Bta (1 mmol, 0.119 g) and water (10 ml) was adjusted to pH 2.2 by a 2 *N* sulfuric acid solution. The synthesis was carried out in a Teflon-lined autoclave. The mixture was heated at 413 K for 3 d, followed by slow cooling to room temperature. The resulting purple crystals were filtered off and washed with distilled water. CHN elemental analysis calculated for $CuC_{12}H_{10}N_6O$: C 45.31, N 26.43, H 3.15%; found: C 45.20, N 26.31, H 3.23%.

Crystal data

$[Cu(C_6H_4N_3)_2(H_2O)]$
$M_r = 317.80$
Monoclinic, $C2/c$
$a = 26.500$ (3) Å
$b = 6.884$ (2) Å
$c = 17.124$ (3) Å
$\beta = 125.609$ (3)°
$V = 2539.8$ (10) Å^3
$Z = 8$
$D_x = 1.662$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.72$ mm^{-1}
$T = 298$ (2) K
Block, purple
0.40 × 0.30 × 0.28 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.54$, $T_{max} = 0.62$
6003 measured reflections
2234 independent reflections
1619 reflections with $I > 2\sigma(I)$
$R_{int} = 0.062$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.104$
$S = 1.01$
2234 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N4^i	1.991 (3)	N3—C2	1.382 (6)
Cu1—N1	1.994 (3)	N4—N5	1.337 (5)
Cu1—N5	2.017 (3)	N4—C7	1.372 (5)
Cu1—N2^i	2.021 (3)	N5—N6	1.331 (4)
N1—N2	1.352 (5)	N6—C8	1.375 (5)
N1—C1	1.360 (5)	C1—C2	1.391 (6)
N2—N3	1.326 (5)	C7—C8	1.400 (6)
N4^i—Cu1—N1	94.28 (14)	N1—Cu1—N5	89.03 (14)
N4^i—Cu1—N5	173.68 (15)	N5—Cu1—N2^i	87.69 (14)

Symmetry code: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

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Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯N3^{i}	0.85	2.33	2.966 (5)	132
O1—H2⋯N6^{ii}	0.85	2.37	2.999 (5)	131

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

H atoms were positioned geometrically and refined as riding [C—H = 0.93Å and U_{iso}(H) = 1.2U_{eq}(C), and O–H = 0.85Å and U_{iso}(H) = 1.5U_{eq}(O) for water H atoms].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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