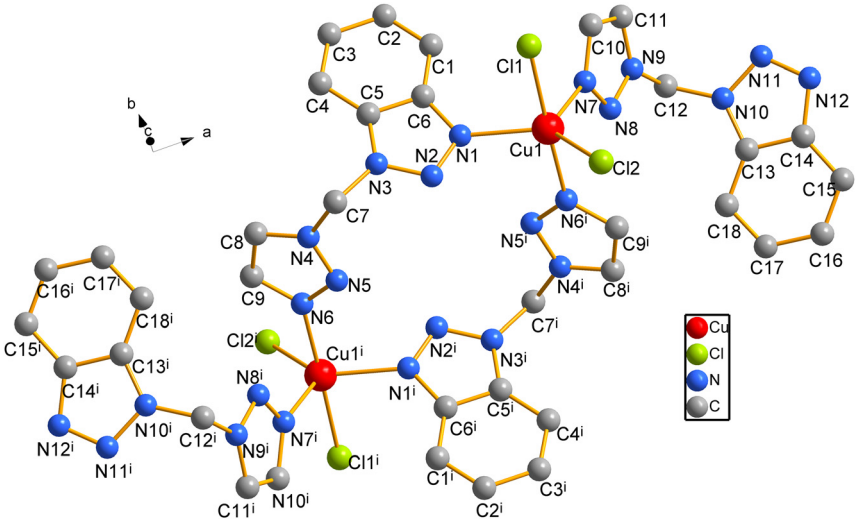
Tongyu Bai, Hanbing Li*, Mengmeng Cao and Xia Wang

Crystal structure of tetrachlorido-bis(1-[(1*H*-triazole-1-yl)methyl]-1*H*-benzotriazole-κ^2*N:N′*) dicopper, $C_{36}H_{32}Cu_2N_{24}Cl_4$



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Abstract

$C_{36}H_{32}Cu_2N_{24}Cl_4$, monoclinic, $P2_1/c$ (no. 14), a = 17.6099(4) Å, b = 8.13871(18) Å, c = 14.8084(3) Å, β = 91.6878(19)°, Z = 2, V = 2,121.45(8) Å^3, $R_{gt}(F)$ = 0.0549, w$R_{ref}(F^2)$ = 0.1597, T = 293(2) 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:	Blue block
Size:	0.13 × 0.08 × 0.06 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	4.08 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max}, completeness:	67.1°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8,031, 3,769, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3,160
$N(param)_{refined}$:	298
Programs:	SHELX[1]

1 Source of materials

All starting materials are commercially available without further purification. 1-[(1H-triazole-1-yl)methyl]-1H-benzotriazole (tmbt) was prepared according to the literature method with some modifications.[2] The ligand 1-[(1H-triazole-1-yl)methyl]-1H–benzotriazole (0.03 mmol, 0.0060 g) was dissolved in 2 mL of methanol solution and the solution was slowly add to 2 mL of $CuCl_2$ (0.06 mmol, 0.0103 g) of methanol solution. The prepared solution was placed at room temperature and blue crystals were obtained after eight days.

2 Experimental details

H atoms were generated geometrically and refined as riding atoms with C–H = 0.93 Å and the and U_{iso}(H) = 1.2 times U_{eq}(C) for aromatic H atoms, with C–H = 0.97 Å and U_{iso}(H) = 1.2 times U_{eq}(C) for methylene H atoms.

***Corresponding author: Hanbing Li**, Henan University of Chinese Medicine, Zhengzhou, 450046, P.R. China, E-mail: lhb8899@163.com. https://orcid.org/0000-0001-6943-2539
Tongyu Bai, Mengmeng Cao and Xia Wang, Henan University of Chinese Medicine, Zhengzhou, 450046, P.R. China. https://orcid.org/0000-0002-7929-0383 (X. Wang)

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.19753 (3)	0.64048 (7)	0.64603 (4)	0.0310 (2)
Cl1	0.20960 (6)	0.81935 (15)	0.76245 (8)	0.0437 (3)
Cl2	0.24586 (7)	0.42454 (14)	0.73346 (7)	0.0434 (3)
N1	0.08430 (18)	0.7260 (4)	0.6247 (2)	0.0305 (7)
N2	0.02879 (18)	0.6251 (4)	0.6407 (2)	0.0306 (7)
N3	−0.03507 (18)	0.7139 (4)	0.6471 (2)	0.0303 (7)
N4	−0.15391 (18)	0.6137 (4)	0.5855 (2)	0.0270 (7)
N5	−0.13698 (18)	0.5005 (4)	0.5235 (2)	0.0288 (7)
N6	−0.18991 (18)	0.5129 (4)	0.4601 (2)	0.0288 (7)
N7	0.26887 (19)	0.7982 (5)	0.5644 (2)	0.0341 (8)
N8	0.2903 (2)	0.7499 (4)	0.4841 (2)	0.0351 (8)
N9	0.33781 (19)	0.8650 (4)	0.4546 (3)	0.0352 (8)
N10	0.4401 (2)	0.7374 (5)	0.3791 (3)	0.0375 (8)
N11	0.5078 (2)	0.8006 (6)	0.4077 (3)	0.0502 (10)
N12	0.5580 (2)	0.6844 (6)	0.4107 (3)	0.0509 (11)
C1	0.0913 (3)	1.0357 (6)	0.6048 (3)	0.0384 (10)
H1	0.1431	1.0430	0.5950	0.046*
C2	0.0468 (3)	1.1714 (6)	0.6048 (3)	0.0443 (11)
H2	0.0686	1.2734	0.5941	0.053*
C3	−0.0317 (3)	1.1624 (6)	0.6206 (3)	0.0434 (11)
H3	−0.0600	1.2589	0.6204	0.052*
C4	−0.0673 (2)	1.0172 (6)	0.6360 (3)	0.0365 (9)
H4	−0.1191	1.0112	0.6464	0.044*
C5	−0.0213 (2)	0.8776 (5)	0.6352 (3)	0.0292 (8)
C6	0.0565 (2)	0.8838 (5)	0.6203 (3)	0.0292 (8)
C7	−0.1059 (2)	0.6311 (5)	0.6665 (3)	0.0301 (8)
H7A	−0.1328	0.6934	0.7113	0.036*
H7B	−0.0948	0.5232	0.6914	0.036*
C8	−0.2176 (2)	0.6951 (6)	0.5618 (3)	0.0355 (9)
H8	−0.2410	0.7780	0.5941	0.043*
C9	−0.2406 (2)	0.6316 (6)	0.4812 (3)	0.0386 (10)
H9	−0.2831	0.6632	0.4468	0.046*
C10	0.3027 (3)	0.9432 (6)	0.5850 (4)	0.0427 (11)
H10	0.2968	1.0028	0.6379	0.051*
C11	0.3470 (3)	0.9870 (6)	0.5149 (4)	0.0436 (11)
H11	0.3768	1.0806	0.5100	0.052*
C12	0.3746 (3)	0.8408 (6)	0.3690 (3)	0.0398 (10)
H12A	0.3388	0.7914	0.3260	0.048*
H12B	0.3897	0.9465	0.3451	0.048*
C13	0.4466 (2)	0.5737 (6)	0.3622 (3)	0.0342 (9)
C14	0.5229 (3)	0.5395 (7)	0.3831 (3)	0.0432 (11)
C15	0.5518 (3)	0.3799 (7)	0.3715 (4)	0.0528 (13)
H15	0.6025	0.3551	0.3844	0.063*
C16	0.5017 (3)	0.2633 (7)	0.3405 (4)	0.0573 (14)
H16	0.5188	0.1562	0.3330	0.069*
C17	0.4252 (3)	0.3000 (7)	0.3195 (4)	0.0541 (13)
H17	0.3936	0.2168	0.2975	0.065*
C18	0.3956 (3)	0.4541 (6)	0.3305 (3)	0.0426 (11)
H18	0.3447	0.4775	0.3176	0.051*

3 Comment

Heterocyclic compounds, as a class of organic compounds, have been widely concerned by researchers because of their properties. For example, the isatin heterocyclic compounds synthesized by the Altamimi, M team have anti-cancer and antibacterial properties.[3] The heterocyclic compounds studied by Zhou M's team can be applied as fluorescent anticancer drugs,[4] and the robust leishmanicidal upshot of some new diphenyl triazine-based molecules synthesized by Singh A's team.[5] Among them, benzotriazole and triazole compounds, as nitrogen heterocyclic thick ring compounds, have abundant electrons and can be coordinated with transition metals to synthesize metal complexes with stable structure and different properties. And widely used in medicine fields. For example, Ricardo A Murcia-Galan's team synthesized Co(II) and Cu(II) complexes containing 1,3-bis(benzotriazol-1-yl)-propan-2-ol and studied their antibacterial activities.[6] Czylkowska and Agnieszka synthesized five metal complexes from triazole derivatives, and found that the anticancer activity of the synthesized metal complexes was significantly stronger than that of the ligands.[7] Zhao Wanling and colleagues studied the synthesis of 7,8-dihydroxyflavone-copper metal complex (CAM–DHF) from flavonoid compounds such as 7,8-dihydroxyflavone found in traditional Chinese medicine and other natural medicines with copper ions. The formation of the complex with flavonoids can reduce the reproductive toxicity of copper ions, and it is speculated to have good biosafety.[8]

X-ray crystallographic analysis shows that the title complex has a binuclear structure and crystallized in a monoclinic $P2_1/c$ space group. As shown in figure, the central atom Cu(II) is coordinated with two Cl ions (Cl1, and Cl2) and three N atoms (N1, N6i and N7 from three tmbt ligands, respectively). The Cu–Cl and Cu–N bonds around Cu1 are of length: Cu1–Cl1: 2.2616(12) Å; Cu1–Cl2: 2.3291(12) Å; Cu1–N1: 2.127(3) Å; Cu1–N6i: 2.008(3) Å; Cu1–N7:2.185(4) Å. The range of bond angles around the metal center Cu(II) is 88.23(10)°–130.93(11)°. In each tmbt ligand, the angle between the benzotriazole ring and the triazole ring is 71.973(137)° and 72.026(116)°, the distance between the benzotriazole rings in two adjacent monodentate coordinated tmbt ligands is 3.982 Å, so it can be inferred that there may be one kind of π–π conjugation between the two adjacent molecules, which makes the centrosymmetric unit extend into a more stable one-dimensional chain structure.

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