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Triaquabis[bis(3,5-dimethyl-1,2,4-triazol-1-yl)-methane-κN^4]copper(II) bis(perchlorate)

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Key indicators

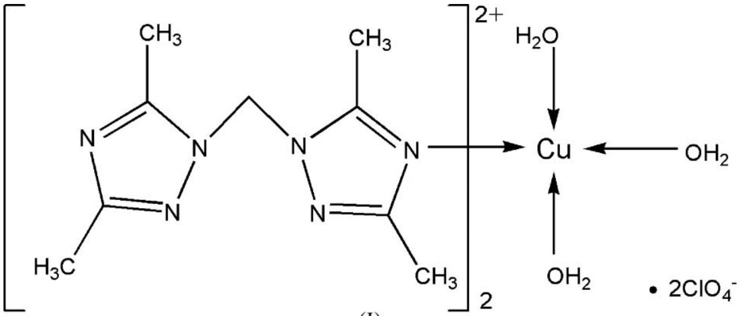
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
Disorder in solvent or counterion
R factor = 0.042
wR factor = 0.119
Data-to-parameter ratio = 11.2

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

The title compound, $[Cu(bdtm)_2(H_2O)_3](ClO_4)_2$ [bdtm is bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane, $C_9H_{14}N_6$], is the first example of a mononuclear copper complex with monodentate bdtm ligands. In the cation, which possesses crystallographically imposed twofold rotation symmetry, the Cu^{II} atom is coordinated by the two N atoms [Cu—N = 2.009 (3) Å] from two symmetry-equivalent bdtm ligands and three O atoms [Cu—O = 1.949 (3) and 2.232 (6) Å] from the water molecules in a distorted trigonal–bipyramidal geometry.

Comment

Since Trofimenko (1970) first synthesized bis(pyrazoly)-alkanes, considerable attention has been attracted to these ligands (Pettinari & Pettinari, 2005) and their modifications (Effendy *et al.*, 2004; Shen *et al.*, 2003; Zhang *et al.*, 2000;). Bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane (bdtm) belongs to the family of the aforementioned compounds. It may coordinate to metal ions either by two endodentate N atoms forming boat-like structures or by two exodentate N atoms forming bridge-like structures (Tang *et al.*, 2000, 2002). In this report, we present the crystal structure of the title compound, (I), which contains a mononuclear copper(II) complex with a monodentate bdtm ligands.



(I)

In (I), the copper(II) complex possesses crystallographically imposed twofold rotation symmetry (Fig. 1). The central Cu^{II} atom is five-coordinated in a distorted trigonal–bipyramidal geometry (Table 1). The equatorial plane is defined by the two exodentate N atoms from two symmetry-related bdtm ligands and one O atom from a water molecule. The axial positions are occupied by two O atoms from two symmetry-related water molecules. To our knowledge, this is the first example of a monodentate coordination mode of the bdtm ligands.

In the crystal structure, intermolecular O—H···O, O—H···N and C—H···O hydrogen bonds (Table 2) stabilize the packing (Fig. 2).

Experimental

Copper(II) perchlorate hexahydrate (0.5 mmol, 186.3 mg) was dissolved in distilled water (5 ml). The solution was added to a solution of bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane (0.5 mmol, 104.4 mg) in ethanol (5 ml), and then the mixture was refluxed for 1.5 h. The mixture was slowly cooled to room temperature and filtered, and the filtrate was slowly evaporated at room temperature. Blue single crystals suitable for X-ray diffraction were obtained after two weeks (yield 35%).

Crystal data

$[Cu(C_9H_{14}N_6)_2(H_2O)_3](ClO_4)_2$
$M_r = 729.01$
Tetragonal, $P4_12_12$
$a = 9.2157$ (3) Å
$c = 37.458$ (3) Å
$V = 3181.2$ (3) Å^3
$Z = 4$

$D_x = 1.522$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.93$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.20 × 0.14 × 0.12 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{min} = 0.855$, $T_{max} = 0.899$

17426 measured reflections
2815 independent reflections
2581 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.119$
$S = 1.07$
2815 reflections
252 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 2.3565P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Absolute structure: Flack (1983), 1078 Friedel pairs
Flack parameter: 0.00 (3)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.949 (3)	Cu1—O2	2.232 (6)
Cu1—N1	2.009 (3)		
O1—Cu1—N1^i	88.70 (12)	O1—Cu1—O2	90.35 (12)
O1—Cu1—N1	91.12 (12)	N1—Cu1—O2	104.88 (9)
N1^i—Cu1—N1	150.25 (19)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A'···N6^{ii}	0.85 (3)	1.83 (3)	2.659 (4)	163 (4)
O1—H1B'···O5^{iii}	0.85 (4)	1.80 (3)	2.641 (7)	171 (5)
O1—H1B'···O5$'^{iii}$	0.85 (4)	2.01 (3)	2.855 (7)	171 (4)
O2—H2A···O3$'^{iv}$	0.85 (5)	1.99 (6)	2.821 (6)	165 (7)
O2—H2A···O4^{iv}	0.85 (5)	2.36 (7)	2.872 (10)	120 (5)
C4—H4A···O5$'^{iv}$	0.96	2.58	3.411 (7)	145
C4—H4C···O6$'^{v}$	0.96	2.55	3.261 (10)	131
C6—H6B···O4$'^{vi}$	0.96	2.24	3.190 (9)	172
C6—H6B···O6^{vi}	0.96	2.54	3.342 (9)	141

Symmetry codes: (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{4}$; (iii) $x + 1, y - 1, z$; (iv) $x, y - 1, z$; (v) $y, x, -z$; (vi) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{4}$.

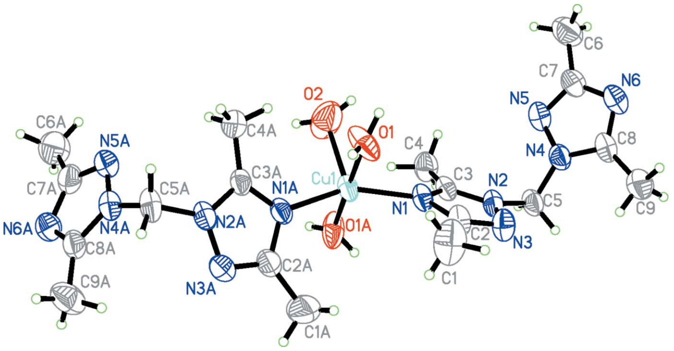


Figure 1
The molecular structure of (I) with the atomic numbering and displacement ellipsoids drawn at the 30% probability level [symmetry code: (A) $y + 1, x - 1, -z$]. Disordered ClO_4^- anions have been omitted for clarity.

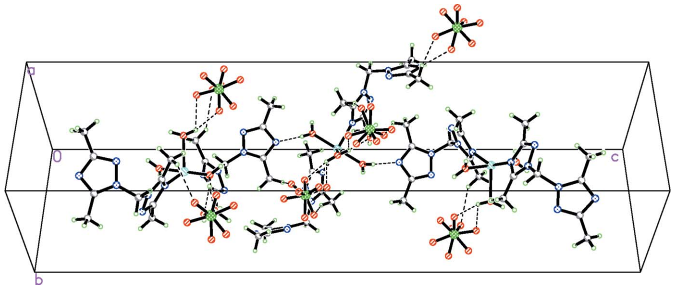


Figure 2
A packing diagram of (I) showing the disordered perchlorate anions, with intermolecular hydrogen bonds as dashed lines.

The water H atoms were located in Fourier difference maps and refined subject to an O—H restraint of 0.85 (2) Å and an H···H restraint of 1.45 (1) Å. The C-bound H atoms were introduced at calculated positions (C—H = 0.96 and 0.97 Å) and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. The perchlorate anion was treated as rotationally disordered between two orientations with occupancies fixed at 0.5.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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References

Bruker (1998). *SMART* (Version 5.0) and *SHELXTL* (Version 6.2). Bruker AXS Inc, Madison, Wisconsin, USA.
Bruker (1999). *SAINT*. Bruker AXS Inc., Madison, Wisconsis, USA.
Effendy, Marchetti, F., Pettinari, C., Pettinari, R., Ricciutelli, M., Skelton, B. W. & White, A. H. (2004). *Inorg. Chem.* **43**, 2157–2165.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Pettinari, C. & Pettinari, R. (2005). *Coord. Chem. Rev.* **249**, 663–691.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2000). *SADABS*. University of Göttingen, Germany.

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Shen, W.-Z., Kang, F., Sun, Y.-J., Chen, P., Yan, S.-P., Liao, D.-Z. & Jiang, Z. H. (2003). *Inorg. Chem. Commun.* **6**, 408–411.
Tang, L.-F., Wang, Z.-H., Chai, J.-F., Jia, W.-L., Xu, Y.-M. & Wang, J.-T. (2000). *Polyhedron*, **19**, 1949–1954.
Tang, L.-F., Wang, Z.-H., Chai, J.-F., Leng, X.-B., Wang, J.-T. & Wang, H.-G. (2002). *J. Organomet. Chem.* **642**, 179–185.
Trofimenko, S. (1970). *J. Am. Chem. Soc.* **92**, 5118–5126.
Zhang, L., Bu, W.-M., Yan, S.-P., Jiang, Z.-H., Liao, D.-Z. & Wang, G.-L. (2000). *Polyhedron*, **19**, 1105–1110.

m3464 Xiang *et al.* • $[Cu(C_9H_{14}N_6)_2(H_2O)_3](ClO_4)_2$ *Acta Cryst.* (2006). E**62**, m3462–m3464