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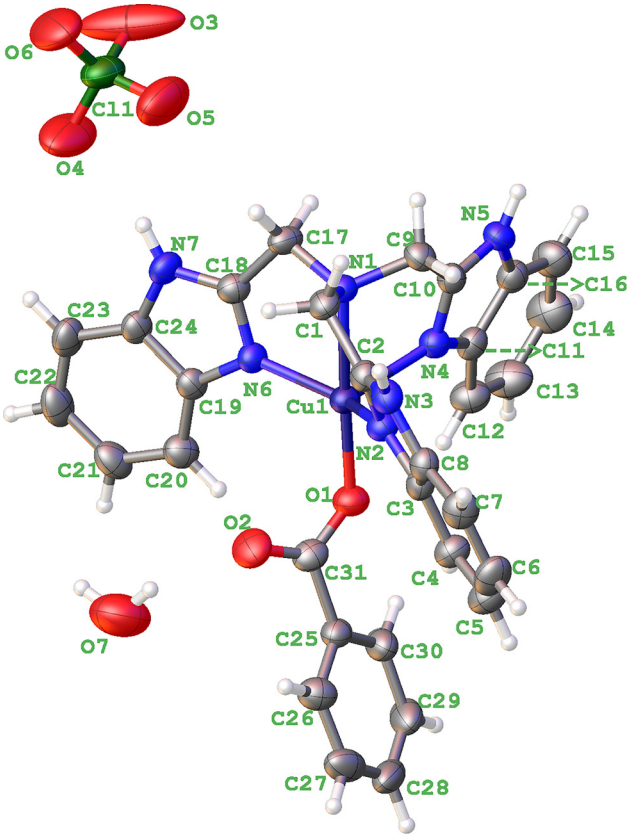
The crystal structure of (tris(2-benzimidazolylmethyl)amine)-benzoato-copper(II) perchlorate monohydrate, $CuC_{31}H_{28}N_7O_7Cl$



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Abstract

$CuC_{31}H_{28}N_7O_7Cl$, triclinic, $P\bar{1}$ (no. 2), a = 10.1386(6) Å, b = 12.1155(8) Å, c = 14.1972(8) Å, α = 100.297(2)°, β = 98.411(2)°, γ = 112.744(2)°, V = 1536.78(16) Å^3, Z = 2, $R_{gt}(F)$ = 0.0613, $wR_{ref}(F^2)$ = 0.1519, T = 250(2) K.

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Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.12 × 0.10 × 0.08 mm
Wavelength:	Ga $K\alpha$ radiation (1.34139 Å)
μ:	4.70 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Photon III, φ and ω
θ_{max}, completeness:	57.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	31,453, 6297, 0.075
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4653
$N(param)_{refined}$:	428
Programs:	Bruker [1], SHELX [2–4], DIAMOND [5], OLEX2 [6]

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Tris(2-benzimidazolylmethyl)amine (NTB) was prepared according to an earlier method [7]. Firstly, ligand ntb (0.081 g, 0.20 mmol) was added to an ethanol (20 ml) solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.074 g, 0.20 mmol). The mixture was stirred at room temperature for 20 min to get a clear blue solution. Then, an ethanol solution (5.0 ml) of sodium benzoate (0.0288 g, 0.20 mmol) was added dropwise to this solution and the green suspension was formed. Lastly, the mixture was refluxed for 30 min at 353 K and then gradually cooled to room temperature. The suspension was filtered and a bright green powder was obtained, washed using ether for three times and dried under the infrared light (0.121 g, yield: 85%). The residual filtrate was allowed to stand for one week. Green crystals suitable for X-ray structure analysis were obtained at the bottom of the vessel.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3026 (4)	0.5266 (3)	0.3699 (3)	0.0350 (8)
H1A	0.297624	0.443128	0.349122	0.042*
H1B	0.206706	0.519292	0.380807	0.042*
C2	0.4204 (4)	0.5994 (3)	0.4616 (3)	0.0326 (8)
C3	0.6344 (4)	0.7281 (3)	0.5567 (3)	0.0332 (8)
C4	0.7797 (4)	0.8134 (3)	0.5969 (3)	0.0402 (9)
H4	0.844504	0.843629	0.557056	0.048*
C5	0.8242 (5)	0.8517 (4)	0.6989 (3)	0.0508 (11)
H5A	0.922297	0.908393	0.728621	0.061*
C6	0.7288 (5)	0.8092 (4)	0.7585 (3)	0.0509 (11)
H6	0.763136	0.839019	0.827346	0.061*
C7	0.5849 (5)	0.7243 (4)	0.7189 (3)	0.0453 (10)
H7A	0.520112	0.694888	0.759010	0.054*
C8	0.5399 (4)	0.6841 (3)	0.6169 (3)	0.0338 (8)
C9	0.3050 (4)	0.7030 (3)	0.3081 (3)	0.0359 (8)
H9A	0.312573	0.734895	0.378061	0.043*
H9B	0.203938	0.678292	0.271531	0.043*
C10	0.4109 (4)	0.8008 (3)	0.2710 (3)	0.0324 (8)
C11	0.6102 (4)	0.9108 (3)	0.2333 (3)	0.0347 (8)
C12	0.7501 (4)	0.9592 (4)	0.2140 (3)	0.0444 (10)
H12	0.821665	0.932055	0.235515	0.053*
C13	0.7784 (5)	1.0481 (4)	0.1623 (4)	0.0577 (12)
H13	0.870874	1.081514	0.147311	0.069*
C14	0.6736 (5)	1.0898 (4)	0.1317 (4)	0.0610 (13)
H14	0.697820	1.151439	0.097107	0.073*
C15	0.5357 (5)	1.0440 (4)	0.1502 (3)	0.0507 (11)
H15	0.465434	1.072703	0.129305	0.061*
C16	0.5060 (4)	0.9529 (3)	0.2014 (3)	0.0377 (9)
C17	0.2744 (4)	0.5132 (4)	0.1923 (3)	0.0381 (9)
H17A	0.240182	0.556654	0.149512	0.046*
H17B	0.189293	0.438679	0.192806	0.046*
C18	0.3853 (4)	0.4778 (3)	0.1539 (3)	0.0346 (8)
C19	0.5974 (4)	0.4846 (3)	0.1355 (3)	0.0331 (8)
C20	0.7452 (4)	0.5135 (4)	0.1403 (3)	0.0415 (9)
H20	0.820159	0.582448	0.187506	0.050*
C21	0.7771 (5)	0.4361 (4)	0.0726 (3)	0.0482 (10)
H21	0.876105	0.453620	0.073284	0.058*
C22	0.6668 (5)	0.3330 (4)	0.0035 (3)	0.0514 (11)
H22	0.693218	0.280833	−0.039373	0.062*
C23	0.5210 (5)	0.3053 (4)	−0.0038 (3)	0.0459 (10)
H23	0.446714	0.236658	−0.051603	0.055*
C24	0.4879 (4)	0.3839 (3)	0.0630 (3)	0.0356 (8)
C25	1.0259 (4)	0.7569 (3)	0.4409 (3)	0.0344 (8)
C26	1.0934 (4)	0.7230 (4)	0.5154 (3)	0.0453 (10)
H26	1.040880	0.649099	0.532003	0.054*
C27	1.2383 (5)	0.7980 (5)	0.5655 (3)	0.0534 (11)
H27	1.282714	0.776753	0.617947	0.064*
C28	1.3171 (5)	0.9033 (4)	0.5386 (4)	0.0559 (12)
H28	1.415919	0.953354	0.571964	0.067*
C29	1.2519 (4)	0.9357 (4)	0.4632 (4)	0.0538 (12)
H29	1.306816	1.006517	0.443713	0.065*
C30	1.1053 (4)	0.8639 (3)	0.4159 (3)	0.0454 (10)
H30	1.059611	0.888482	0.366336	0.054*
C31	0.8657 (4)	0.6789 (4)	0.3920 (3)	0.0372 (9)
Cl1	−0.02683 (11)	0.20570 (11)	−0.06739 (8)	0.0573 (3)
Cu1	0.58207 (5)	0.66700 (5)	0.32064 (4)	0.03158 (19)
N1	0.3424 (3)	0.5950 (3)	0.2939 (2)	0.0305 (6)
N2	0.5550 (3)	0.6740 (3)	0.4580 (2)	0.0327 (7)
N3	0.4067 (3)	0.6014 (3)	0.5544 (2)	0.0362 (7)
H3	0.327868	0.558207	0.572021	0.043*
N4	0.5473 (3)	0.8152 (3)	0.2766 (2)	0.0327 (7)
N5	0.3798 (3)	0.8820 (3)	0.2280 (2)	0.0359 (7)
H5	0.296590	0.888357	0.218795	0.043*
N6	0.5283 (3)	0.5416 (3)	0.1933 (2)	0.0325 (7)
N7	0.3560 (3)	0.3835 (3)	0.0771 (2)	0.0395 (7)
H7	0.268823	0.330854	0.041989	0.047*
O1	0.7955 (3)	0.7341 (2)	0.35524 (19)	0.0408 (6)
O2	0.8106 (3)	0.5669 (3)	0.3910 (2)	0.0524 (8)
O3	−0.0648 (4)	0.2634 (7)	−0.1372 (4)	0.172 (3)
O4	0.1035 (4)	0.1932 (5)	−0.0742 (4)	0.128 (2)
O5	0.0037 (5)	0.2821 (5)	0.0254 (3)	0.1167 (17)
O6	−0.1499 (4)	0.0938 (4)	−0.0786 (4)	0.1058 (15)
O7	0.9594 (5)	0.4327 (5)	0.2954 (4)	0.1051 (14)
H7B	0.897568	0.452785	0.321219	0.158*
H7C	0.912689	0.372704	0.243210	0.158*

Experimental details

Hydrogen atoms bonded to carbon atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms with C–H = 0.94 Å (aromatic), 0.98 Å (methylene) and U_{iso}(H) = 1.2U_{eq} (aromatic and methylene). Hydrogen atoms bonded to nitrogen, water oxygen atoms were initially found from the difference maps and then refined to be at their ideal positions with N–H = 0.87 Å and O–H = 0.86 Å. Their thermal factors were set as U_{iso}(H) = 1.2U_{eq}(N) and 1.5U_{eq}(O).

Comment

Multi-benzimidazole ligand tris(2-benzimidazolylmethyl)-amine (NTB) has been often used as a histidine-like mimic to model the active sites of metalloproteins [8–13]. A number of mononuclear copper complexes related with NTB have been synthesized and reported. In these analogs, there may be a coligand such as nitrate, chloride, azide and water molecule around the copper coordination sphere, which can regulate its redox properties and further influence the enzymatic-mimicking activities. As a continuation of our studies [14].

In the crystal of the title compound(I), its asymmetric unit was composed of each one $[Cu(NTB)(PhCOO)]^+$, one

perchlorate anion and one water solvent molecule. In (I), NTB acts as a tetradentate ligand, coordinating through the tertiary N atom and three benzimidazole (bzim) N atoms to the metal ion. There is also a benzoate oxygen atom mono-dentated coordinated to the copper atom, forming a distorted trigonal bipyramidal coordination configuration with a τ parameter of 0.608 [15]. The three benzimidazole N2, N4 and N6 atoms constitute of the equatorial plane, and the amine N1 and carboxylated O1 atoms reside at the axial positions. The tertiary N1 atom presents the Cu–N1 bond length about 0.14 Å longer than the mean value of the three Cu–N_{bzim} bond lengths. This should result from steric requirements of the trigonal ligand NTB. The cis angles around the copper center are ranging from 79.09(1)° to 107.83(1)° and the two larger trans angles are 139.08(1)° and 175.55(1)° for N2–Cu1–N6 and N1–Cu1–O1, respectively, which are very similar to some analogs [16–18].

In the crystal packing, the component ions are linked into a complex structure by a combination of N–H···O, O–H···O, $\pi\cdots\pi$ and C–H···π interactions [19].

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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