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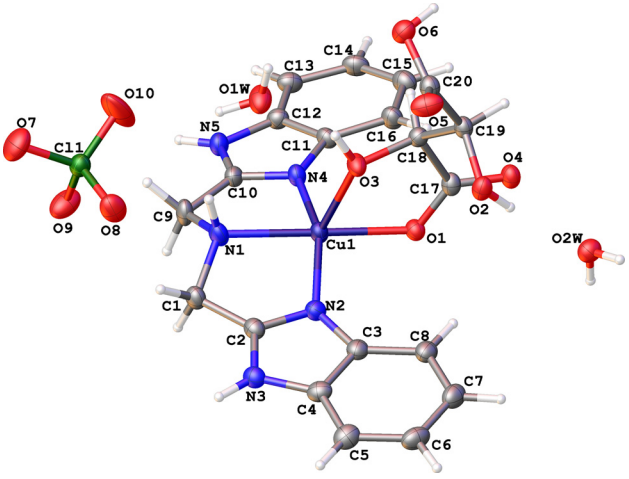
The crystal structure of (bis(benzimidazol-2-yl-methyl)amine-κ^3N,N',N'')-(dihydrogen L-malate-κ^2O,O')copper(II) perchlorate dihydrate, $CuC_{20}H_{24}ClN_5O_{12}$



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Abstract

$CuC_{20}H_{24}ClN_5O_{12}$, monoclinic, $P\bar{1}$ (no. 4), a = 7.4467(4) Å, b = 17.3823(9) Å, c = 9.6974(5) Å, α = 90°, β = 103.373(2)°, γ = 90°, V = 1221.20(11) Å^3, Z = 2, $R_{gt}(F)$ = 0.0642, $wR_{ref}(F^2)$ = 0.1757, T = 100(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

Bis(benzimidazol-2-yl-methyl)amine (IDB) was prepared according to an earlier described method [7]. IDB (0.277 g, 1.0 mmol) and L-malic acid (0.134 g, 1.0 mmol) were firstly dissolved in hot methanol (30.0 mL) and then a solution of $Cu(ClO_4)_2(H_2O)_6$ (0.371 g, 1.0 mmol) in 20.0 mL methanol was added drop by drop. The mixed solution was stirred for 1 h at 60 °C. Then, the reaction mixture was filtered and the filtrate solution was evaporated at room temperature for two weeks. Some blue crystals were obtained at the bottom of the glass vessel (0.40 g, yield: 64 %).

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.16 × 0.12 × 0.10 mm
Wavelength:	Ga $K\alpha$ radiation (1.34139 Å)
μ:	5.94 mm^{-1}
Diffractometer, scan mode:	Bruker Photon III, φ and ω
θ_{max}, completeness:	54.9°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	25,044, 4607, 0.099
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3932
$N(param)_{refined}$:	373
Programs:	Bruker [1], SHELX [2, 3, 6], Diamond [4], Olex2 [5]

2 Experimental details

Hydrogen atoms bonded to carbon atoms were placed in their geometrically idealized positions and restrained to ride on their parent atoms with C–H = 0.95 Å (aromatic), 0.99 Å (methylene), 1.00 Å (methine) and U_{iso}(H) = 1.2U_{eq} (aromatic, methylene and methine). Hydrogen atoms bonded to nitrogen and oxygen atoms were initially found from the difference maps and restrained to be at their indicative positions using command 'AFIX'. The thermal factors of these hydrogen atoms were set 1.2 times (for N) or 1.5 times (for O) of their parent atoms. During the refinement, the perchlorate anion was found to be disordered over two positions with the final occupancies being 0.87(1):0.13(1) for the major and minor components. Commands DFIX, DANG and EADP were used to constrain the Cl–O,O···O distances and thermal factors.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6343 (13)	0.3976 (5)	0.8240 (9)	0.0458 (19)
H1A	0.536673	0.402955	0.877406	0.055*
H1B	0.745638	0.375556	0.887761	0.055*
C2	0.6775 (11)	0.4737 (5)	0.7694 (9)	0.0407 (18)
C3	0.7466 (11)	0.5585 (5)	0.6256 (9)	0.0429 (19)
C4	0.7391 (11)	0.5968 (5)	0.7502 (10)	0.045 (2)
C5	0.7714 (13)	0.6748 (6)	0.7690 (12)	0.055 (2)
H5	0.765751	0.700269	0.854549	0.066*
C6	0.8128 (13)	0.7138 (6)	0.6549 (12)	0.059 (3)
H6	0.834786	0.767640	0.661520	0.070*
C7	0.8227 (13)	0.6746 (6)	0.5299 (12)	0.055 (2)
H7	0.853594	0.702884	0.454745	0.066*
C8	0.7896 (12)	0.5978 (5)	0.5125 (10)	0.047 (2)
H8	0.795624	0.572243	0.427064	0.057*
C9	0.6120 (14)	0.2649 (5)	0.7188 (9)	0.050 (2)
H9B	0.507455	0.237811	0.744546	0.060*
H9A	0.723289	0.257576	0.796307	0.060*
C10	0.6444 (12)	0.2333 (5)	0.5830 (9)	0.0403 (18)
C11	0.6884 (11)	0.2283 (5)	0.3705 (8)	0.0405 (18)
C12	0.6975 (12)	0.1532 (5)	0.4223 (9)	0.0432 (18)
C13	0.7313 (13)	0.0896 (5)	0.3468 (10)	0.049 (2)
H13	0.738172	0.038900	0.384037	0.059*
C14	0.7544 (13)	0.1060 (6)	0.2121 (10)	0.052 (2)
H14	0.781257	0.064796	0.155650	0.062*
C15	0.7404 (14)	0.1787 (6)	0.1569 (10)	0.054 (2)
H15	0.754667	0.185910	0.062876	0.065*
C16	0.7063 (13)	0.2417 (6)	0.2324 (9)	0.048 (2)
H16	0.695453	0.291871	0.192646	0.058*
C17	0.6145 (12)	0.4388 (5)	0.2397 (8)	0.0386 (17)
C18	0.4088 (10)	0.4368 (5)	0.2403 (8)	0.0367 (16)
H18	0.352877	0.388333	0.193599	0.044*
C19	0.3103 (11)	0.5060 (5)	0.1594 (8)	0.0388 (17)
H19	0.312744	0.500843	0.057115	0.047*
C20	0.1093 (12)	0.5117 (5)	0.1709 (9)	0.0432 (19)
Cu1	0.65223 (15)	0.38791 (7)	0.52418 (11)	0.0379 (3)
N1	0.5700 (12)	0.3473 (4)	0.6979 (7)	0.0505 (18)
H1	0.432310	0.351136	0.673812	0.061*
N2	0.7072 (10)	0.4811 (4)	0.6400 (7)	0.0411 (15)
N3	0.6977 (9)	0.5407 (4)	0.8394 (8)	0.0434 (16)
H3	0.686548	0.547896	0.926919	0.052*
N4	0.6545 (9)	0.2787 (4)	0.4771 (7)	0.0391 (14)
N5	0.6680 (10)	0.1591 (4)	0.5585 (8)	0.0443 (16)
H5A	0.665389	0.120872	0.617484	0.053*
O1	0.7324 (7)	0.4245 (3)	0.3569 (6)	0.0396 (12)
O2	0.6586 (9)	0.4545 (3)	0.1274 (6)	0.0439 (13)
O3	0.3936 (7)	0.4373 (4)	0.3837 (6)	0.0453 (14)
H3A	0.279 (5)	0.429 (7)	0.385 (12)	0.068*
O4	0.3975 (9)	0.5756 (3)	0.2117 (6)	0.0440 (13)
H4	0.497117	0.579858	0.185692	0.066*
O5	0.0426 (9)	0.5700 (4)	0.2072 (9)	0.0608 (18)
O6	0.0183 (9)	0.4470 (4)	0.1397 (7)	0.0491 (14)
H6A	0.019407	0.433993	0.056518	0.074*
Cl1[a]	0.1526 (5)	0.3263 (2)	0.8571 (4)	0.0460 (8)
O7[a]	0.0261 (13)	0.3024 (6)	0.9402 (11)	0.079 (3)
O8[a]	0.1815 (14)	0.4066 (4)	0.8631 (9)	0.068 (3)
O9[a]	0.3253 (11)	0.2911 (5)	0.9247 (13)	0.076 (3)
O10[a]	0.091 (3)	0.3002 (8)	0.7186 (10)	0.138 (7)
Cl1A[b]	0.150 (4)	0.3403 (14)	0.819 (3)	0.0460 (8)
O7A[b]	0.098 (8)	0.356 (3)	0.951 (4)	0.079 (3)
O8A[b]	0.224 (7)	0.4098 (18)	0.770 (5)	0.068 (3)
O9A[b]	0.288 (7)	0.280 (2)	0.833 (7)	0.076 (3)
O10A[b]	−0.013 (7)	0.319 (4)	0.712 (6)	0.138 (7)
O1W	0.0989 (9)	0.3964 (5)	0.4683 (8)	0.0634 (18)
H1WA	0.112523	0.375842	0.551277	0.095*
H1WB	−0.011267	0.407532	0.419137	0.095*
O2W	0.6867 (9)	0.6229 (4)	0.1044 (7)	0.0492 (14)
H2WA	0.671867	0.669088	0.069096	0.074*
H2WB	0.803817	0.614028	0.137396	0.074*

[a]Occupancy: 0.867 (10), [b]occupancy: 0.133 (10).

3 Comment

Cu(II)-containing complexes are of great interest in relation of the active site of natural superoxidase dismutase (SOD), hemerythrin and nuclease [8–10]. These model compounds can be used as mimics aiming to provide further insight into the mechanism of metal sites in complex biological systems. Some of the important considerations in the preparation of model compounds include donor atoms and the resulting geometry around the metal center. Although there is each one copper(II) and one zinc(II) ions in the active site of the natural SOD, research indicates the two back-to-back single-electron redox reactions occur only around the Cu(II) ion which plays a decisive role in the whole catalytic process, and the metal zinc ion only stabilize the skeleton of the enzymatic protein. Therefore, much synthesis of superoxide dismutase model compounds have mainly focused on the micking of copper metal complexes containing imidazole or benzimidazole ligands due to their structurally similarity.

The crystal of the title compund (I) crystallized in the chiral space group $P2_1$ because of the use of the chiral ligand L-malic acid. Its asymmetric unit was composed of each one $[Cu(IDB)(L\text{-}mal)]^+$ cation, one counter perchlorate anion and two water molecules. In (I), IDB acts as a tridentate ligand coordinating through one tertiary N atom (N1) and two benzimidazole (bzim) N atoms (N2 and N4) to copper. And the L-malate anion coordinates to the central copper ion in a way of bidentated ligand via the O1 and O3 atoms. Thus, a distorted five-coordinated environment was formed around the copper center with a τ parameter of 0.35 showing a moderately distortion of the square-pyramidal polyhedron [11]. The donor sets of N1/N2/N4/O1 constitute the basic plane and O3 atom resides at the apical position. The Cu1–N1 (2.049(7) Å) bond distance is slightly longer that

the other two Cu–N2 (1.957(7) Å) and Cu1–N4 (1.954(7) Å), which should be ascribed to the steric hindrance originating from the IDB ligand. The Cu1–O1 of 1.960(5) Å is apparently shorter than the Cu1–O3 (2.256(5) Å) which also meets the requirement of the copper center. The bond angles around Cu1 atom from 76.0(2) to 178.8(2)° are comparable to some analogs [12–14].

Analysis by *Platon* [15] indicates that in this component $[Cu(IDB)(L\text{-}mal)]^+$, the ClO_4^- ions and two water solvent molecules are linked into a complex three-dimensional hydrogen-bonded network by the extensive N–H···O and O–H···O hydrogen bonds. Also there are two intermolecular $\pi\cdots\pi$ interactions observed between the benzene ring (C3–C8) and the adjacent imidazole ring [N4/N5/C10–C12, $(1 - x, 1/2 + y, 1 - z)$] and the benzene ring [C11–C16, $(2 - x, 1/2 + y, 1 - z)$]. Their centroid-to-centroid distances are of 3.538(4) and 3.664(4) Å, respectively, showing moderate noncovalent interactions, which further consolidate the crystal structure.

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