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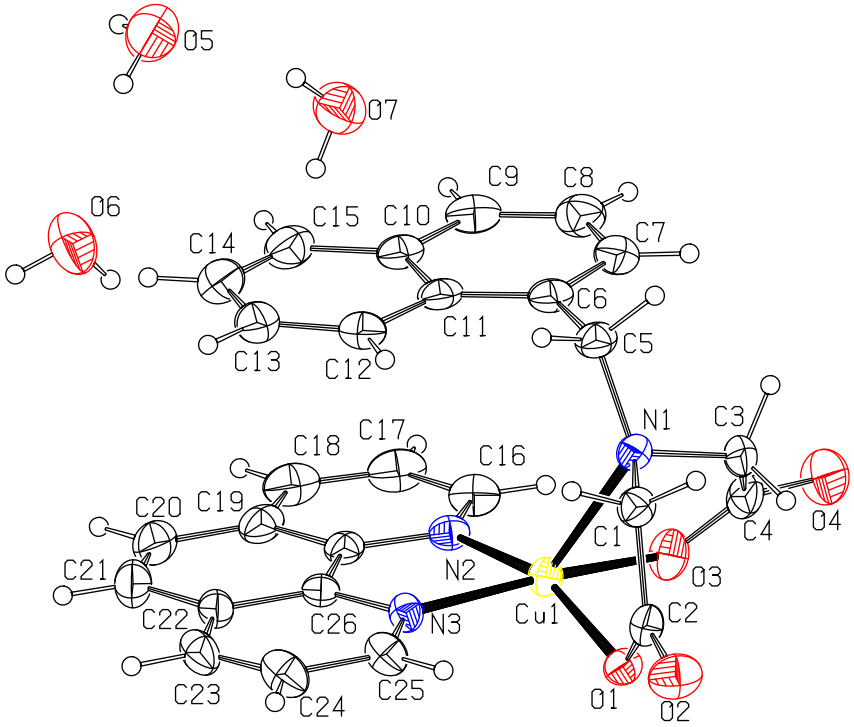
Crystal structure of (2,2′-((naphthalen-1-ylmethyl)azanediyl)diacetato-κ^3*N*,*O*,*O*′)-(1,10-phenanthroline-κ^2*N*,*N*′)-copper(II) trihydrate, $CuC_{27}H_{27}N_3O_7$



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Abstract

$CuC_{27}H_{27}N_3O_7$, orthorhombic, $Pca2_1$ (no. 29), a = 22.9142(18) Å, b = 7.3271(6) Å, c = 14.7386(11) Å, V = 2474.5(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0443, $wR_{ref}(F^2)$ = 0.0990, T = 294(2) K.

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The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.12 × 0.10 × 0.10 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.94 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16,736, 5352, 0.044
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 4224
$N(param)_{refined}$:	352
Programs:	Bruker [1], SHELX [2–4], Diamond [5], Olex2 [6], PLATON [7]

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

Source of material

All the reagents and solvents were used as obtained without further purification. *N*-(1-naphtylmethyl)iminodiacetic acid

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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	0.79889 (19)	0.0923 (6)	0.7026 (3)	0.0415 (10)
H1A	0.796156	0.103621	0.768000	0.050*
H1B	0.831649	0.165665	0.682380	0.050*
C2	0.80975 (17)	−0.1037 (6)	0.6783 (4)	0.0407 (13)
C3	0.7529 (2)	0.1837 (7)	0.5623 (3)	0.0471 (11)
H3A	0.790791	0.134267	0.546237	0.057*
H3B	0.753626	0.313105	0.548430	0.057*
C4	0.7082 (2)	0.0957 (7)	0.5034 (3)	0.0503 (12)
C5	0.72674 (19)	0.3387 (6)	0.7046 (4)	0.0447 (11)
H5A	0.748847	0.438085	0.677900	0.054*
H5B	0.735941	0.334250	0.768755	0.054*
C6	0.6621 (2)	0.3763 (6)	0.6930 (4)	0.0454 (12)
C7	0.6413 (3)	0.4520 (7)	0.6144 (4)	0.0565 (14)
H7	0.668053	0.483274	0.569552	0.068*
C8	0.5816 (3)	0.4851 (8)	0.5976 (4)	0.0612 (14)
H8	0.569028	0.531602	0.542281	0.073*
C9	0.5430 (2)	0.4465 (6)	0.6653 (6)	0.0600 (12)
H9	0.503533	0.469497	0.656043	0.072*
C10	0.5613 (2)	0.3725 (6)	0.7492 (4)	0.0471 (12)
C11	0.62194 (19)	0.3358 (6)	0.7624 (4)	0.0459 (11)
C12	0.6385 (2)	0.2628 (7)	0.8493 (4)	0.0513 (12)
H12	0.677440	0.234785	0.860642	0.062*
C13	0.5979 (3)	0.2347 (7)	0.9148 (4)	0.0594 (14)
H13	0.609583	0.189958	0.970977	0.071*
C14	0.5394 (3)	0.2713 (8)	0.8995 (5)	0.0668 (16)
H14	0.512392	0.249521	0.945380	0.080*
C15	0.5211 (2)	0.3376 (8)	0.8198 (5)	0.0637 (16)
H15	0.481668	0.360990	0.810825	0.076*
C16	0.5594 (2)	−0.0296 (7)	0.6214 (4)	0.0520 (12)
H16	0.570885	0.009587	0.564113	0.062*
C17	0.4999 (2)	−0.0310 (8)	0.6431 (4)	0.0612 (17)
H17	0.472371	0.006018	0.600509	0.073*
C18	0.4824 (2)	−0.0871 (7)	0.7274 (5)	0.0650 (17)
H18	0.442959	−0.087960	0.742080	0.078*
C19	0.5238 (2)	−0.1434 (7)	0.7916 (4)	0.0516 (13)
C20	0.5114 (3)	−0.2058 (8)	0.8812 (5)	0.0674 (17)
H20	0.472947	−0.207897	0.901185	0.081*
C21	0.5543 (3)	−0.2623 (8)	0.9383 (4)	0.0654 (16)
H21	0.544662	−0.302776	0.996143	0.078*
C22	0.6135 (2)	−0.2604 (7)	0.9110 (3)	0.0478 (12)
C23	0.6606 (3)	−0.3184 (7)	0.9660 (3)	0.0560 (13)
H23	0.653960	−0.360566	1.024601	0.067*
C24	0.7149 (3)	−0.3116 (7)	0.9323 (4)	0.0574 (13)
H24	0.746119	−0.348886	0.968119	0.069*
C25	0.7251 (2)	−0.2501 (7)	0.8455 (3)	0.0464 (11)
H25	0.763284	−0.248458	0.824130	0.056*
C26	0.62714 (19)	−0.1986 (6)	0.8241 (3)	0.0377 (10)
C27	0.58245 (18)	−0.1398 (6)	0.7638 (3)	0.0395 (10)
Cu1	0.68688 (2)	−0.09753 (6)	0.66375 (4)	0.03550 (14)
N1	0.74485 (13)	0.1624 (4)	0.6610 (3)	0.0365 (7)
N2	0.59960 (14)	−0.0822 (4)	0.6798 (3)	0.0380 (10)
N3	0.68280 (14)	−0.1932 (5)	0.7912 (2)	0.0361 (8)
O1	0.76685 (11)	−0.1993 (4)	0.6493 (2)	0.0406 (7)
O2	0.85943 (14)	−0.1634 (5)	0.6899 (3)	0.0609 (11)
O3	0.67791 (14)	−0.0349 (6)	0.5360 (2)	0.0523 (9)
O4	0.7047 (2)	0.1460 (6)	0.4242 (3)	0.0796 (12)
O5	0.3772 (3)	0.6113 (7)	0.8548 (4)	0.0957 (15)
H5C	0.341481	0.602977	0.853320	0.143*
H5D	0.387848	0.521768	0.883678	0.143*
O6	0.3787 (2)	0.2318 (7)	0.8910 (4)	0.0844 (14)
H6A	0.375941	0.177076	0.842656	0.127*
H6B	0.366220	0.160028	0.928970	0.127*
O7	0.3900 (2)	0.5306 (5)	0.6648 (4)	0.0810 (10)
H7A	0.386941	0.420147	0.672546	0.121*
H7B	0.391386	0.573174	0.716178	0.121*

(H_2NamIDA) was prepared in its acid form according to an earlier reported method [8]. A small amounts of $Cu_2CO_3(OH)_2$ (0.44 g, 2.0 mmol), 1,10-phenanthroline (0.36 g, 2.0 mmol) and H_2NamIDA (0.6 g, 2.2 mmol) were added into a flask in 50.0 mL distilled water. The solution was heated (50 °C) and stirred for 2 h. The residue was filtered and stood at room temperature for three days. Block blue crystals are formed (Yield: 60%, 0.683 g, based on metal salt).

Experimental details

H atoms were treated as riding, with C–H distances of 0.93 Å (aromatic) and 0.97 Å (methylene); U_{iso}(H) = 1.2U_{eq} (aromatic and methylene C). H atoms bonded to water O atoms were initially found in difference maps, and refined with constraint of O–H = 0.82 Å and U_{iso}(H) values were set equal to 1.5 times of their parent atoms.

Comment

2,2′-(1-naphthylmethyl)iminodiacetic acid (H_2NamIDA) is a frequently used organic starting material in the synthesis of metal-organic compounds as supra-molecular building blocks or as biological probe [9–12]. As the continuation of our earlier work aiming to design new useful DNA cleaving agents [13, 14], we have synthesized new mixed ligated copper(II) complexes formed by NamIDA and 1,10-phenanthroline.

The title compound was crystallized in the orthorhombic acentric $Pca2_1$ space group. In its asymmetric unit, there is a neutral metal coordination ion and three free water molecules. The central copper (II) is five-coordinated by a $\{N_3O_2\}$ donor set from each one NamIDA dianionic ligands and one phenanthroline molecule. The coordination

configuration around Cu(II) center can be best described as a distorted square pyramidal polyhedron with a τ parameter of 0.13 [15]. The square plane is constituted by each two carboxylate oxygen and two phenanthroline nitrogen atoms, and the aliphatic amine N1 atom resides at the axial position. The Cu–O (1.990(3) Å and 1.949(3) Å) bond distances are slightly shorter than the Cu–N bond lengths (2.017(3) Å and 2.008(4) Å). The axial Cu1–N1 bond (2.323(3) Å) are apparently longer than the four basal Cu–O and Cu–N bond which is similar to some analogs [9, 11].

In the crystal, the coordination ions are linked into a two-dimensional network parallel to the (100) plane by six O–H···O hydrogen bonds. Due to the two aromatic naphthyl and phenanthroline rings existing in the molecular structure, there are also strong π···π stacking interactions, which further consolidated the crystal packing. For instance, the centroid-to-centroid distance between the six-numbered C16–C19/C27/N2 and C10–C15 rings is only 3.525(2) Å with a dihedral angle of 3.3(1)°. There is also another π···π stacking interaction between the C19–C22/C26/C27 and C10–C15 rings with the centroid-to-centroid distance and dihedral angle of 3.653(3) Å and 2.4(1)°, respectively [7].

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