Crystal structure of bis[(μ_2-hydroxo)-aqua-(1,10-phenanthroline-*N*,*N'*)copper(II)] phenylacetate hexahydrate, $[Cu(C_{12}H_8N_2)(OH)(H_2O)]_2[C_8H_7O_2]_2 \cdot 6H_2O$

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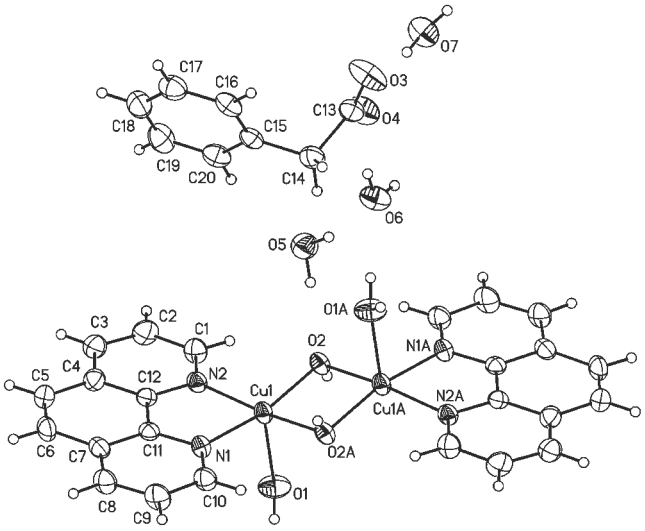

Abstract

$C_{40}H_{48}Cu_2N_4O_{14}$, triclinic, $P\bar{1}$ (no. 2), a = 9.307(2) Å, b = 10.092(2) Å, c = 11.587(2) Å, α = 73.34(3)°, β = 76.32(3)°, γ = 82.69(3)°, V = 1010.9 Å^3, Z = 1, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.137, T = 293 K.

Source of material

Dropwise addition of 1.0 ml of Na_2CO_3 (1 M solution) to a aqueous solution of $CuCl_2 \cdot 2H_2O$ (0.170 g, 1.0 mmol) in 5.0 ml of H_2O gave a blue precipitate, which was separated by centrifugation and washed with water until no Cl anions were detectable in the supernatant. The collected blue precipitate was transferred to a mixture solution of ethanol and water (1:1 *v*/*v*, 10 ml), to which 1,10-phenanthroline (phen, 0.198 g, 1.00 mmol) and phenyl- acetic acid (0.136 g, 1.00 mmol) were added successively. The resulting blue solution (pH = 7.82) was allowed to stand at room temperature. Blue block-like crystals were grown by slow evaporation for over 7 days.

Discussion

The crystal structure of the title compound is composed of a dinuclear cation $[Cu(C_{12}H_8N_2)(OH)(H_2O)]_2^{2+}$, an anion $(C_8H_7O_2)_2^{2-}$ and six lattice water molecules. The local coordination of copper(II) ion is tetragonal pyramidal. Two nitrogen atoms of phen and two hydroxyl oxygen atoms are located in the equatorial plane of the tetragonal pyramid with d(Cu—N1) = 2.011 Å, d(Cu—N2) = 2.032 Å, d(Cu—O2) = 1.940 Å, d(Cu—O2A) ($-x$+1,$-y$,$-z$) = 1.959 Å, and an aqua oxygen O1 occupies the axial position with d(Cu—O1) = 2.402 Å which is longer than literature reported 2.265 Å [1]. Elongation is due to the Jahn-Teller effect. According to Addison's definition [2], the τ index about the central Cu atom is 0.213, suggesting that the square pyramidal coordination geometry is slightly distorted with the Cu atom deviated from the basal plane by 0.200(3) Å towards the apical O1 atom. Within each complex cation, both phenanthroline ligands exhibit nearly perfect planarity and constitute an orthogonal system with the coordinating carboxylate group of the phenylacetate anion. The complex cation displays a similar configuration to the observed in a succinato complex $[Cu(phen)_2(C_4H_4O_4)]$ [3] and all the bonding parameters are normal [4]. Surprisedly, a different crystal structure of $[Cu(phen)_2(C_8H_7O_2)](C_8H_7O_2) \cdot 6H_2O$ was reported by us, which grown in same experimental condition [5].

Different $[Cu(C_{12}H_8N_2)(OH)(H_2O)]_2^{2+}$ units indicate significant π-π stacking interactions making a contribution to formation of two-dimensional layers with the interplanner distance of neighboring aromatic rings is 3.17 Å. In the phenylacetate anion, two oxygen atoms are in a common plane and six carbon atoms reside in the other plane, the dihedral angle between the being 26.5°. Through extensive hydrogen bonds between the carboxylate oxygen atoms of free phenyl- acetate, μ_2-OH-, guest and coordination water molecules, along with π-π stacking interactions, title compound exhibits a three-dimensional supramolecular framework.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.210 × 0.220 × 0.370 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.26 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, ω
$2\theta_{max}$:	54.88°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9947, 4551
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3733
$N(param)_{refined}$:	271
Programs:	SHELXS-97 [6], SHELXL-97 [7], ORTEP [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2B)	2*i*	0.5029	0.4436	0.8796	0.034
H(1B)	2*i*	0.5884	0.7469	0.6997	0.054

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(1C)	2*i*	0.5380	0.8350	0.8019	0.054
H(10A)	2*i*	0.6480	0.7588	1.1022	0.043
H(3A)	2*i*	1.2074	0.4651	0.6349	0.046
H(9A)	2*i*	0.8293	0.8661	1.1418	0.050
H(6A)	2*i*	1.2607	0.7399	0.8829	0.044
H(8A)	2*i*	1.0724	0.8440	1.0405	0.045
H(20A)	2*i*	0.8757	0.0128	1.2514	0.047
H(1A)	2*i*	0.7741	0.4035	0.7323	0.043
H(14A)	2*i*	0.6492	0.0015	1.4022	0.048
H(14B)	2*i*	0.6519	–0.0591	1.5426	0.048
H(5A)	2*i*	1.3061	0.6112	0.7456	0.046

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(2A)	2*i*	1.0058	0.3690	0.6141	0.048
H(16A)	2*i*	0.8815	–0.2050	1.5977	0.047
H(17A)	2*i*	1.1368	–0.2295	1.5460	0.056
H(18A)	2*i*	1.2613	–0.1369	1.3454	0.059
H(19A)	2*i*	1.1298	–0.0171	1.1990	0.059
H(7B)	2*i*	0.4356	–0.4945	1.3824	0.221
H(7C)	2*i*	0.5111	–0.3752	1.3507	0.221
H(6B)	2*i*	0.4553	–0.0473	1.1483	0.060
H(6C)	2*i*	0.5222	–0.0489	1.2250	0.060
H(5B)	2*i*	0.6063	0.2253	0.9295	0.057
H(5C)	2*i*	0.5893	0.1072	1.0345	0.057

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*	0.64093(4)	0.56138(4)	0.93934(3)	0.0252(2)	0.0302(2)	0.0280(2)	–0.0071(1)	–0.0041(1)	–0.0109(2)
O(2)	2*i*	0.5292(2)	0.4169(2)	0.9292(2)	0.031(1)	0.030(1)	0.027(1)	–0.0097(8)	–0.0035(8)	–0.0091(9)
N(2)	2*i*	0.8304(3)	0.5182(3)	0.8232(2)	0.028(1)	0.027(1)	0.031(1)	–0.005(1)	–0.008(1)	–0.009(1)
N(1)	2*i*	0.7776(3)	0.6721(3)	0.9804(2)	0.027(1)	0.031(1)	0.028(1)	–0.007(1)	–0.005(1)	–0.008(1)
O(4)	2*i*	0.5846(3)	–0.2141(3)	1.3656(2)	0.077(2)	0.048(2)	0.044(2)	–0.013(1)	–0.024(1)	–0.012(1)
C(11)	2*i*	0.9200(3)	0.6586(3)	0.9202(3)	0.029(1)	0.021(1)	0.026(1)	–0.002(1)	–0.011(1)	–0.001(1)
O(1)	2*i*	0.5643(3)	0.7355(3)	0.7891(2)	0.067(2)	0.037(1)	0.030(1)	0.005(1)	–0.016(1)	–0.004(1)
C(4)	2*i*	1.0933(3)	0.5595(3)	0.7669(3)	0.030(2)	0.033(2)	0.033(2)	–0.001(1)	–0.007(1)	–0.007(1)
C(13)	2*i*	0.6136(4)	–0.2087(3)	1.4639(3)	0.042(2)	0.032(2)	0.035(2)	–0.004(1)	–0.008(1)	–0.011(1)
O(3)	2*i*	0.5950(4)	–0.3020(3)	1.5605(3)	0.111(3)	0.048(2)	0.041(2)	–0.035(2)	–0.020(2)	–0.004(1)
C(10)	2*i*	0.7456(4)	0.7485(3)	1.0609(3)	0.037(2)	0.034(2)	0.039(2)	–0.006(1)	–0.005(1)	–0.016(1)
C(3)	2*i*	1.1138(4)	0.4791(4)	0.6821(3)	0.037(2)	0.037(2)	0.040(2)	–0.001(1)	–0.003(1)	–0.010(2)
C(7)	2*i*	1.0358(3)	0.7213(3)	0.9393(3)	0.033(2)	0.027(2)	0.034(2)	–0.008(1)	–0.013(1)	–0.002(1)
C(12)	2*i*	0.9489(3)	0.5776(3)	0.8338(3)	0.028(1)	0.022(1)	0.029(1)	–0.002(1)	–0.007(1)	–0.005(1)
C(9)	2*i*	0.8549(4)	0.8138(4)	1.0849(3)	0.048(2)	0.043(2)	0.044(2)	–0.009(2)	–0.011(2)	–0.023(2)
C(6)	2*i*	1.1826(4)	0.7001(4)	0.8708(3)	0.027(2)	0.039(2)	0.044(2)	–0.009(1)	–0.012(1)	–0.006(2)
C(8)	2*i*	0.9994(4)	0.8007(4)	1.0248(3)	0.039(2)	0.038(2)	0.043(2)	–0.008(1)	–0.016(2)	–0.015(2)
C(20)	2*i*	0.9278(4)	–0.0379(4)	1.3109(3)	0.056(2)	0.033(2)	0.034(2)	–0.006(2)	–0.011(2)	–0.012(1)
C(1)	2*i*	0.8540(4)	0.4432(4)	0.7417(3)	0.037(2)	0.041(2)	0.035(2)	–0.006(1)	–0.009(1)	–0.016(2)
C(15)	2*i*	0.8505(4)	–0.0954(3)	1.4301(3)	0.041(2)	0.026(2)	0.033(2)	–0.008(1)	–0.005(1)	–0.011(1)
C(14)	2*i*	0.6832(4)	–0.0774(4)	1.4622(4)	0.044(2)	0.033(2)	0.046(2)	–0.004(1)	–0.005(2)	–0.017(2)
C(5)	2*i*	1.2096(4)	0.6231(4)	0.7887(3)	0.027(2)	0.036(2)	0.048(2)	–0.002(1)	–0.006(1)	–0.007(2)
C(2)	2*i*	0.9939(4)	0.4219(4)	0.6699(3)	0.044(2)	0.042(2)	0.040(2)	0.002(2)	–0.007(2)	–0.023(2)
C(16)	2*i*	0.9307(4)	–0.1666(4)	1.5172(3)	0.053(2)	0.033(2)	0.030(2)	–0.014(2)	–0.007(2)	–0.004(1)
C(17)	2*i*	1.0839(5)	–0.1817(4)	1.4862(4)	0.056(2)	0.039(2)	0.049(2)	–0.006(2)	–0.020(2)	–0.010(2)
C(18)	2*i*	1.1586(4)	–0.1258(4)	1.3664(4)	0.044(2)	0.046(2)	0.060(2)	–0.010(2)	–0.005(2)	–0.017(2)
C(19)	2*i*	1.0803(5)	–0.0546(4)	1.2795(4)	0.054(2)	0.054(2)	0.037(2)	–0.016(2)	0.006(2)	–0.016(2)
O(7)	2*i*	0.4819(3)	–0.4312(3)	1.3165(2)	0.066(2)	0.054(2)	0.040(1)	–0.014(1)	–0.015(1)	–0.016(1)
O(6)	2*i*	0.4960(3)	–0.0077(3)	1.1817(2)	0.068(2)	0.038(1)	0.043(1)	–0.006(1)	–0.010(1)	–0.006(1)
O(5)	2*i*	0.6451(3)	0.1402(3)	0.9504(3)	0.048(2)	0.044(2)	0.048(2)	–0.002(1)	–0.004(1)	–0.012(1)

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