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Crystal structure of aqua-(2,9-dimethyl-1,10-phenanthroline-*N,N'*)-diformato-copper(II), $Cu(C_{14}H_{12}N_2)(H_2O)(HCOO)_2$

J.-G. Pan, J.-L. Lin and Y.-Q. Zheng*

Ningbo University, Institute of Inorganic Chemistry, Municipal Key Laboratory of Solid Materials Chemistry, Ningbo, Zhejiang, 315211 P. R. China

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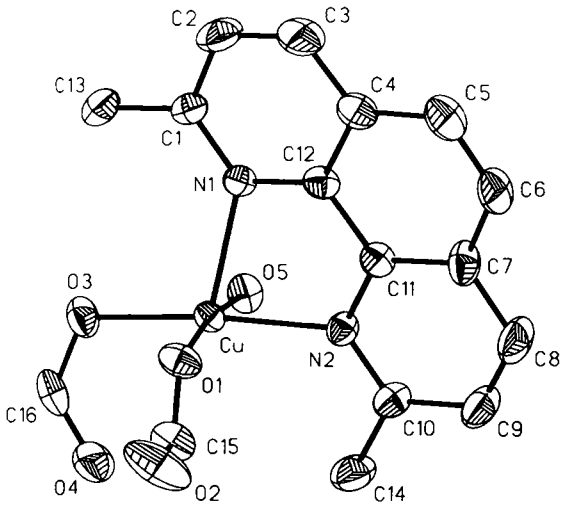

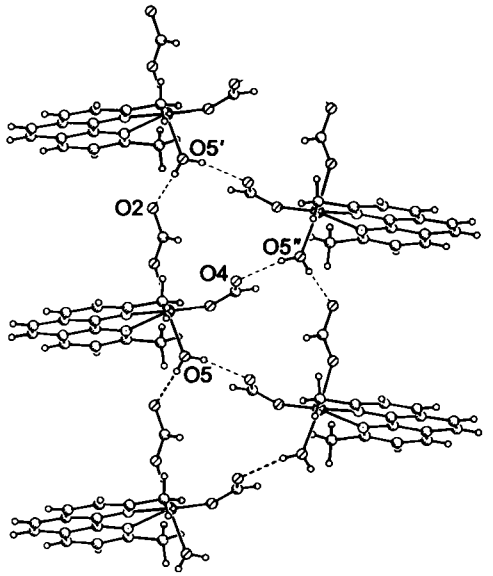

Abstract

$C_{16}H_{16}CuN_2O_5$, orthorhombic, $Pna2_1$ (no. 33), $a = 7.680(2)$ Å, $b = 14.873(3)$ Å, $c = 14.011(3)$ Å, $V = 1600.4$ Å^3, $Z = 4$, $R_{gt}(F) = 0.040$, $wR_{ref}(F^2) = 0.102$, $T = 293$ K.

Source of material

Dropwise addition of 2.0 ml (1.0 M) Na_2CO_3 to an aqueous solution of 0.075 g (0.442 mol) $CuCl_2 \cdot 2H_2O$ in 5.0 ml H_2O yielded pale blue deposit, which was separated by centrifugation and washed with doubly distilled water until no Cl^- anions are detectable in the supernatant. Such freshly prepared precipitate was then added to a solution of 0.100 g (0.442 mmol) 2,9-dimethyl-1,10-phenanthroline in a mixed solvent consisting of 15.0 ml H_2O and 15.0 ml methanol. To the mixture 1.77 ml (1.0 M) formic acid was dropped and the precipitate was slowly dissolved under continuous stirring. The resulting blue solution (pH = 3.94) was allowed to stand at room temperature, and slow evaporation for one week afforded blue plate-like crystals.

Experimental details

All hydrogen atoms were located from Fourier difference maps. During refinement, those H atom parameter which did not converge were fixed on the initial values. The correct absolute structure was confirmed by a Flack parameter of x = 0.02(2).

Discussion

The title structure consists of the $[Cu(C_{14}H_{12}N_2)(H_2O)(HCOO)_2]$ complex molecules, in which the Cu atoms are each square pyramidally coordinated by two nitrogen atoms of one 2,9-dimethyl-1,10-phenanthroline ligand and three oxygen atoms of aqua ligand and two formate anions with the apex occupied by one pyridyl N atoms (figure, top). The aromatic N-donor ligand exhibits an interesting coordination fashion to chelate central cupric ions with the nitrogen atoms situated at the apical and basal sites, respectively. This differs from that observed in a previously reported aqua-carbonato-(2,9-dimethyl-1,10-phenanthroline-*N,N'*)-copper(II) dihydrate, $[Cu(C_{14}H_{12}N_2)(H_2O)(CO_3)] \cdot 2H_2O$, where the two nitrogen atoms of the chelating aromatic ligand reside at the basal positions around the square pyramidally coordinated Cu atoms [1]. The apical and basal Cu—N bond distances are 2.250(4) Å and 2.041(4) Å, respectively, the latter being slightly shorter than the corresponding one in the carbonato compound [1], and both Cu—O bond distances to the formate anions averaged at 1.956 Å are slightly shorter than that to the aqua ligand (1.978(3) Å) suggesting that the anionic ligand possess better coordinating capability. The *cis* bond angles at the central Cu atom from the apical N1 atom fall in the region 78.4° – 107.0°, indicating a significant deviation from the value for a perfect square pyramidal geometry. The Cu atom is found to be shifted by 0.128 Å from the basal plane toward the apical nitrogen atom. Two crystallographically different formate anions coordinate the Cu atoms in *syn* and *anti* fashions, respectively. As expected, the C—O bond lengths to the coordinating oxygen atoms in the carboxylate anions are considerably longer than those to the others, the difference of 0.051 Å being larger than the corresponding one (0.030 Å) found in the diformato-bis(1,10-phenanthroline-*N,N'*)manganese(II) pentahydrate reported by us [2]. Interestingly, replacement of the chelating carbonato ligand in the $[Cu(C_{14}H_{12}N_2)(H_2O)(CO_3)]$ complex molecule by two monodentate formato ligands results in a different square pyramidal CuN_2O_5 coordination sphere in the present complex molecule.

* Correspondence author (e-mail: zhengcm@nbu.edu.cn)

Within the crystal structure, the aqua and formato ligands of each $[Cu(C_{14}H_{12}N_2)(H_2O)(HCOO)_2]$ complex molecule function as H-bond donors and acceptors, respectively, to two neighbors and from two neighbors, resulting in hydrogen bonded double chains with the aromatic ligands outside (figure, bottom). The formed double chains extend infinitely along [100]. The substituted phenanthroline ligands of one double chain protrude into the grooves between adjacent aromatic planes of the neighboring double chain, yielding layers parallel to (001). It is found that the assembly of the double chains is due to interchain π-π stacking interactions [3] between substituted phenanthroline ligands (mean interplanar distances: 3.44 Å, 3.85 Å). The layers are further stacked along [001] to meet requirement of close packing and weak interlayer C–H···O hydrogen bonding interactions between aromatic CH and aqua oxygen atom make a contribution to stabilization of the crystal structure.

Table 1. Data collection and handling.

Crystal:	blue, plate-like, size 0.178 × 0.333 × 0.422 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.94 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2524, 2055
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1809
$N(param)_{refined}$:	226
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*a*	0.0554	0.6387	0.2158	0.061
H(3)	4*a*	0.0878	0.7713	0.2942	0.066
H(5)	4*a*	0.1716	0.8551	0.4480	0.063
H(6)	4*a*	0.2617	0.8470	0.6014	0.060
H(8)	4*a*	0.3501	0.7542	0.7443	0.063
H(9)	4*a*	0.4016	0.6153	0.8082	0.056
H(13A)	4*a*	0.1452	0.4222	0.3164	0.075
H(13B)	4*a*	0.1779	0.4686	0.2176	0.075
H(13C)	4*a*	–0.0113	0.4629	0.2591	0.075
H(14A)	4*a*	0.3773	0.4084	0.6782	0.071
H(14B)	4*a*	0.3161	0.4409	0.7792	0.071
H(14C)	4*a*	0.5118	0.4509	0.7493	0.071
H(15)	4*a*	0.6742	0.4145	0.5540	0.048
H(16A)	4*a*	0.4034	0.2195	0.4204	0.048
H(5A)	4*a*	0.015(7)	0.424(4)	0.537(5)	0.04(2)
H(5B)	4*a*	0.062(7)	0.347(4)	0.550(4)	0.04(1)

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	4*a*	0.30612(5)	0.44434(3)	0.50256(2)	0.0232(2)	0.0224(2)	0.0246(2)	0.0010(2)	0.0006(3)	0.0003(3)
N(1)	4*a*	0.1934(5)	0.5557(2)	0.4132(3)	0.027(2)	0.026(2)	0.025(2)	–0.001(1)	–0.004(2)	0.001(1)
C(1)	4*a*	0.1353(7)	0.5574(3)	0.3237(4)	0.041(3)	0.039(2)	0.024(2)	0.004(2)	–0.008(2)	0.001(2)
C(2)	4*a*	0.0953(9)	0.6389(4)	0.2785(4)	0.074(4)	0.048(3)	0.031(2)	0.005(3)	–0.020(3)	0.008(2)
C(3)	4*a*	0.114(1)	0.7176(4)	0.3251(5)	0.082(4)	0.034(2)	0.050(3)	0.008(3)	–0.017(3)	0.014(2)
C(4)	4*a*	0.1736(7)	0.7190(3)	0.4199(4)	0.052(3)	0.030(2)	0.040(3)	0.004(2)	–0.004(2)	0.007(2)
C(5)	4*a*	0.1947(9)	0.7994(4)	0.4753(5)	0.081(5)	0.021(2)	0.056(4)	0.006(3)	–0.006(3)	0.002(2)
C(6)	4*a*	0.248(1)	0.7943(4)	0.5665(5)	0.076(4)	0.022(2)	0.053(4)	0.003(3)	–0.006(3)	–0.009(3)
C(7)	4*a*	0.2829(8)	0.7104(3)	0.6109(4)	0.056(3)	0.030(2)	0.034(3)	–0.004(2)	0.005(2)	–0.008(2)
C(8)	4*a*	0.3371(9)	0.7029(4)	0.7070(4)	0.079(4)	0.040(3)	0.037(3)	–0.008(3)	–0.012(3)	–0.016(2)
C(9)	4*a*	0.3699(8)	0.6207(4)	0.7444(4)	0.061(3)	0.050(3)	0.029(2)	–0.008(3)	–0.010(3)	–0.007(2)
C(10)	4*a*	0.3562(8)	0.5434(3)	0.6873(4)	0.039(2)	0.037(2)	0.025(2)	–0.006(2)	–0.006(2)	0.000(2)
N(2)	4*a*	0.3076(5)	0.5493(2)	0.5964(3)	0.033(2)	0.027(2)	0.021(2)	–0.004(1)	–0.002(2)	–0.001(1)
C(11)	4*a*	0.2698(7)	0.6320(3)	0.5585(4)	0.036(2)	0.028(2)	0.027(2)	–0.000(2)	0.003(2)	0.003(2)
C(12)	4*a*	0.2132(6)	0.6340(3)	0.4605(4)	0.033(2)	0.021(2)	0.031(2)	–0.002(2)	–0.001(2)	0.005(2)
C(13)	4*a*	0.1095(9)	0.4701(4)	0.2749(4)	0.063(4)	0.051(3)	0.035(3)	0.009(3)	–0.018(3)	–0.011(2)
C(14)	4*a*	0.3936(9)	0.4529(4)	0.7270(4)	0.058(4)	0.053(3)	0.031(2)	–0.001(3)	–0.010(3)	0.006(2)
O(1)	4*a*	0.5418(4)	0.4805(2)	0.4654(3)	0.024(1)	0.043(2)	0.042(2)	0.004(1)	0.003(1)	0.009(2)
C(15)	4*a*	0.6811(5)	0.4557(3)	0.5042(8)	0.031(2)	0.040(2)	0.049(3)	–0.002(2)	0.003(3)	0.007(4)
O(2)	4*a*	0.8245(4)	0.4822(3)	0.4806(5)	0.028(2)	0.058(2)	0.125(6)	0.003(2)	0.009(2)	0.024(3)
O(3)	4*a*	0.3162(4)	0.3373(2)	0.4220(3)	0.047(2)	0.027(1)	0.038(2)	0.005(1)	0.005(2)	–0.003(2)
C(16)	4*a*	0.3952(7)	0.2707(3)	0.4582(5)	0.044(3)	0.025(2)	0.050(3)	0.002(2)	0.009(3)	–0.006(2)
O(4)	4*a*	0.4614(6)	0.2664(3)	0.5371(4)	0.064(3)	0.035(2)	0.057(3)	0.007(2)	–0.011(2)	–0.003(2)
O(5)	4*a*	0.0873(4)	0.4009(2)	0.5608(3)	0.030(2)	0.034(2)	0.035(2)	–0.005(2)	0.003(2)	–0.003(2)

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