Crystal structure of chloro-(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')-(4-hydroxybenzoato-κ^2O,O')copper(II)—methanol (2/1), $C_{21.5}H_{19}ClCuN_2O_{3.5}$

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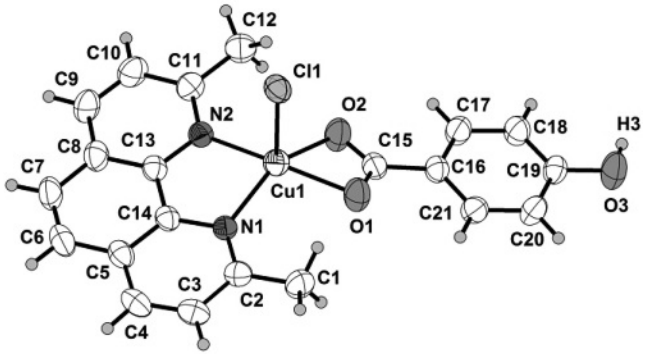

Abstract

$C_{21.5}H_{19}ClCuN_2O_{3.5}$, monoclinic, $P2_1/n$ (no. 14), a = 10.421(1) Å, b = 11.582(1) Å, c = 17.438(2) Å, β = 104.358(1)°, V = 2038.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.0319, $wR_{ref}(F^2)$ = 0.0986, T = 291 K.

Table 1. Data collection and handling.

Crystal:	green blocks, size 0.39×0.45×0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.30 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15137, 3775
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3161
$N(param)_{refined}$:	274
Programs:	SHELX [8], DIAMOND [9]

Source of material

All of reagents were commercially available and of analytical grade. 4-Hydroxybenzoic acid (0.138 g, 1 mmol), NaOH (0.037 g, 1 mmol) and $CuCl_2$ (0.087 g, 0.5 mmol) were successively dissolved in a water-methanol (v:v = 10:1) mixture (10 ml). This solution was added to a solution of 2,9-dimethyl-1,10-phenanthroline hemihydrate (0.110 g, 0.5 mmol) in methanol (10 ml). The mixture was stirred at 323 K and then refluxed for 10 h, cooled to room temperature and filtered. Green crystals of the title compound were collected from the filtrate after ten days.

Discussion

1,10-Phenanthroline (*phen*) plays an important role for coordination chemistry, supramolecular assembly and organometallic chemistry due to two special bidentate N-donor sites [1, 2]. A variety of substituted derivatives of *phen* have been used as chelating ligands [1]. Among them, 2,9-dimethyl-1,10-phenanthroline (*dmphen*) is often used as a versatile ligand, and a series of Cu(II)-*dmphen* complexes [3-5] have been prepared and reported. In this contribution, the binary complex of Cu^{II} ion with *dmphen* and 4-hydroxybenzoic acid was synthesized and its crystal structure was determined. Each central metal Cu^{II} ion is in a distorted square-pyramidal geometry five-coordinated by one bidentate *dmphen* ligand and one bidentate 4-hydroxyben-zoic anion, forming the basis of the coordination polyhedron, and one chlorido ligand acting as the apex with a distance of 2.4351(8) Å. The coordination environment of Cu(II) is similar to previous reports [6, 7]. Additionally, one half solvent methanol molecule is present in the asymmetric unit. Strong O–H···Cl^i classic hydrogen bond between the hydroxyl group of 4-hydroxybenzoic anion and neighboring chloride anion (Symmetry code: **i** x+1, y, z) was also found. The crystal packing is further stabilized by π-π interactions between the *dmphen* rings of neighboring molecules, with a distance between their ring centroids of 3.758 Å.

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(3)	4*e*		1.4464	0.2349	0.2457	0.091
H(1A)	4*e*		0.6770	–0.0727	0.2181	0.085
H(1B)	4*e*		0.5797	–0.0785	0.2737	0.085
H(1C)	4*e*		0.6348	0.0410	0.2541	0.085
H(3A)	4*e*		0.3852	–0.1563	0.1912	0.065
H(4)	4*e*		0.2026	–0.1365	0.0882	0.065
H(6)	4*e*		0.0840	–0.0250	–0.0354	0.065
H(7)	4*e*		0.0864	0.1195	–0.1222	0.069
H(9)	4*e*		0.2086	0.2877	–0.1657	0.070
H(10)	4*e*		0.3914	0.4036	–0.1418	0.067
H(12A)	4*e*		0.6417	0.4159	0.0279	0.087
H(12B)	4*e*		0.5941	0.4668	–0.0578	0.087
H(12C)	4*e*		0.6859	0.3576	–0.0425	0.087
H(17)	4*e*		1.0444	0.2984	0.0985	0.059
H(18)	4*e*		1.2714	0.3017	0.1474	0.059
H(20)	4*e*		1.2417	0.0592	0.3062	0.059
H(21)	4*e*		1.0141	0.0572	0.2570	0.055
H(4A)	4*e*	0.5	0.0552	0.5074	0.9410	0.205
H(22A)	4*e*	0.5	0.0236	0.3204	0.9457	0.233
H(22B)	4*e*	0.5	–0.0732	0.4047	0.8888	0.233
H(22C)	4*e*	0.5	–0.1007	0.3697	0.9701	0.233

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*e*		0.62475(3)	0.18900(3)	0.10575(2)	0.0318(2)	0.0444(2)	0.0382(2)	–0.0024(1)	0.0060(1)	0.0010(1)
Cl(1)	4*e*		0.56253(7)	0.34533(6)	0.18268(4)	0.0447(4)	0.0472(4)	0.0524(4)	–0.0031(3)	0.0118(3)	–0.0107(3)
O(1)	4*e*		0.7868(2)	0.1341(2)	0.1840(1)	0.035(1)	0.065(1)	0.053(1)	–0.0026(9)	0.0093(9)	0.008(1)
O(2)	4*e*		0.8027(2)	0.2391(2)	0.0840(1)	0.036(1)	0.063(1)	0.053(1)	–0.0001(9)	0.0072(9)	0.011(1)
O(3)	4*e*		1.4110(2)	0.1861(2)	0.2677(1)	0.033(1)	0.083(2)	0.062(1)	0.003(1)	0.0065(9)	0.013(1)
N(1)	4*e*		0.4903(2)	0.0617(2)	0.1103(1)	0.036(1)	0.035(1)	0.039(1)	0.0008(9)	0.0084(9)	–0.0023(9)
N(2)	4*e*		0.4926(2)	0.2328(2)	0.0062(1)	0.039(1)	0.040(1)	0.035(1)	–0.0006(9)	0.0087(9)	–0.0006(9)
C(1)	4*e*		0.6059(3)	–0.0341(3)	0.2336(2)	0.055(2)	0.054(2)	0.057(2)	–0.001(2)	0.007(1)	0.017(1)
C(2)	4*e*		0.4911(3)	–0.0218(2)	0.1636(2)	0.046(2)	0.039(1)	0.046(2)	0.000(1)	0.015(1)	–0.000(1)
C(3)	4*e*		0.3824(3)	–0.0975(3)	0.1545(2)	0.061(2)	0.043(2)	0.061(2)	–0.010(1)	0.020(2)	0.004(1)
C(4)	4*e*		0.2736(3)	–0.0860(3)	0.0932(2)	0.053(2)	0.048(2)	0.065(2)	–0.018(1)	0.019(2)	–0.009(1)
C(5)	4*e*		0.2688(3)	0.0025(2)	0.0374(2)	0.041(1)	0.045(2)	0.048(2)	–0.005(1)	0.012(1)	–0.013(1)
C(6)	4*e*		0.1582(3)	0.0223(3)	–0.0282(2)	0.040(2)	0.061(2)	0.060(2)	–0.011(1)	0.008(1)	–0.018(2)
C(7)	4*e*		0.1597(3)	0.1083(3)	–0.0799(2)	0.044(2)	0.067(2)	0.052(2)	–0.003(2)	–0.007(1)	–0.010(2)
C(8)	4*e*		0.2719(3)	0.1826(3)	–0.0708(2)	0.044(2)	0.055(2)	0.040(2)	0.001(1)	0.002(1)	–0.008(1)
C(9)	4*e*		0.2788(3)	0.2738(3)	–0.1220(2)	0.058(2)	0.067(2)	0.040(2)	0.004(2)	–0.007(1)	0.005(1)
C(10)	4*e*		0.3877(3)	0.3422(3)	–0.1080(2)	0.065(2)	0.058(2)	0.041(2)	0.005(2)	0.005(1)	0.012(1)
C(11)	4*e*		0.4955(3)	0.3209(2)	–0.0426(2)	0.049(2)	0.049(2)	0.039(2)	0.002(1)	0.012(1)	0.002(1)
C(12)	4*e*		0.6150(3)	0.3971(3)	–0.0274(2)	0.060(2)	0.054(2)	0.059(2)	–0.007(2)	0.013(2)	0.015(2)
C(13)	4*e*		0.3822(3)	0.1650(2)	–0.0071(2)	0.039(1)	0.041(1)	0.034(1)	0.000(1)	0.008(1)	–0.007(1)
C(14)	4*e*		0.3810(2)	0.0737(2)	0.0483(2)	0.038(1)	0.037(1)	0.037(1)	–0.001(1)	0.010(1)	–0.009(1)
C(15)	4*e*		0.8593(3)	0.1849(2)	0.1459(2)	0.036(1)	0.042(1)	0.045(2)	–0.002(1)	0.009(1)	–0.006(1)
C(16)	4*e*		1.0056(3)	0.1806(2)	0.1745(2)	0.033(1)	0.044(2)	0.043(2)	–0.000(1)	0.009(1)	–0.002(1)
C(17)	4*e*		1.0838(3)	0.2515(3)	0.1412(2)	0.041(2)	0.053(2)	0.052(2)	0.002(1)	0.007(1)	0.012(1)
C(18)	4*e*		1.2197(3)	0.2538(3)	0.1703(2)	0.038(1)	0.056(2)	0.055(2)	–0.003(1)	0.014(1)	0.009(1)
C(19)	4*e*		1.2787(3)	0.1843(2)	0.2339(2)	0.032(1)	0.050(2)	0.046(2)	0.006(1)	0.009(1)	–0.002(1)
C(20)	4*e*		1.2018(3)	0.1089(3)	0.2653(2)	0.043(2)	0.054(2)	0.049(2)	0.010(1)	0.010(1)	0.013(1)
C(21)	4*e*		1.0656(3)	0.1075(2)	0.2357(2)	0.042(2)	0.044(2)	0.053(2)	0.001(1)	0.015(1)	0.006(1)
O(4)	4*e*	0.5	0.032(1)	0.4686(7)	0.9747(5)	0.22(1)	0.088(6)	0.105(7)	–0.018(6)	0.048(6)	0.010(4)
C(22)	4*e*	0.5	–0.033(1)	0.387(2)	0.9432(7)	0.13(1)	0.25(2)	0.082(8)	0.02(1)	0.032(7)	0.03(1)

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