Crystal structure of (1-cyclopropyl-6-fluoro-7-chloro-1,4-dihydro-4-oxo-3-quinolinecarboxylato)chloro(2,2′-bipyridine)copper(II) dihydrate, $CuCl(C_{10}H_8N_2)(C_{13}H_8NClFO_3) \cdot 2H_2O$

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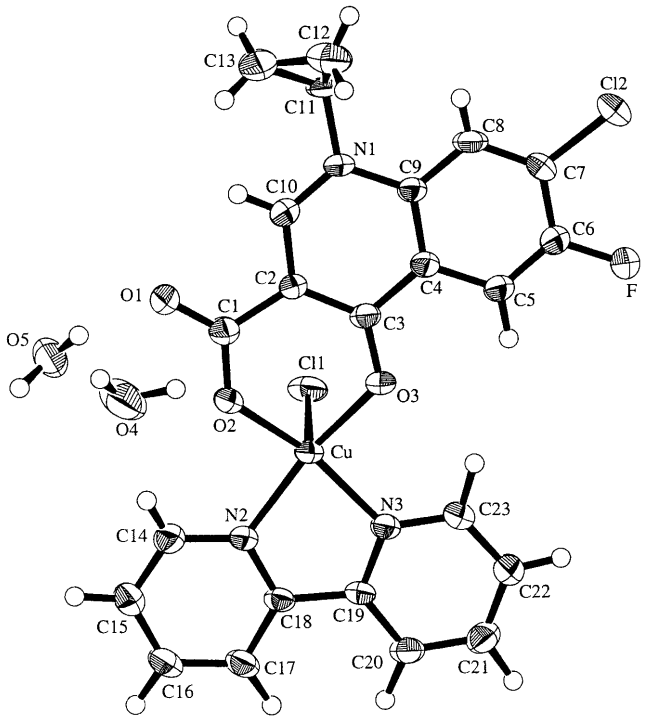

Abstract

$C_{23}H_{20}Cl_2CuFN_3O_5$, triclinic, $P\bar{1}$ (No. 2), a = 10.329(2) Å, b = 11.417(4) Å, c = 10.225(3) Å, α = 95.77(3)°, β = 99.10(2)°, γ = 98.65(2)°, V = 1167.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.050, $wR_{obs}(F)$ = 0.061, T = 293 K.

Source of material

The compound was obtained in water/ethanol media, by mixing solutions containing 2,2-bipyridine (bipy, 1 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol), Hcip (1-cyclopropyl-6-fluoro-7-chloro-1,4-dihydro-4-oxo-3-quinolinecarboxylic acid, 1 mmol) and NaOH (1 mmol). The pH of the resulting solution was adjusted to about 7.5 with dilute HCl. Then the solution was slowly evaporated at room temperature, and blue crystals were formed in a period of two months. Elemental analysis: found – C, 48.47%; N, 7.58%; H, 3.54%; calculated for $C_{23}H_{20}O_5N_3FCuCl_2$ – C, 48.30%; N, 7.35%; H, 3.52%;

Discussion

Quinolones, such as ciprofloxacin, norfloxacin and ofloxacin, are representatives of a class of synthetic antimicrobial drugs, which exhibit excellent activity against many Gram-positive and Gram-negative bacterial pathogens [1-3]. The coordination chemistry of quinolines with transition and non-transition metal ions has been the subject of a number of literature reports [4]. In this paper, we report a quaternary complex of copper(II) with a quinolone ligand, $[CuCl(C_{10}H_8N_2)(C_{13}H_8NClFO_3)] \cdot 2H_2O$ (**I**). In the title complex, the copper atom is five-coordinated with a square pyramidal environment, involving two nitrogen atoms from one 2,2′-bipy, one chloride anion and two oxygen atoms from one cip$^-$ ligand. Atoms O2, O3, N2 and N3 are sitting in a basal plane, while Cl1 is in apical position with a longer Cu—Cl1 distance. The cip$^-$ ligand is coordinated to Cu^{II} ion via the *keto* and the oxygen atom of the carboxylate group to form a six-membered ring. Compared with complex $[Cu(Hcpf)(bipy)(Cl)_{0.7}(NO_3)_{0.3}](NO_3) \cdot 2H_2O$ (**II**) [5], the Cl$^-$ anion (Cl2) in **I** could be replaced by other anions, such as acetate and nitrate. As expected, the distance Cu—O(COO$^-$) of 1.923(3) Å is similar to those in previous structures, such as **II**, $[Cu(phen)(nal)(H_2O)](NO_3) \cdot 3H_2O$ (**III**), $[Cu(phen)(cnx)(H_2O)](NO_3) \cdot H_2O$ (**IV**) and $[Cu(bpy)(oxo)](NO_3) \cdot H_2O$ (**V**) [6,7]. The Cu—O(*keto*) distance in **I** (1.976(3) Å) is longer than those observed in **II**, **III**, **IV** and **V**. The Cu—N distances (1.992(4) Å and 2.020(4) Å) are as observed in the structures of the analogous **II** and **III**. Interestingly, the distances between π-π stacked cip$^-$ rings from neighboring molecules and between cip$^-$ ring and bipy ring from another molecule are about 3.68 Å and 3.5 Å, respectively. The latter distance indicates a strong stacking interaction.

Table 1. Data collection and handling.

Crystal:	blue prismatic, size 0.20 × 0.23 × 0.30 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	12.13 cm^{-1}
Diffractometer, scan mode:	AFC7R, $\omega/2\theta$
$2\theta_{max}$:	50.0°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3882, 2918
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2918
$N(param)_{refined}$:	317
Programs:	SHELXS-86 [8], teXsan [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*i*	0.5205	0.2526	0.7377	0.050
H(2)	2*i*	0.2433	0.5107	0.5851	0.050
H(3)	2*i*	0.3482	0.3398	0.2129	0.050
H(4)	2*i*	0.2953	0.5742	0.3751	0.050
H(5)	2*i*	0.0582	0.4013	0.3573	0.050
H(6)	2*i*	0.0563	0.5298	0.3542	0.050
H(7)	2*i*	0.1537	0.5297	0.1650	0.050
H(8)	2*i*	0.1505	0.3982	0.1544	0.050
H(9)	2*i*	0.6860	–0.0389	0.1352	0.050
H(10)	2*i*	0.7919	–0.1690	0.0328	0.050
H(11)	2*i*	0.9508	–0.2573	0.1744	0.050
H(12)	2*i*	0.9783	–0.2080	0.4189	0.050
H(13)	2*i*	0.9795	–0.1676	0.6212	0.050
H(14)	2*i*	0.9697	–0.1057	0.8450	0.050
H(15)	2*i*	0.8264	0.0445	0.8967	0.050
H(16)	2*i*	0.6948	0.1167	0.7145	0.050
H(17)	2*i*	0.7677	0.1947	0.0396	0.050
H(18)	2*i*	0.8179	0.2228	0.1806	0.050
H(19)	2*i*	0.5235	0.1427	0.9707	0.050
H(20)	2*i*	0.5570	0.0539	0.8780	0.050

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	2*i*	0.65888(6)	0.07378(5)	0.41371(6)	0.0385(4)	0.0263(3)	0.0294(3)	0.0159(3)	0.0016(3)	0.0023(2)
Cl(1)	2*i*	0.8225(1)	0.2603(1)	0.4166(1)	0.0472(8)	0.0242(6)	0.0548(8)	0.0120(6)	0.0052(6)	0.0055(6)
Cl(2)	2*i*	0.2671(2)	0.5448(1)	0.8623(1)	0.102(1)	0.0554(9)	0.0430(8)	0.0465(9)	0.0148(8)	–0.0043(7)
F	2*i*	0.4374(3)	0.3710(3)	0.9242(3)	0.082(2)	0.046(2)	0.029(2)	0.029(2)	0.002(2)	0.000(1)
O(1)	2*i*	0.4302(4)	0.1811(3)	0.1090(3)	0.071(3)	0.056(2)	0.029(2)	0.038(2)	0.004(2)	0.004(2)
O(2)	2*i*	0.5420(3)	0.0820(3)	0.2498(3)	0.052(2)	0.034(2)	0.030(2)	0.022(2)	0.000(2)	–0.002(1)
O(3)	2*i*	0.5466(3)	0.1553(3)	0.5196(3)	0.046(2)	0.034(2)	0.033(2)	0.023(2)	0.007(2)	0.007(1)
O(4)	2*i*	0.8572(5)	0.2104(4)	0.0924(5)	0.073(3)	0.078(3)	0.077(3)	0.038(3)	–0.005(2)	–0.020(3)
O(5)	2*i*	0.5989(4)	0.1343(3)	0.9312(4)	0.059(3)	0.054(2)	0.045(2)	0.014(2)	0.012(2)	–0.006(2)
N(1)	2*i*	0.3237(4)	0.4041(3)	0.3870(4)	0.041(2)	0.025(2)	0.033(2)	0.015(2)	0.004(2)	0.007(2)
N(2)	2*i*	0.7526(4)	–0.0438(3)	0.3201(4)	0.038(2)	0.023(2)	0.029(2)	0.010(2)	0.003(2)	0.002(2)
N(3)	2*i*	0.7551(4)	0.0153(3)	0.5723(4)	0.033(2)	0.024(2)	0.032(2)	0.009(2)	0.003(2)	0.002(2)
C(1)	2*i*	0.4758(5)	0.1666(4)	0.2240(5)	0.036(3)	0.036(3)	0.033(3)	0.015(2)	0.002(2)	0.003(2)
C(2)	2*i*	0.4460(5)	0.2457(4)	0.3371(4)	0.037(3)	0.026(2)	0.026(2)	0.011(2)	0.002(2)	0.004(2)
C(3)	2*i*	0.4796(5)	0.2320(4)	0.4741(5)	0.031(3)	0.022(2)	0.032(3)	0.007(2)	–0.001(2)	0.004(2)
C(4)	2*i*	0.4304(5)	0.3110(4)	0.5673(5)	0.038(3)	0.021(2)	0.030(3)	0.006(2)	0.004(2)	0.003(2)
C(5)	2*i*	0.4599(5)	0.3051(4)	0.7062(5)	0.042(3)	0.026(3)	0.031(3)	0.009(2)	0.002(2)	0.005(2)
C(6)	2*i*	0.4104(5)	0.3776(4)	0.7930(5)	0.052(3)	0.030(3)	0.030(3)	0.010(2)	0.002(2)	0.005(2)
C(7)	2*i*	0.3317(5)	0.4597(4)	0.7485(5)	0.057(4)	0.026(3)	0.034(3)	0.013(2)	0.007(2)	–0.004(2)
C(8)	2*i*	0.3035(5)	0.4697(4)	0.6155(5)	0.043(3)	0.025(2)	0.042(3)	0.015(2)	–0.002(2)	0.005(2)
C(9)	2*i*	0.3516(5)	0.3960(4)	0.5242(4)	0.035(3)	0.021(2)	0.030(3)	0.007(2)	0.002(2)	0.004(2)
C(10)	2*i*	0.3714(5)	0.3326(4)	0.3023(5)	0.044(3)	0.031(3)	0.030(3)	0.010(2)	0.003(2)	0.007(2)
C(11)	2*i*	0.2462(5)	0.4945(4)	0.3400(5)	0.043(3)	0.029(3)	0.046(3)	0.021(2)	0.001(2)	0.010(2)
C(12)	2*i*	0.1014(6)	0.4737(5)	0.3299(7)	0.052(4)	0.042(3)	0.072(4)	0.019(3)	0.003(3)	0.004(3)
C(13)	2*i*	0.1586(8)	0.4716(7)	0.2091(6)	0.108(6)	0.084(5)	0.049(4)	0.068(5)	–0.005(4)	0.006(3)
C(14)	2*i*	0.7454(5)	–0.0683(4)	0.1874(5)	0.042(3)	0.032(3)	0.033(3)	0.009(2)	–0.001(2)	0.003(2)
C(15)	2*i*	0.8125(5)	–0.1490(5)	0.1323(5)	0.048(3)	0.037(3)	0.035(3)	0.011(3)	0.005(2)	–0.003(2)
C(16)	2*i*	0.8937(5)	–0.2062(4)	0.2151(5)	0.051(3)	0.033(3)	0.045(3)	0.017(3)	0.009(3)	–0.004(2)
C(17)	2*i*	0.9062(5)	–0.1811(4)	0.3530(5)	0.044(3)	0.025(3)	0.041(3)	0.010(2)	0.005(2)	–0.003(2)
C(18)	2*i*	0.8312(5)	–0.0999(4)	0.4019(5)	0.031(3)	0.019(2)	0.034(3)	0.006(2)	0.001(2)	0.000(2)
C(19)	2*i*	0.8339(4)	–0.0658(4)	0.5452(5)	0.031(3)	0.020(2)	0.035(3)	0.008(2)	0.005(2)	0.003(2)
C(20)	2*i*	0.9099(5)	–0.1124(4)	0.6457(5)	0.038(3)	0.028(3)	0.041(3)	0.012(2)	0.001(2)	0.005(2)
C(21)	2*i*	0.9043(5)	–0.0729(5)	0.7787(5)	0.044(3)	0.040(3)	0.036(3)	0.011(3)	–0.001(2)	0.009(2)
C(22)	2*i*	0.8252(5)	0.0100(5)	0.8056(5)	0.047(3)	0.043(3)	0.033(3)	0.018(3)	0.006(2)	0.002(2)
C(23)	2*i*	0.7530(5)	0.0531(4)	0.7012(5)	0.042(3)	0.033(3)	0.036(3)	0.015(2)	0.007(2)	0.002(2)

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