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The mixed-ligand copper(II) complex (2,2′-bipyridine)[1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazin-4-ium-1-yl)quinoline-3-carboxylato]nitratocopper(II) nitrate dihydrate

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The drug norfloxacin and ligand 2,2′-bipyridine coordinate to copper(II) yielding a mixed-ligand complex, $[Cu(C_{16}H_{18}FN_3O_3)(NO_3)(C_{10}H_8N_2)](NO_3)\cdot2H_2O$ or $[Cu(H\text{-}Norf)(NO_3)(bpy)](NO_3)\cdot2H_2O$. The Cu^{II} atom has a five-coordinate environment with square-based pyramidal geometry, which involves two N atoms from the 2,2′-bipyridine ligand, two O atoms from the norfloxacinate ligand and one nitrate O atom. Weak interactions between O and Cu result in a centrosymmetric dimer.

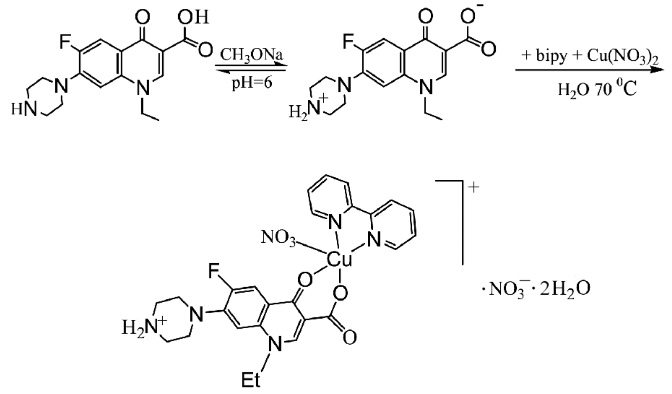
Key indicators

Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.080
Data-to-parameter ratio = 11.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Norfloxacin [H-Norf, 1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)quinoline-3-carboxylic acid)], serving as a fluoroquinolone antimicrobial agent, is widely used as an antibacterial drug. Treatment with this drug leads to double-stranded DNA breaks and cell death (Froelich-Ammon & Osheroff, 1995; Shea & Hiasa, 2000), which is thought to take place through the formation of intermediate copper or iron complexes (Mendoza-Diaz *et al.*, 1993). However, reports of the crystal structures of norfloxacin directly chelated to metal ions are rare (Chen *et al.*, 2001, 2000). As an extension of our research on the coordination behavior of norfloxacin with metal ions, we have synthesized a new mixed-ligand complex, $[Cu(bpy)(H\text{-}Norf)(NO_3)](NO_3)\cdot2H_2O$. We report here the preparation and crystal structure of the title complex, (I).



(I)

In the mixed-ligand complex, copper(II) is five-coordinate, with two N atoms from bpy, two O atoms from H-Norf and one O atom from the NO_3^- ion (Table 1), leading to a square-based pyramid. H-Norf chelates to copper(II) by using O2 and O3 to form a hexagonal ring structure, which is similar to that of the mixed-ligand complex of copper(I), $[Cu(PPh_3)_2(H\text{-}Norf)](ClO_4)$ (Chen *et al.*, 2001). Atoms Cu, O2, O3, N1 and

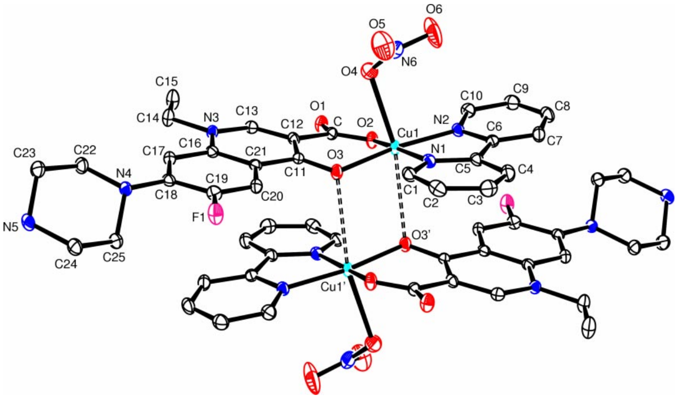


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of the dimer cation of the title complex, with displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. Primed atoms are related to their umpromed equivalents by inversion symmetry.

N2 constitute a nearly square plane, whereas atom O4 from the NO_3^- ion is located at the apex of the pyramid and is weakly bonded to the Cu atom. The title complex with square-based pyramidal geometry is similar to the copper(II) complex $[Cu_2(cfc)_2(bpy)_2(pip)]\cdot 6H_2O$ reported by Wang *et al.* (2003). An important feature of the crystal structure is the weak attraction between Cu and O from H-Norf [O3′···Cu = 2.8723 (15) Å], which results in the formation of a dimer (Fig. 1). The occurrence of a centrosymmetric dimer connected by such a long O···Cu distance is rather rare (Zang *et al.*, 1990). The H atoms of the water molecules and of the amine group build up an intricate hydrogen-bond network with O and N atoms (Table 2)

Experimental

Norfloxacin (0.5 mmol) was dissolved in H_2O (25 ml) and the pH value of this solution was adjusted to 6 with CH_3ONa. 2,2′-Bipyridine(0.5 mmol) was added and the solution was heated to 343 K. $Cu(NO_3)_2\cdot 3H_2O$(0.5 mmol) was then added and the solution was stirred for 1 h. Crystals were obtained by cooling the solution, after a few days.

Crystal data

$[Cu(C_{16}H_{18}FN_3O_3)(NO_3)(C_{10}H_8N_2)](NO_3)\cdot 2H_2O$
M_r = 699.12
Monoclinic, $P2_1/n$
a = 13.9080 (8) Å
b = 13.8441 (8) Å
c = 14.4835 (9) Å
β = 93.173 (3)°
V = 2784.4 (3) Å^3
Z = 4
D_x = 1.668 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6954 reflections
θ = 1.5–25.0°
μ = 0.87 mm^{-1}
T = 130 K
Prism, blue
0.32 × 0.20 × 0.15 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.770, T_{max} = 0.852
17 478 measured reflections
4902 independent reflections
4561 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.0°
h = −16 → 15
k = −16 → 16
l = −16 → 17

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.081
S = 1.09
4902 reflections
428 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 2.0954P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O2	1.9217 (15)	Cu—N1	1.9983 (18)
Cu—O3	1.9289 (14)	Cu—O4	2.3760 (16)
Cu—N2	1.9967 (17)		
O2—Cu—O3	93.45 (6)	N2—Cu—N1	81.16 (7)
O2—Cu—N2	92.17 (7)	O2—Cu—O4	89.69 (6)
O3—Cu—N2	171.98 (7)	O3—Cu—O4	89.45 (6)
O2—Cu—N1	170.82 (6)	N2—Cu—O4	96.31 (6)
O3—Cu—N1	92.60 (6)	N1—Cu—O4	97.27 (6)

Table 2
Hydrogen-bond geometry (Å, °).

	D—H	H···A	D···A	D—H···A
O10—H3···O4	0.857 (17)	2.02 (2)	2.843 (3)	161 (3)
O10—H3···O6	0.857 (17)	2.49 (2)	3.167 (4)	137 (3)
O10—H3···N6	0.857 (17)	2.57 (2)	3.371 (3)	157 (3)
O10—H4···O9	0.847 (17)	2.03 (2)	2.829 (3)	156 (3)
O10—H4···O8	0.847 (17)	2.65 (2)	3.345 (3)	140 (3)
O10—H4···N7	0.847 (17)	2.700 (19)	3.517 (3)	163 (3)
O11—H1···O5^{i}	0.848 (17)	1.99 (2)	2.795 (3)	157 (3)
O11—H2···O8^{ii}	0.858 (17)	2.08 (2)	2.908 (3)	164 (3)
O11—H2···O7^{ii}	0.858 (17)	2.40 (2)	3.103 (3)	139 (3)
O11—H2···N7^{ii}	0.858 (17)	2.574 (18)	3.417 (3)	168 (3)
N5—H5A···O1^{iii}	0.90	1.79	2.686 (2)	176
N5—H5B···O10^{i}	0.90	2.07	2.850 (3)	144

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$; (iii) $x-1, y, z$.

All H atoms, except for the water H atoms, were placed in calculated positions and included in the final cycles of refinement in the riding-model approximation, with N—H distances of 0.90 Å, and C—H distances of 0.93 (aromatic H atoms), 0.97 (methylene groups) and 0.96 Å (methyl group), and with U_{iso}(H)= $1.2U_{eq}$(C,N) [or $1.5U_{eq}$(C)]. The water H atoms were located in Fourier syntheses, but their positional and displacement parameters were refined with O—H distance restraints of 0.85 Å and H···H restraints of 1.39 Å. U_{iso}(H) values for the water H atoms were set equal to $1.5U_{eq}$(O).

Data collection: *CrystalClear* (Rigaku/MSC, 2004); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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