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A copper(II) complex of 1,10-phenanthroline and enrofloxacin

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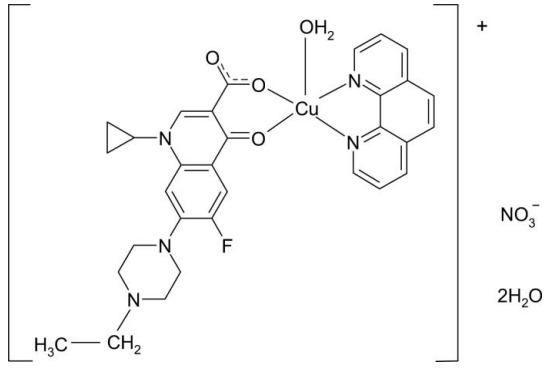
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.008 Å; R factor = 0.061; wR factor = 0.129; data-to-parameter ratio = 13.2.

The asymmetric unit of the title complex, aqua[1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylato](1,10-phenanthroline)copper(II) nitrate dihydrate, $[Cu(C_{19}H_{21}FN_3O_3)(C_{12}H_8N_2)(H_2O)]NO_3\cdot 2H_2O$, contains one $[Cu(erx)(phen)(H_2O)]^+$ cation, one NO_3^- anion and two solvent water molecules (erx is enrofloxacin and phen is 1,10-phenanthroline). The Cu^{II} ion adopts a slightly distorted square-pyramidal geometry, coordinated by two O atoms of the erx ligand and two N atoms of the phen ligand in the basal plane, and by a water molecule in the apical position. The Cu^{II} ion deviates from the basal plane by 0.1439 (7) Å. The piperazine ring belonging to erx has a slightly twisted chair conformation. Coordinated and uncoordinated water molecules participate in a hydrogen-bonding network including both cations and anions, to produce a three-dimensional supramolecular structure.

Related literature

A similar arrangement to that of the title compound has been observed in [Cu(erx)(phen)Cl] (Efthimiadou *et al.*, 2006), where erx and phen occupy the four positions in the basal plane, while the Cl atom is in the apical position. Metal-to-ligand distances are also similar to those found in related compounds with cinoxacin (Mendoza-Díaz *et al.*, 1987) and ciprofloxacin (Saha *et al.*, 2005; Drevenšek *et al.*, 2003). A trigonality index may by computed for Cu^{II} (Addison *et al.*, 1984). Quinolone–metal complexes have been studied in relation to their biological activity and structural properties (Mendoza-Díaz & Ireta-Moreno, 1994; Turel *et al.*, 1997; Wallis *et al.*, 1996).



Experimental

Crystal data

$[Cu(C_{19}H_{21}FN_3O_3)(C_{12}H_8N_2)(H_2O)]NO_3\cdot 2H_2O$
M_r = 718.2
Triclinic, $P\overline{1}$
a = 10.819 (4) Å
b = 12.019 (5) Å
c = 12.968 (6) Å
α = 76.75 (3)°
β = 87.91 (3)°
γ = 80.37 (2)°
V = 1618.3 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.74 mm^{-1}
T = 298 (2) K
0.27 × 0.24 × 0.22 mm

Data collection

Siemens $P4$ diffractometer
Absorption correction: ψ scan (*XSCANS*; Siemens, 1993)
T_{min} = 0.824, T_{max} = 0.853
6697 measured reflections
5711 independent reflections
3170 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
3 standard reflections
every 97 reflections
intensity decay: 3.6%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.129
S = 1.03
5711 reflections
434 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1D···O03	0.84	2.10	2.879 (7)	155
O2W—H2C···O01	0.88	2.37	3.194 (7)	157
O2W—H2C···O02	0.88	2.28	3.031 (8)	144
O2W—H2D···O3W	0.88	2.26	3.066 (7)	152
O3W—H3C···O2^{i}	0.86	2.17	3.005 (5)	166
O3W—H3D···O3^{ii}	0.85	2.00	2.845 (6)	179

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $x-1, y, z$.

Data collection: *XSCANS* (Siemens, 1993); cell refinement: *XSCANS*; data reduction: *XSCANS*; 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: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2143).

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supplementary materials

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A copper(II) complex of 1,10-phenanthroline and enrofloxacin

J. Recillas-Mota, M. Flores-Alamo, R. Moreno-Esparza and J. Gracia-Mora

Comment

The quinolones complexation with metal ions is known to enhance biological activities of the quinolone antibiotics, probably because of the higher liposolubility leading to greater intracellular accumulation (Mendoza-Díaz & Ireta-Moreno, 1994). The study of mixed-ligands coordination compounds with enrofloxacin is thus relevant, in order to improve the activity of this antibiotic used in veterinary medicine. Several fluoroquinolones-metal complexes have been isolated and their crystal structures reported (Mendoza-Díaz *et al.*, 1987; Wallis *et al.*, 1996; Turel *et al.*, 1997), most of them with ciprofloxacin. As part of our studies on different bioactive antibiotics, the title compound, (I), is a mixed-ligands metal complex, which, besides enrofloxacin (erx), includes the *N*,*N*′-bidentate ligand 1,10-phenanthroline (phen). It could contribute to the development of a new type of drug with biological activity.

The asymmetric unit of (I) consists of one $[Cu(erx)(phen)(H_2O)]^+$ cation, one NO_3^- anion and two lattice water molecules (Fig. 1). The Cu^{II} ion is coordinated by two enrofloxacin O atoms and two N atoms of 1,10 phenanthroline in the basal plane, and by a H_2O molecule in the axial position. It adopts a slightly distorted square-pyramidal geometry [trigonality index (Addison *et al.*, 1984): $\tau = 0.02$] with an O1—Cu—O2 angle of 92.94 (14)° and a N1—Cu—N2 angle of 82.08 (17)°. The Cu^{II} ion deviates from the basal plane by 0.1439 (7) Å. The apical site is occupied by a water molecule, with a bond length Cu1—O1w of 2.253 (4) Å and an angle of 89.69 (12)° with the best plane of four atoms at the base of the pyramid. The uncoordinated carboxylate atom O3 [Cu1···O3 = 4.020 (4) Å] lies above the basal plane of the pyramid. The *trans* atom system of the basal plane gives angles O1—Cu—N1 = 169.36 (16)° and O2—Cu—N2 = 170.46 (16)°.

An arrangement similar to that of (I) has been observed in [Cu(erx)(phen)Cl] (Efthimiadou *et al.*, 2006), where the enrofloxacin and the phenanthroline occupy the four positions in the basal plane, while the apical position is occupied by a Cl^- ion. Metal-to-ligand distances in (I) are also similar to those found in related compounds with cinoxacin [1-ethyl-1,4-dihydro-4-oxo-1,3-dioxolo[4,5*g*]cinnoline-3-carboxylic acid, cnx], namely $[Cu(phen)(cnx)(H_2O)]NO_3{\cdot}2H_2O$ (Mendoza-Díaz *et al.*, 1987), or ciprofloxacin [1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid, *cf.*H] (Saha *et al.*, 2005; Drevenšek *et al.*, 2003) all of them presenting small trigonality indexes.

The crystal structure of (I) is dominated by layered structures. All units are connected *via* O—H···O hydrogen bonds (Table 1), forming an infinite one-dimensional chain along [001]. Additionally, complex cations are also connected through weak π–π interactions, completing the three-dimensional supramolecular arrangement.

Experimental

Enrofloxacin (360 mg, 1 mmol) was dissolved in CH_3CN—H_2O (3:2, 15 ml) and NaOH (40 mg, 1 mmol) was added. After 20 min. of stirring, $Cu(NO_3)_2{\cdot}5H_2O$ (240 mg, 1 mmol) in CH_3CN—H_2O (20 ml) and phen (180 mg, 1 mmol) in CH_3CN—H_2O (10 ml) were added dropwise. The reaction mixture was stirred for 50 min. The green solution was reduced

in volume and left for slow evaporation. Green crystals of (I) deposited over a few days. Yield: 646 mg, 90%. A suitable green single-crystal was carefully selected out of the mother liquor and mounted with mineral oil in a glass capillary for subsequent data collection. The crystals decompose rapidly by contact with air, with probable release of water.

Refinement

H atoms bonded to O atoms were found in a difference map and their coordinates refined with O—H bond lengths constrained to 0.84–0.88 Å and U_{iso} = 1.5U_{eq}(carrier O). H atoms attached to C atoms were placed in geometrically idealized positions, and refined as riding on their parent atoms, with C—H distances fixed to 0.93 (aromatic CH), 0.96 (methyl CH_3), 0.97 (methylene CH_2) or 0.98 Å (methine CH), and with U_{iso} = 1.5U_{eq}(C) for the methyl group and U_{iso}(H) = 1.2U_{eq}(C) otherwise.

Figures

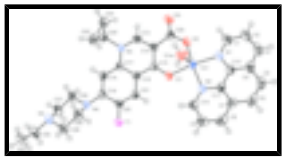


Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms. The anion and solvent molecules were omitted for clarity.

aqua[1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluoro-4-oxo-1,4- dihydroquinoline-3-carboxylato](1,10-phenanthroline)copper(II) nitrate dihydrate

Crystal data

$[Cu(C_{19}H_{21}FN_3O_3)(C_{12}H_8N_2)(H_2O_1)]NO_3{\cdot}2H_2O$	Z = 2
M_r = 718.2	F_{000} = 746
Triclinic, $P\overline{1}$	D_x = 1.474 Mg m^{-3}
a = 10.819 (4) Å	Mo $K\alpha$ radiation λ = 0.71073 Å
b = 12.019 (5) Å	Cell parameters from 50 reflections
c = 12.968 (6) Å	θ = 3.8–23.9º
α = 76.75 (3)º	μ = 0.74 mm^{-1}
β = 87.91 (3)º	T = 298 (2) K
γ = 80.37 (2)º	Block, green
V = 1618.3 (12) Å^3	0.27 × 0.24 × 0.22 mm

Data collection

Siemens P4 diffractometer	R_{int} = 0.035
Radiation source: fine-focus sealed tube	θ_{max} = 25.1º
Monochromator: graphite	θ_{min} = 1.6º
T = 298(2) K	h = −1→12
2θ/ω scans	k = −14→14
Absorption correction: ψ scan (XSCANS; Siemens, 1993)	l = −15→15

T_{min} = 0.824, T_{max} = 0.853
6697 measured reflections
5711 independent reflections
3170 reflections with $I > 2\sigma(I)$

3 standard reflections
every 97 reflections
intensity decay: 3.6%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.129$
$S = 1.03$
5711 reflections
434 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.4734P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7460 (6)	0.6938 (5)	0.4278 (4)	0.0567 (16)
H1	0.8137	0.7218	0.449	0.068*
C2	0.7685 (6)	0.6165 (5)	0.3609 (5)	0.0646 (18)
H2	0.8489	0.597	0.3356	0.078*
C3	0.6713 (6)	0.5696 (5)	0.3330 (4)	0.0597 (17)
H3	0.6855	0.5166	0.29	0.072*
C4	0.5490 (6)	0.6022 (4)	0.3700 (4)	0.0492 (15)
C5	0.4388 (7)	0.5585 (5)	0.3482 (5)	0.0618 (18)
H5	0.4461	0.5044	0.3064	0.074*
C6	0.3262 (6)	0.5939 (5)	0.3867 (5)	0.0626 (18)
H6	0.2574	0.5639	0.3704	0.075*
C7	0.3083 (5)	0.6771 (5)	0.4525 (4)	0.0470 (14)
C8	0.1942 (6)	0.7186 (5)	0.4960 (5)	0.0583 (16)
H8	0.1214	0.6926	0.4827	0.07*
C9	0.1895 (5)	0.7977 (5)	0.5584 (4)	0.0537 (15)
H9	0.1139	0.8252	0.5873	0.064*
C10	0.2993 (5)	0.8361 (4)	0.5778 (4)	0.0437 (13)
H10	0.2951	0.8894	0.6202	0.052*
C11	0.4145 (5)	0.7207 (4)	0.4766 (4)	0.0383 (13)
C12	0.5349 (5)	0.6835 (4)	0.4353 (4)	0.0399 (13)
C13	0.7644 (5)	1.0355 (4)	0.7580 (4)	0.0390 (13)
H13	0.8515	1.0247	0.758	0.047*
C14	0.7075 (5)	0.9895 (4)	0.6880 (4)	0.0351 (12)
C15	0.5749 (5)	1.0025 (4)	0.6883 (4)	0.0345 (12)
C16	0.5078 (4)	1.0642 (4)	0.7631 (4)	0.0329 (11)
C17	0.5737 (5)	1.1117 (4)	0.8305 (4)	0.0329 (12)

C18	0.5072 (5)	1.1760 (4)	0.8994 (4)	0.0394 (13)
H18	0.5515	1.2064	0.9435	0.047*
C19	0.3777 (5)	1.1947 (4)	0.9025 (4)	0.0376 (12)
C20	0.3156 (5)	1.1416 (4)	0.8364 (4)	0.0423 (13)
C21	0.3771 (5)	1.0788 (4)	0.7702 (4)	0.0403 (13)
H21	0.3321	1.0452	0.7293	0.048*
C22	0.7761 (5)	1.1298 (5)	0.9055 (4)	0.0459 (14)
H22	0.7736	1.0835	0.9781	0.055*
C23	0.7825 (6)	1.2536 (5)	0.8956 (5)	0.0641 (17)
H23A	0.782	1.2813	0.9603	0.077*
H23B	0.7402	1.309	0.8358	0.077*
C24	0.8955 (6)	1.1718 (6)	0.8735 (5)	0.077 (2)
H24A	0.9216	1.1779	0.8004	0.093*
H24B	0.9633	1.1502	0.9248	0.093*
C25	0.7914 (5)	0.9325 (4)	0.6140 (4)	0.0411 (13)
C26	0.3700 (5)	1.3449 (4)	1.0030 (4)	0.0481 (14)
H26A	0.4181	1.3862	0.9468	0.058*
H26B	0.4276	1.3007	1.0589	0.058*
C27	0.2754 (5)	1.4304 (4)	1.0459 (4)	0.0531 (15)
H27A	0.3186	1.4831	1.0718	0.064*
H27B	0.2191	1.4757	0.9895	0.064*
C28	0.1357 (5)	1.2918 (5)	1.0910 (4)	0.0499 (14)
H28A	0.0774	1.3376	1.0364	0.06*
H28B	0.088	1.2501	1.1472	0.06*
C29	0.2275 (5)	1.2062 (4)	1.0451 (4)	0.0491 (15)
H29A	0.2812	1.1562	1.1011	0.059*
H29B	0.1816	1.158	1.0155	0.059*
C30	0.1149 (6)	1.4505 (5)	1.1817 (5)	0.0653 (18)
H30A	0.0488	1.4898	1.1313	0.078*
H30B	0.16	1.5088	1.1959	0.078*
C31	0.0562 (6)	1.3940 (6)	1.2832 (5)	0.082 (2)
H31A	−0.0021	1.348	1.2677	0.123*
H31B	0.0129	1.4527	1.3168	0.123*
H31C	0.1204	1.3454	1.3297	0.123*
Cu1	0.57945 (6)	0.84081 (6)	0.55762 (5)	0.0410 (2)
F1	0.1881 (3)	1.1611 (3)	0.8365 (2)	0.0651 (10)
N01	0.3156 (6)	0.6901 (5)	0.8300 (4)	0.0649 (14)
N1	0.6331 (4)	0.7290 (3)	0.4623 (3)	0.0416 (11)
N2	0.4095 (4)	0.7998 (3)	0.5383 (3)	0.0380 (11)
N3	0.7045 (4)	1.0947 (3)	0.8261 (3)	0.0356 (10)
N4	0.3054 (4)	1.2660 (3)	0.9618 (3)	0.0397 (10)
N5	0.2019 (4)	1.3690 (3)	1.1333 (3)	0.0453 (11)
O01	0.3491 (5)	0.7816 (5)	0.8383 (4)	0.1054 (18)
O1	0.5090 (3)	0.9650 (3)	0.6268 (3)	0.0418 (9)
O2	0.7439 (3)	0.8813 (3)	0.5512 (3)	0.0485 (10)
O02	0.2046 (5)	0.6808 (5)	0.8384 (5)	0.121 (2)
O1W	0.6097 (4)	0.7053 (3)	0.7104 (3)	0.0628 (11)
H1C	0.6676	0.6892	0.7558	0.094*
H1D	0.5437	0.6983	0.7454	0.094*

O03	0.3973 (5)	0.6117 (5)	0.8137 (4)	0.1022 (17)
O3	0.9053 (3)	0.9349 (3)	0.6145 (3)	0.0630 (11)
O2W	0.0721 (5)	0.9211 (4)	0.8484 (4)	0.1185 (19)
H2C	0.1372	0.8658	0.8557	0.178*
H2D	0.0777	0.9454	0.7795	0.178*
O3W	0.0751 (4)	1.0871 (4)	0.6304 (3)	0.0894 (15)
H3C	0.1166	1.0938	0.5724	0.134*
H3D	0.0237	1.0423	0.6254	0.134*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.056 (4)	0.052 (4)	0.064 (4)	0.000 (3)	0.006 (3)	−0.024 (3)
C2	0.068 (5)	0.060 (4)	0.067 (4)	0.006 (4)	0.010 (4)	−0.029 (4)
C3	0.085 (5)	0.042 (3)	0.050 (4)	0.007 (4)	0.005 (4)	−0.021 (3)
C4	0.073 (4)	0.033 (3)	0.041 (3)	−0.001 (3)	−0.007 (3)	−0.013 (3)
C5	0.090 (5)	0.047 (4)	0.055 (4)	−0.009 (4)	−0.008 (4)	−0.025 (3)
C6	0.082 (5)	0.054 (4)	0.062 (4)	−0.026 (4)	−0.020 (4)	−0.021 (3)
C7	0.047 (4)	0.042 (3)	0.051 (3)	−0.008 (3)	−0.013 (3)	−0.006 (3)
C8	0.050 (4)	0.056 (4)	0.070 (4)	−0.021 (3)	−0.013 (3)	−0.006 (3)
C9	0.042 (4)	0.052 (4)	0.065 (4)	−0.008 (3)	0.008 (3)	−0.011 (3)
C10	0.044 (3)	0.045 (3)	0.043 (3)	−0.008 (3)	0.004 (3)	−0.014 (3)
C11	0.051 (4)	0.032 (3)	0.032 (3)	−0.006 (3)	−0.005 (3)	−0.007 (2)
C12	0.051 (4)	0.033 (3)	0.034 (3)	−0.001 (3)	−0.005 (3)	−0.007 (2)
C13	0.028 (3)	0.041 (3)	0.050 (3)	−0.010 (2)	0.005 (3)	−0.014 (3)
C14	0.034 (3)	0.031 (3)	0.041 (3)	−0.005 (2)	0.003 (2)	−0.011 (2)
C15	0.042 (3)	0.033 (3)	0.030 (3)	−0.007 (3)	−0.003 (2)	−0.011 (2)
C16	0.033 (3)	0.036 (3)	0.032 (3)	−0.009 (2)	0.000 (2)	−0.009 (2)
C17	0.037 (3)	0.029 (3)	0.034 (3)	−0.009 (2)	0.004 (2)	−0.008 (2)
C18	0.043 (3)	0.043 (3)	0.038 (3)	−0.012 (3)	−0.002 (3)	−0.018 (3)
C19	0.042 (3)	0.038 (3)	0.035 (3)	−0.008 (3)	0.003 (2)	−0.012 (2)
C20	0.028 (3)	0.049 (3)	0.056 (3)	−0.010 (3)	0.006 (3)	−0.022 (3)
C21	0.039 (3)	0.049 (3)	0.041 (3)	−0.012 (3)	0.000 (3)	−0.020 (3)
C22	0.047 (4)	0.055 (4)	0.042 (3)	−0.013 (3)	−0.006 (3)	−0.020 (3)
C23	0.070 (4)	0.061 (4)	0.073 (4)	−0.026 (4)	−0.002 (4)	−0.028 (3)
C24	0.045 (4)	0.118 (6)	0.097 (5)	−0.029 (4)	0.010 (4)	−0.071 (5)
C25	0.040 (4)	0.038 (3)	0.048 (3)	−0.005 (3)	−0.004 (3)	−0.015 (3)
C26	0.056 (4)	0.045 (3)	0.052 (3)	−0.015 (3)	0.012 (3)	−0.025 (3)
C27	0.074 (4)	0.038 (3)	0.051 (3)	−0.011 (3)	0.013 (3)	−0.018 (3)
C28	0.048 (4)	0.054 (4)	0.052 (3)	−0.014 (3)	0.011 (3)	−0.019 (3)
C29	0.058 (4)	0.046 (3)	0.048 (3)	−0.016 (3)	0.015 (3)	−0.016 (3)
C30	0.071 (4)	0.055 (4)	0.073 (4)	0.006 (3)	0.015 (4)	−0.033 (3)
C31	0.080 (5)	0.087 (5)	0.084 (5)	−0.003 (4)	0.035 (4)	−0.042 (4)
Cu1	0.0408 (4)	0.0434 (4)	0.0450 (4)	−0.0071 (3)	0.0033 (3)	−0.0229 (3)
F1	0.0330 (18)	0.102 (3)	0.080 (2)	−0.0126 (18)	0.0059 (16)	−0.060 (2)
N01	0.069 (4)	0.072 (4)	0.048 (3)	−0.015 (4)	0.002 (3)	0.002 (3)
N1	0.043 (3)	0.040 (3)	0.044 (3)	−0.003 (2)	0.004 (2)	−0.018 (2)
N2	0.042 (3)	0.036 (3)	0.037 (2)	−0.003 (2)	0.000 (2)	−0.012 (2)

N3	0.036 (3)	0.037 (2)	0.037 (2)	−0.008 (2)	0.001 (2)	−0.016 (2)
N4	0.044 (3)	0.039 (2)	0.043 (3)	−0.013 (2)	0.008 (2)	−0.019 (2)
N5	0.053 (3)	0.037 (3)	0.047 (3)	−0.002 (2)	0.004 (2)	−0.017 (2)
O01	0.111 (4)	0.079 (4)	0.131 (5)	−0.027 (3)	−0.010 (3)	−0.024 (3)
O1	0.040 (2)	0.045 (2)	0.047 (2)	−0.0076 (17)	0.0045 (17)	−0.0246 (18)
O2	0.039 (2)	0.061 (2)	0.056 (2)	−0.0132 (19)	0.0109 (18)	−0.032 (2)
O02	0.067 (4)	0.158 (6)	0.128 (5)	−0.039 (4)	−0.004 (3)	0.004 (4)
O1W	0.061 (3)	0.075 (3)	0.050 (2)	−0.012 (2)	−0.002 (2)	−0.009 (2)
O03	0.106 (4)	0.093 (4)	0.121 (4)	−0.016 (3)	0.025 (3)	−0.055 (3)
O3	0.035 (2)	0.083 (3)	0.085 (3)	−0.012 (2)	0.010 (2)	−0.048 (2)
O2W	0.106 (4)	0.116 (4)	0.122 (4)	0.009 (4)	−0.020 (3)	−0.021 (4)
O3W	0.094 (4)	0.128 (4)	0.070 (3)	−0.058 (3)	0.019 (3)	−0.044 (3)

Geometric parameters (Å, °)

C1—N1	1.321 (6)	C23—C24	1.498 (8)
C1—C2	1.398 (7)	C23—H23A	0.97
C1—H1	0.93	C23—H23B	0.97
C2—C3	1.369 (8)	C24—H24A	0.97
C2—H2	0.93	C24—H24B	0.97
C3—C4	1.413 (8)	C25—O3	1.238 (6)
C3—H3	0.93	C25—O2	1.293 (5)
C4—C12	1.420 (6)	C26—N4	1.468 (6)
C4—C5	1.442 (8)	C26—C27	1.511 (6)
C5—C6	1.339 (8)	C26—H26A	0.97
C5—H5	0.93	C26—H26B	0.97
C6—C7	1.442 (7)	C27—N5	1.487 (6)
C6—H6	0.93	C27—H27A	0.97
C7—C8	1.400 (7)	C27—H27B	0.97
C7—C11	1.413 (7)	C28—N5	1.469 (6)
C8—C9	1.376 (7)	C28—C29	1.516 (6)
C8—H8	0.93	C28—H28A	0.97
C9—C10	1.395 (7)	C28—H28B	0.97
C9—H9	0.93	C29—N4	1.474 (6)
C10—N2	1.325 (6)	C29—H29A	0.97
C10—H10	0.93	C29—H29B	0.97
C11—N2	1.368 (6)	C30—N5	1.473 (6)
C11—C12	1.432 (7)	C30—C31	1.507 (8)
C12—N1	1.364 (6)	C30—H30A	0.97
C13—N3	1.341 (5)	C30—H30B	0.97
C13—C14	1.376 (6)	C31—H31A	0.96
C13—H13	0.93	C31—H31B	0.96
C14—C15	1.418 (6)	C31—H31C	0.96
C14—C25	1.498 (6)	Cu1—O2	1.915 (3)
C15—O1	1.290 (5)	Cu1—O1	1.949 (3)
C15—C16	1.454 (6)	Cu1—N2	2.021 (4)
C16—C21	1.397 (6)	Cu1—N1	2.029 (4)
C16—C17	1.417 (6)	Cu1—O1W	2.253 (4)
C17—N3	1.397 (6)	N01—O02	1.223 (6)

C17—C18	1.413 (6)	N01—O02	1.223 (6)
C18—C19	1.382 (7)	N01—O03	1.230 (6)
C18—H18	0.93	N01—O03	1.230 (6)
C19—N4	1.404 (5)	N01—O01	1.242 (6)
C19—C20	1.425 (6)	N01—O01	1.242 (6)
C20—C21	1.356 (6)	O1W—H1C	0.8422
C20—F1	1.360 (5)	O1W—H1D	0.8373
C21—H21	0.93	O2W—H2C	0.8754
C22—C24	1.476 (7)	O2W—H2D	0.8768
C22—C23	1.477 (7)	O3W—H3C	0.8564
C22—N3	1.484 (6)	O3W—H3D	0.8496
C22—H22	0.98		
N1—C1—C2	123.1 (6)	O3—C25—C14	119.2 (4)
N1—C1—H1	118.4	O2—C25—C14	119.6 (5)
C2—C1—H1	118.4	N4—C26—C27	109.9 (4)
C3—C2—C1	119.4 (6)	N4—C26—H26A	109.7
C3—C2—H2	120.3	C27—C26—H26A	109.7
C1—C2—H2	120.3	N4—C26—H26B	109.7
C2—C3—C4	119.7 (5)	C27—C26—H26B	109.7
C2—C3—H3	120.2	H26A—C26—H26B	108.2
C4—C3—H3	120.2	N5—C27—C26	110.6 (4)
C3—C4—C12	116.8 (5)	N5—C27—H27A	109.5
C3—C4—C5	125.5 (5)	C26—C27—H27A	109.5
C12—C4—C5	117.7 (5)	N5—C27—H27B	109.5
C6—C5—C4	121.7 (5)	C26—C27—H27B	109.5
C6—C5—H5	119.2	H27A—C27—H27B	108.1
C4—C5—H5	119.2	N5—C28—C29	110.8 (4)
C5—C6—C7	122.1 (6)	N5—C28—H28A	109.5
C5—C6—H6	119	C29—C28—H28A	109.5
C7—C6—H6	119	N5—C28—H28B	109.5
C8—C7—C11	116.4 (5)	C29—C28—H28B	109.5
C8—C7—C6	125.8 (5)	H28A—C28—H28B	108.1
C11—C7—C6	117.8 (5)	N4—C29—C28	111.3 (4)
C9—C8—C7	120.2 (5)	N4—C29—H29A	109.4
C9—C8—H8	119.9	C28—C29—H29A	109.4
C7—C8—H8	119.9	N4—C29—H29B	109.4
C8—C9—C10	119.4 (5)	C28—C29—H29B	109.4
C8—C9—H9	120.3	H29A—C29—H29B	108
C10—C9—H9	120.3	N5—C30—C31	113.9 (5)
N2—C10—C9	122.7 (5)	N5—C30—H30A	108.8
N2—C10—H10	118.6	C31—C30—H30A	108.8
C9—C10—H10	118.6	N5—C30—H30B	108.8
N2—C11—C7	123.3 (5)	C31—C30—H30B	108.8
N2—C11—C12	116.5 (5)	H30A—C30—H30B	107.7
C7—C11—C12	120.3 (5)	C30—C31—H31A	109.5
N1—C12—C4	122.7 (5)	C30—C31—H31B	109.5
N1—C12—C11	116.9 (4)	H31A—C31—H31B	109.5
C4—C12—C11	120.4 (5)	C30—C31—H31C	109.5
N3—C13—C14	125.4 (5)	H31A—C31—H31C	109.5

N3—C13—H13	117.3	H31B—C31—H31C	109.5
C14—C13—H13	117.3	O2—Cu1—O1	92.94 (14)
C13—C14—C15	118.2 (4)	O2—Cu1—N2	170.46 (16)
C13—C14—C25	117.0 (4)	O1—Cu1—N2	92.85 (15)
C15—C14—C25	124.8 (4)	O2—Cu1—N1	90.95 (16)
O1—C15—C14	125.1 (4)	O1—Cu1—N1	169.36 (16)
O1—C15—C16	117.4 (4)	N2—Cu1—N1	82.08 (17)
C14—C15—C16	117.5 (4)	O2—Cu1—O1W	96.03 (15)
C21—C16—C17	118.3 (4)	O1—Cu1—O1W	94.13 (14)
C21—C16—C15	121.2 (4)	N2—Cu1—O1W	91.11 (15)
C17—C16—C15	120.6 (4)	N1—Cu1—O1W	95.31 (15)
N3—C17—C18	121.2 (4)	O02—N01—O03	122.7 (7)
N3—C17—C16	118.7 (4)	O02—N01—O03	122.7 (7)
C18—C17—C16	120.1 (4)	O02—N01—O03	122.7 (7)
C19—C18—C17	121.4 (4)	O02—N01—O03	122.7 (7)
C19—C18—H18	119.3	O02—N01—O01	119.7 (7)
C17—C18—H18	119.3	O02—N01—O01	119.7 (7)
C18—C19—N4	124.4 (4)	O03—N01—O01	117.6 (6)
C18—C19—C20	116.6 (4)	O03—N01—O01	117.6 (6)
N4—C19—C20	118.9 (4)	O02—N01—O01	119.7 (7)
C21—C20—F1	119.2 (4)	O02—N01—O01	119.7 (7)
C21—C20—C19	123.2 (5)	O03—N01—O01	117.6 (6)
F1—C20—C19	117.5 (4)	O03—N01—O01	117.6 (6)
C20—C21—C16	120.4 (4)	C1—N1—C12	118.3 (4)
C20—C21—H21	119.8	C1—N1—Cu1	129.6 (4)
C16—C21—H21	119.8	C12—N1—Cu1	112.1 (3)
C24—C22—C23	61.0 (4)	C10—N2—C11	118.0 (4)
C24—C22—N3	118.9 (5)	C10—N2—Cu1	129.5 (3)
C23—C22—N3	119.6 (5)	C11—N2—Cu1	112.4 (3)
C24—C22—H22	115.5	C13—N3—C17	119.6 (4)
C23—C22—H22	115.5	C13—N3—C22	120.4 (4)
N3—C22—H22	115.5	C17—N3—C22	119.6 (4)
C22—C23—C24	59.5 (4)	C19—N4—C26	116.7 (4)
C22—C23—H23A	117.8	C19—N4—C29	115.1 (4)
C24—C23—H23A	117.8	C26—N4—C29	110.4 (4)
C22—C23—H23B	117.8	C28—N5—C30	111.8 (4)
C24—C23—H23B	117.8	C28—N5—C27	108.2 (4)
H23A—C23—H23B	115	C30—N5—C27	111.8 (4)
C22—C24—C23	59.5 (3)	C15—O1—Cu1	122.0 (3)
C22—C24—H24A	117.8	C25—O2—Cu1	127.3 (3)
C23—C24—H24A	117.8	Cu1—O1W—H1C	131.2
C22—C24—H24B	117.8	Cu1—O1W—H1D	113
C23—C24—H24B	117.8	H1C—O1W—H1D	105.3
H24A—C24—H24B	115	H2C—O2W—H2D	96.6
O3—C25—O2	121.2 (5)	H3C—O3W—H3D	104.8
N1—C1—C2—C3	−3.3 (9)	O2—Cu1—N1—C1	8.1 (5)
C1—C2—C3—C4	1.6 (9)	O1—Cu1—N1—C1	119.6 (9)
C2—C3—C4—C5	−179.0 (6)	N2—Cu1—N1—C1	−178.4 (5)
C3—C4—C5—C6	179.8 (6)	O1W—Cu1—N1—C1	−88.0 (5)

C5—C6—C7—C8	−179.9 (6)	O2—Cu1—N1—C12	−174.2 (3)
C6—C7—C8—C9	179.6 (5)	O1—Cu1—N1—C12	−62.7 (10)
C6—C7—C11—N2	−179.9 (4)	N2—Cu1—N1—C12	−0.7 (3)
C8—C7—C11—C12	−179.8 (5)	O1W—Cu1—N1—C12	89.7 (3)
C5—C4—C12—N1	178.9 (5)	C9—C10—N2—C11	−0.4 (7)
C3—C4—C12—C11	−179.6 (5)	C9—C10—N2—Cu1	−178.8 (4)
C5—C4—C12—C11	−0.6 (7)	C7—C11—N2—C10	0.6 (7)
N2—C11—C12—N1	0.8 (7)	C12—C11—N2—C10	180.0 (4)
C7—C11—C12—N1	−179.7 (5)	C7—C11—N2—Cu1	179.2 (4)
N2—C11—C12—C4	−179.6 (4)	C12—C11—N2—Cu1	−1.4 (5)
C7—C11—C12—C4	−0.2 (7)	O1—Cu1—N2—C10	−9.8 (4)
N3—C13—C14—C15	−1.5 (7)	N1—Cu1—N2—C10	179.6 (5)
N3—C13—C14—C25	176.4 (4)	O1W—Cu1—N2—C10	84.3 (4)
C13—C14—C15—O1	179.3 (4)	O1—Cu1—N2—C11	171.7 (3)
C25—C14—C15—O1	1.6 (8)	N1—Cu1—N2—C11	1.1 (3)
C13—C14—C15—C16	0.1 (7)	O1W—Cu1—N2—C11	−94.1 (3)
C25—C14—C15—C16	−177.7 (4)	C14—C13—N3—C17	1.1 (7)
O1—C15—C16—C21	2.0 (7)	C14—C13—N3—C22	173.7 (5)
C14—C15—C16—C21	−178.7 (5)	C18—C17—N3—C13	−178.4 (4)
O1—C15—C16—C17	−177.6 (4)	C16—C17—N3—C13	0.8 (7)
C14—C15—C16—C17	1.7 (7)	C18—C17—N3—C22	8.9 (7)
C21—C16—C17—N3	178.2 (4)	C16—C17—N3—C22	−171.8 (4)
C15—C16—C17—N3	−2.2 (7)	C24—C22—N3—C13	40.1 (7)
C21—C16—C17—C18	−2.6 (7)	C23—C22—N3—C13	111.2 (6)
C15—C16—C17—C18	177.1 (4)	C24—C22—N3—C17	−147.3 (5)
N3—C17—C18—C19	178.8 (5)	C23—C22—N3—C17	−76.2 (6)
C16—C17—C18—C19	−0.4 (7)	C18—C19—N4—C26	14.4 (7)
C17—C18—C19—N4	−174.1 (4)	C20—C19—N4—C26	−162.4 (5)
C17—C18—C19—C20	2.7 (7)	C18—C19—N4—C29	−117.5 (5)
C18—C19—C20—C21	−2.2 (8)	C20—C19—N4—C29	65.7 (6)
N4—C19—C20—C21	174.8 (5)	C27—C26—N4—C19	169.1 (4)
C18—C19—C20—F1	−178.5 (5)	C27—C26—N4—C29	−56.9 (5)
N4—C19—C20—F1	−1.5 (7)	C28—C29—N4—C19	−169.6 (4)
F1—C20—C21—C16	175.5 (5)	C28—C29—N4—C26	55.6 (6)
C19—C20—C21—C16	−0.7 (8)	C29—C28—N5—C30	−178.1 (4)
C17—C16—C21—C20	3.1 (7)	C29—C28—N5—C27	58.3 (5)
C15—C16—C21—C20	−176.6 (5)	C31—C30—N5—C28	69.4 (6)
N3—C22—C23—C24	−108.7 (6)	C31—C30—N5—C27	−169.0 (5)
N3—C22—C24—C23	109.8 (6)	C26—C27—N5—C28	−60.4 (5)
C13—C14—C25—O3	−4.0 (7)	C26—C27—N5—C30	176.0 (5)
C15—C14—C25—O3	173.8 (5)	C14—C15—O1—Cu1	21.5 (7)
C13—C14—C25—O2	175.6 (5)	C16—C15—O1—Cu1	−159.3 (3)
C15—C14—C25—O2	−6.7 (8)	O2—Cu1—O1—C15	−30.0 (4)
N4—C26—C27—N5	60.1 (6)	N2—Cu1—O1—C15	157.6 (4)
N5—C28—C29—N4	−57.1 (6)	N1—Cu1—O1—C15	−141.3 (8)
C2—C1—N1—C12	3.1 (8)	O1W—Cu1—O1—C15	66.2 (4)
C2—C1—N1—Cu1	−179.3 (4)	O3—C25—O2—Cu1	166.3 (4)
C4—C12—N1—C1	−1.4 (8)	C14—C25—O2—Cu1	−13.3 (7)
C11—C12—N1—C1	178.1 (5)	O1—Cu1—O2—C25	26.9 (4)

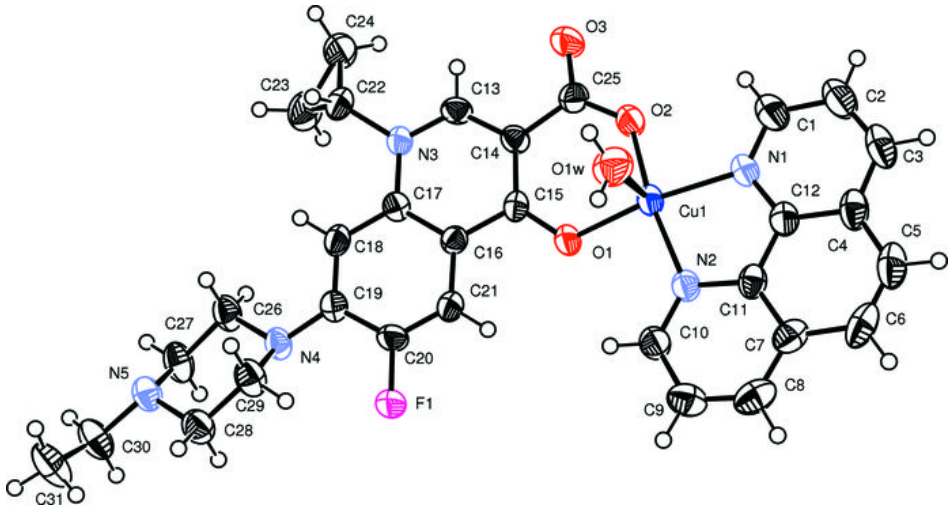
C4—C12—N1—Cu1	−179.4 (4)	N1—Cu1—O2—C25	−163.0 (4)
C11—C12—N1—Cu1	0.2 (5)	O1W—Cu1—O2—C25	−67.6 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1D···O03	0.84	2.10	2.879 (7)	155
O2W—H2C···O01	0.88	2.37	3.194 (7)	157
O2W—H2C···O02	0.88	2.28	3.031 (8)	144
O2W—H2D···O3W	0.88	2.26	3.066 (7)	152
O3W—H3C···O2^{i}	0.86	2.17	3.005 (5)	166
O3W—H3D···O3^{ii}	0.85	2.00	2.845 (6)	179

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+1; (ii) *x*−1, *y*, *z*.

Fig. 1


C24
O3
C23
C22
C13
C25
O2
C1
C2
N3
C14
O1w
N1
C3
C17
C15
Cu1
C12
C18
C16
O1
C4
C5
N2
C19
C21
C26
C11
C27
C10
C6
N4
C20
C7
N5
C29
F1
C8
C28
C9
C30
C31