Crystal structure of *di*-aqua-*bis*-[1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluor-4-oxo-1,4-dihydrochinolin-3-carboxylic acid]zinc(II)bibenzene-1,4-dicarboxylate octahydrate, $[Zn(C_{19}H_{22}N_3FO_3)_2(H_2O)_2]\cdot 2(C_8H_5O_4)\cdot 8(H_2O)$, $C_{54}H_{74}F_2N_6O_{24}Zn$

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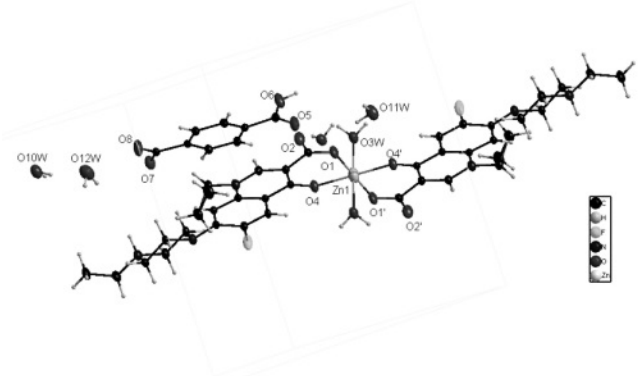

Abstract

$C_{54}H_{74}F_2N_6O_{24}Zn$, monoclinic, $P2_1/n$ (no. 14), a = 13.5443(3) Å, b = 13.7558(4) Å, c = 16.6644(4) Å, β = 106.666(2)°, V = 2974.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.0550, $wR_{ref}(F^2)$ = 0.1444, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.20×0.23×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.06 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	22589, 5231
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3723
$N(param)_{refined}$:	472
Programs:	SHELX [4]

Source of material

A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.25 mmol), enrofloxacin (0.5 mmol), 1,4-benzenedicarboxylic acid (0.25 mmol), sodium hydroxide (1 mmol), and water (15 mL) was stirred for 30 min in air. The mixture was then transferred to a 25-mL Teflon-lined autoclave, which was heated to 455K for 72 h under autogenous pressure. After cooling, the bomb was opened and colourless blocks of title compound were recovered from the reaction mixture by vacuum filtration and rinsed with water. Crystals suitable for single crystal X-ray diffraction were selected directly from the sample as prepared.

Discussion

Enrofloxacin (Henro), $C_{19}H_{22}FN_3O_3$ (systematic name: 1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluor-4-oxo-1,4-dihydrochinolin-3-carboxylic acid), is a member of the fluoroquinolone (flqu) family of antibiotics [1], widely used in veterinary clinical practice because of its wide antibiotic spectrum and its excellent bactericidal activity [1, 2]. Our interest in enrofloxacin and related fluoroquinolones is focused on their potential as multidentate/bridging ligands in coordination chemistry. The cadmium and lead complexe of enrofloxacin anion had been reported [3]. In the title compound, $[Zn(C_{19}H_{22}N_3FO_3)_2(H_2O)_2]\cdot 2(C_8H_5O_4)\cdot 8(H_2O)$, the Zn^{II} ion (site symmetry 1) exhibits a distorted ZnO_6 octahedral geometry defined by two neutral bidentate O,O-bonded 1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluor-4-oxo-1,4-dihydrochinolin-3-carboxylate (Henro) zwitterions and two water molecules. The charge-balancing benzene-1,4-dicarboxylate (1,4-bdc) anion is also centrosymmetric. An extensive network of O–H···O and O–H···N hydrogen bonds helps to establish the crystal packing.

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

Atom	Site	x	y	z	U_{iso}
H(5)	4*e*	0.2080	0.4391	0.0396	0.042
H(16A)	4*e*	0.0081	0.5559	0.3028	0.045
H(16B)	4*e*	0.0826	0.4687	0.3388	0.045
H(20A)	4*e*	–0.0603	0.3644	0.3214	0.050
H(20B)	4*e*	–0.0679	0.4513	0.3805	0.050
H(21A)	4*e*	–0.0846	0.4679	0.0988	0.050
H(21B)	4*e*	–0.0924	0.5559	0.1566	0.050
H(22A)	4*e*	–0.2377	0.4573	0.1386	0.058
H(22B)	4*e*	–0.1674	0.3666	0.1721	0.058
H(24A)	4*e*	0.3173	0.5525	0.4578	0.074
H(24B)	4*e*	0.3628	0.4773	0.4012	0.074
H(25A)	4*e*	–0.2174	0.4457	0.4137	0.109
H(25B)	4*e*	–0.3360	0.4265	0.3778	0.109
H(25C)	4*e*	–0.2893	0.5260	0.3607	0.109
H(26A)	4*e*	–0.3226	0.4252	0.2428	0.070
H(26B)	4*e*	–0.2481	0.3468	0.2960	0.070
H(27A)	4*e*	0.4642	0.6540	0.4750	0.091
H(27B)	4*e*	0.5098	0.5788	0.4184	0.091
H(2)	4*e*	0.182(2)	0.559(2)	0.292(2)	0.04(1)
H(3)	4*e*	0.496(3)	0.655(3)	0.289(2)	0.05(1)
H(4)	4*e*	0.310(3)	0.674(3)	0.356(2)	0.06(1)
H(6)	4*e*	–0.175(3)	0.530(3)	0.269(2)	0.05(1)
H(7)	4*e*	0.109(3)	0.697(3)	0.003(3)	0.06(1)
H(8)	4*e*	–0.012(3)	0.704(3)	0.081(2)	0.05(1)
H(9)	4*e*	0.204(3)	0.831(3)	0.273(2)	0.06(1)
H(10)	4*e*	0.326(3)	0.825(3)	0.198(2)	0.05(1)
H(5C)	4*e*	0.412(4)	0.820(4)	0.031(3)	0.09(2)
H(1W)	4*e*	0.536(3)	0.353(2)	0.116(2)	0.07(1)
H(2W)	4*e*	0.591(4)	0.333(2)	0.069(3)	0.10(2)
H(3W)	4*e*	0.755(1)	0.677(3)	0.269(2)	0.09(2)
H(4W)	4*e*	0.843(2)	0.694(2)	0.262(2)	0.06(1)

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Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(5W)	4*e*	0.429(3)	0.837(5)	0.906(2)	0.16(3)
H(6W)	4*e*	0.520(2)	0.838(3)	0.953(3)	0.09(2)
H(7W)	4*e*	0.704(3)	0.671(4)	0.082(3)	0.11(2)

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(8W)	4*e*	0.788(3)	0.717(4)	0.103(2)	0.11(2)
H(9W)	4*e*	0.630(3)	0.764(2)	0.898(2)	0.08(2)
H(10W)	4*e*	0.680(4)	0.771(3)	0.973(2)	0.11(2)

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}
C(1)	4*e*	0.2858(2)	0.5163(2)	0.1429(2)	0.025(2)	0.037(2)	0.028(2)	0.003(1)	0.007(1)	0.001(1)
C(2)	4*e*	0.3775(3)	0.5361(2)	0.1165(2)	0.033(2)	0.037(2)	0.034(2)	0.002(2)	0.014(2)	0.003(2)
C(3)	4*e*	0.2771(2)	0.5481(2)	0.2202(2)	0.031(2)	0.033(2)	0.028(2)	–0.001(2)	0.007(2)	–0.001(1)
C(4)	4*e*	0.2271(3)	0.7614(3)	0.0920(2)	0.037(2)	0.037(2)	0.037(2)	–0.001(2)	0.014(2)	–0.002(2)
C(5)	4*e*	0.2039(2)	0.4629(3)	0.0908(2)	0.033(2)	0.048(2)	0.025(2)	–0.003(2)	0.011(2)	–0.005(2)
C(6)	4*e*	0.0860(3)	0.7683(2)	0.1839(2)	0.038(2)	0.036(2)	0.032(2)	–0.003(2)	0.013(2)	–0.000(2)
C(7)	4*e*	0.2558(3)	0.8000(3)	0.1721(2)	0.037(2)	0.046(2)	0.039(2)	–0.010(2)	0.012(2)	–0.007(2)
C(8)	4*e*	0.1048(2)	0.4819(2)	0.1914(2)	0.028(2)	0.041(2)	0.033(2)	0.003(2)	0.012(2)	0.002(2)
C(9)	4*e*	0.4438(3)	0.6178(3)	0.2488(2)	0.030(2)	0.049(2)	0.041(2)	–0.006(2)	0.011(2)	–0.006(2)
C(10)	4*e*	0.0078(3)	0.7746(3)	0.2332(2)	0.041(2)	0.043(2)	0.040(2)	0.001(2)	0.018(2)	0.000(2)
C(11)	4*e*	0.1859(3)	0.5328(3)	0.2427(2)	0.032(2)	0.039(2)	0.031(2)	–0.001(2)	0.012(2)	–0.001(2)
C(12)	4*e*	0.1186(3)	0.4464(3)	0.1159(2)	0.033(2)	0.046(2)	0.033(2)	–0.006(2)	0.009(2)	–0.009(2)
C(13)	4*e*	0.0591(3)	0.7267(3)	0.1047(2)	0.035(2)	0.051(2)	0.036(2)	–0.010(2)	0.009(2)	–0.007(2)
C(14)	4*e*	0.4566(3)	0.5912(3)	0.1734(2)	0.031(2)	0.044(2)	0.036(2)	–0.001(2)	0.012(2)	–0.003(2)
C(15)	4*e*	0.1854(3)	0.8033(3)	0.2178(2)	0.043(2)	0.045(2)	0.036(2)	–0.008(2)	0.013(2)	–0.007(2)
C(16)	4*e*	0.0168(3)	0.4861(3)	0.2999(2)	0.030(2)	0.052(2)	0.031(2)	–0.001(2)	0.011(2)	–0.002(2)
C(17)	4*e*	0.2975(3)	0.7620(3)	0.0372(2)	0.043(2)	0.049(2)	0.040(2)	–0.000(2)	0.015(2)	–0.004(2)
C(18)	4*e*	0.1296(3)	0.7225(3)	0.0592(2)	0.040(2)	0.052(2)	0.033(2)	–0.004(2)	0.011(2)	–0.009(2)
C(19)	4*e*	0.5559(3)	0.6243(3)	0.1582(2)	0.034(2)	0.044(2)	0.045(2)	–0.004(2)	0.015(2)	0.000(2)
C(20)	4*e*	–0.0697(3)	0.4342(3)	0.3237(2)	0.036(2)	0.050(2)	0.040(2)	0.002(2)	0.015(2)	0.004(2)
C(21)	4*e*	–0.0840(2)	0.4860(3)	0.1552(2)	0.029(2)	0.063(3)	0.035(2)	0.000(2)	0.011(2)	–0.003(2)
C(22)	4*e*	–0.1730(3)	0.4365(3)	0.1771(2)	0.034(2)	0.068(3)	0.045(2)	–0.007(2)	0.014(2)	–0.009(2)
C(23)	4*e*	0.3570(3)	0.6226(3)	0.3583(2)	0.046(2)	0.062(3)	0.037(2)	–0.009(2)	0.014(2)	–0.016(2)
C(24)	4*e*	0.3583(3)	0.5437(4)	0.4193(3)	0.063(3)	0.085(3)	0.037(2)	–0.012(3)	0.014(2)	–0.004(2)
C(25)	4*e*	–0.2773(4)	0.4573(4)	0.3673(3)	0.068(3)	0.089(4)	0.080(4)	–0.015(3)	0.050(3)	–0.008(3)
C(26)	4*e*	–0.2604(3)	0.4161(3)	0.2886(3)	0.046(2)	0.072(3)	0.066(3)	–0.016(2)	0.029(2)	–0.005(2)
C(27)	4*e*	0.4495(3)	0.6068(4)	0.4299(3)	0.059(3)	0.125(5)	0.038(3)	–0.022(3)	0.005(2)	–0.018(3)
F(1)	4*e*	0.0436(2)	0.3887(2)	0.0668(1)	0.041(1)	0.089(2)	0.056(1)	–0.029(1)	0.022(1)	–0.038(1)
N(1)	4*e*	0.3603(2)	0.5958(2)	0.2745(2)	0.032(2)	0.048(2)	0.031(2)	–0.007(1)	0.012(1)	–0.007(1)
N(2)	4*e*	0.0153(2)	0.4583(2)	0.2142(2)	0.027(2)	0.049(2)	0.032(2)	–0.001(1)	0.012(1)	–0.001(1)
N(3)	4*e*	–0.1710(2)	0.4621(2)	0.2653(2)	0.035(2)	0.045(2)	0.046(2)	–0.005(2)	0.020(2)	–0.003(2)
O(1)	4*e*	0.5768(2)	0.5971(2)	0.0926(2)	0.042(2)	0.065(2)	0.050(2)	–0.017(1)	0.027(1)	–0.012(1)
O(2)	4*e*	0.6129(2)	0.6790(2)	0.2122(2)	0.035(1)	0.070(2)	0.057(2)	–0.018(1)	0.015(1)	–0.019(2)
O(3)	4*e*	0.5669(2)	0.3831(2)	0.0864(2)	0.055(2)	0.058(2)	0.055(2)	0.005(2)	0.032(2)	0.006(2)
O(4)	4*e*	0.3792(2)	0.5040(2)	0.0457(2)	0.036(1)	0.060(2)	0.034(1)	–0.007(1)	0.016(1)	–0.008(1)
O(5)	4*e*	0.2789(2)	0.7201(2)	–0.0289(2)	0.057(2)	0.085(2)	0.053(2)	–0.017(2)	0.030(2)	–0.025(2)
O(6)	4*e*	0.3811(2)	0.8139(2)	0.0680(2)	0.057(2)	0.092(2)	0.052(2)	–0.031(2)	0.029(2)	–0.022(2)
O(7)	4*e*	–0.0817(2)	0.7446(2)	0.1983(2)	0.039(2)	0.078(2)	0.048(2)	–0.009(1)	0.015(1)	–0.007(1)
O(8)	4*e*	0.0370(2)	0.8083(2)	0.3058(2)	0.052(2)	0.105(3)	0.048(2)	–0.014(2)	0.026(2)	–0.029(2)
O(9)	4*e*	0.8160(2)	0.6588(2)	0.2918(2)	0.046(2)	0.056(2)	0.056(2)	0.002(2)	0.022(2)	0.007(1)
O(10)	4*e*	0.4628(3)	0.8617(3)	0.9525(2)	0.068(2)	0.081(2)	0.060(2)	–0.007(2)	0.030(2)	0.001(2)
O(11)	4*e*	0.7520(3)	0.6863(3)	0.0607(2)	0.057(2)	0.099(3)	0.051(2)	–0.017(2)	0.017(2)	–0.006(2)
O(12)	4*e*	0.6513(3)	0.8090(3)	0.9329(3)	0.073(3)	0.102(3)	0.074(2)	–0.009(2)	0.021(2)	0.013(3)
Zn(1)	2*b*	½	½	0	0.0356(4)	0.0559(4)	0.0397(4)	–0.0074(3)	0.0204(3)	–0.0069(3)

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References

1. Hooper D., Wolfson J.: The fluoroquinolones: Structures, mechanisms of action and resistance and spectra of activity in vitro. Antimicrob. Agents Chemother. **28** (1985) 581-586.
2. Mizuki, Y.; Fujiwara, I.; Yamaguchi, T.: Pharmacokinetic interactions related to the chemical structures of fluoroquinolones. J. Antimicrob. Chemother. **37** (Suppl A) (1996) 41-55.
3. An, Z.; Gao, J.; Harrison, William, T. A.: Two binuclear complexes containing the enrofloxacinate anion: $Cd_2(C_{19}H_{21}N_3O_3F)_4(H_2O)2{\cdot}4H_2O$ and $Pb_2(C_{19}H_{21}N_3O_3F)_4{\cdot}4H_2O$. J. Coord. Chem. **63** (2010) 3871-3879.
4. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.