Crystal structure of diaqua-bis[1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluor-4-oxo-1,4-dihydrochinolin-3-carboxylic acid]manganese(II)-benzene-1-carboxyl-4-carboxylate octahydrate, $C_{54}H_{74}F_2MnN_6O_{24}$

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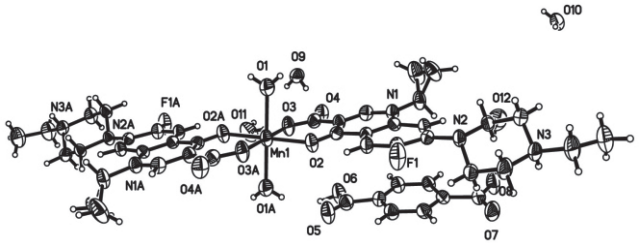
Received February 02, 2015, accepted July 03, 2015, available online July 13, 2015, CCDC no. 1267/4353



Abstract

$C_{54}H_{74}F_2MnN_6O_{24}$, monoclinic, $P2_1/n$ (no. 14), a = 13.5493(4) Å, b = 13.8063(4) Å, c = 16.7349(4) Å, β = 106.935(2)°, V = 2994.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.0629, $wR_{ref}(F^2)$ = 0.1500, T = 296 K.

Table 1. Data collection and handling.

Crystal:	pink prisms, size 0.23×0.24×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.13 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	22980, 5269
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3554
$N(param)_{refined}$:	400
Programs:	SHELX [6]

Source of material

A mixture of $Mn(CH_3COO)_2{\cdot}4H_2O$ (0.20 mmol), enrofloxacin (0.40 mmol), benzene-1,4-dicarboxylic acid (0.20 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 hydrothermal autoclave. The autoclave was heated to 443K for 48 h under autogenous pressure. After cooling, pink single crystals of title compound suitable for X-ray analysis were obtained from the reaction mixture.

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, widely used in veterinary clinical practice because of its wide antibiotic spectrum and its excellent bactericidal activity [1]. Our interest in enrofloxacin and related fluoroquinolones is focused on their potential as multidentate/bridging ligands in coordination chemistry. The cadmium, lead, copper, zinc and cobalt complexes of the enrofloxacin anion have been reported [2–5]. In the title compound, $[Mn(C_{19}H_{22}N_3FO_3)_2(H_2O)_2]{\cdot}2(C_8H_5O_4){\cdot}8(H_2O)$, the Mn^{II} atom (site symmetry $\bar{1}$) exhibits a distorted $[MnO_6]$ octahedral geometry defined by two 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. There is a benzene-1-carboxyl-4-carboxylate (1,4-*bdc*) anion fore the charge balancing. 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(8)	4*e*	0.2074	0.5585	0.0438	0.045
H(9A)	4*e*	0.0803	0.5332	0.3399	0.044
H(9B)	4*e*	0.0060	0.4462	0.3036	0.044
H(10)	4*e*	0.1771	0.4410	0.2956	0.041
H(11)	4*e*	0.4927	0.3445	0.2896	0.049
H(14)	4*e*	0.2031	0.1706	0.2699	0.049
H(16)	4*e*	0.3199	0.1743	0.1933	0.053
H(17)	4*e*	–0.0060	0.3032	0.0831	0.050
H(18)	4*e*	0.1106	0.3083	0.0069	0.053
H(20A)	4*e*	–0.0698	0.5498	0.3807	0.052
H(20B)	4*e*	–0.0626	0.6365	0.3218	0.052
H(22A)	4*e*	–0.0945	0.4462	0.1573	0.053
H(22B)	4*e*	–0.0860	0.5344	0.1004	0.053
H(23A)	4*e*	–0.1676	0.6353	0.1746	0.061
H(23B)	4*e*	–0.2392	0.5463	0.1393	0.061
H(24A)	4*e*	0.3610	0.5207	0.4038	0.079
H(24B)	4*e*	0.3134	0.4470	0.4597	0.079
H(25A)	4*e*	0.4590	0.3433	0.4784	0.099
H(25B)	4*e*	0.5065	0.4170	0.4225	0.099
H(26A)	4*e*	–0.3254	0.5764	0.2417	0.073
H(26B)	4*e*	–0.2506	0.6542	0.2953	0.073
H(27A)	4*e*	–0.2894	0.4751	0.3599	0.108
H(27B)	4*e*	–0.3411	0.5725	0.3745	0.108
H(27C)	4*e*	–0.2218	0.5580	0.4127	0.108
H(1A)	4*e*	0.3049	0.3218	0.3610	0.076
H(2A)	4*e*	–0.1783	0.4713	0.2680	0.076
H(1W)	4*e*	0.5978	0.6695	0.0725	0.076
H(2W)	4*e*	0.5388	0.6562	0.1171	0.076
H(3W)	4*e*	0.7531	0.3256	0.2726	0.076
H(4W)	4*e*	0.8387	0.3052	0.2616	0.076
H(5W)	4*e*	0.4238	0.1651	0.9095	0.076
H(6W)	4*e*	0.5158	0.1656	0.9546	0.076
H(7W)	4*e*	0.7045	0.327	0.0882	0.076
H(8W)	4*e*	0.7942	0.2936	0.1046	0.076
H(9W)	4*e*	0.1277	0.2618	0.3987	0.076
H(10W)	4*e*	0.1857	0.2711	0.4716	0.076
H(1M)	4*e*	0.409(4)	0.180(4)	0.022(3)	0.11(2)

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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*	0.2842(2)	0.4817(2)	0.1471(2)	0.025(2)	0.037(2)	0.031(2)	0.000(1)	0.008(2)	0.000(2)
C(2)	4*e*	0.1032(2)	0.5187(2)	0.1940(2)	0.029(2)	0.038(2)	0.033(2)	–0.002(2)	0.011(2)	–0.001(2)
C(3)	4*e*	0.3754(2)	0.4612(3)	0.1210(2)	0.028(2)	0.043(2)	0.037(2)	–0.001(2)	0.010(2)	–0.005(2)
C(4)	4*e*	0.4551(3)	0.4061(3)	0.1785(2)	0.029(2)	0.050(2)	0.036(2)	0.005(2)	0.012(2)	0.005(2)
C(5)	4*e*	0.2740(2)	0.4505(3)	0.2235(2)	0.029(2)	0.039(2)	0.029(2)	0.003(2)	0.008(2)	–0.002(2)
C(6)	4*e*	0.0847(3)	0.2333(3)	0.1833(2)	0.040(2)	0.038(2)	0.034(2)	0.000(2)	0.013(2)	–0.003(2)
C(7)	4*e*	0.2260(3)	0.2387(3)	0.0911(2)	0.037(2)	0.040(2)	0.041(2)	0.002(2)	0.015(2)	0.004(2)
C(8)	4*e*	0.2029(2)	0.5354(3)	0.0949(2)	0.031(2)	0.052(2)	0.033(2)	0.002(2)	0.013(2)	0.006(2)
C(9)	4*e*	0.0146(3)	0.5157(3)	0.3007(2)	0.032(2)	0.051(2)	0.030(2)	0.000(2)	0.012(2)	–0.001(2)
C(10)	4*e*	0.1833(2)	0.4661(3)	0.2457(2)	0.033(2)	0.042(2)	0.031(2)	0.004(2)	0.014(2)	0.004(2)
C(11)	4*e*	0.4406(3)	0.3803(3)	0.2530(2)	0.031(2)	0.046(2)	0.044(2)	0.007(2)	0.009(2)	0.007(2)
C(12)	4*e*	0.2958(3)	0.2369(3)	0.0369(3)	0.042(2)	0.055(3)	0.044(3)	0.003(2)	0.013(2)	0.004(2)
C(13)	4*e*	0.1182(3)	0.5533(3)	0.1194(2)	0.031(2)	0.050(2)	0.039(2)	0.008(2)	0.012(2)	0.012(2)
C(14)	4*e*	0.1837(3)	0.1969(3)	0.2164(2)	0.043(2)	0.048(2)	0.033(2)	0.004(2)	0.013(2)	0.004(2)
C(15)	4*e*	0.0072(3)	0.2279(3)	0.2320(2)	0.040(2)	0.049(2)	0.041(2)	–0.001(2)	0.017(2)	–0.003(2)
C(16)	4*e*	0.2538(3)	0.1993(3)	0.1706(2)	0.041(2)	0.050(2)	0.042(2)	0.010(2)	0.015(2)	0.007(2)
C(17)	4*e*	0.0592(3)	0.2761(3)	0.1051(2)	0.035(2)	0.052(2)	0.035(2)	0.006(2)	0.006(2)	0.001(2)
C(18)	4*e*	0.1288(3)	0.2791(3)	0.0593(2)	0.042(2)	0.056(3)	0.032(2)	0.005(2)	0.009(2)	0.009(2)
C(19)	4*e*	0.5548(3)	0.3740(3)	0.1640(2)	0.033(2)	0.048(2)	0.045(2)	0.001(2)	0.013(2)	0.000(2)
C(20)	4*e*	–0.0719(3)	0.5669(3)	0.3240(2)	0.039(2)	0.049(2)	0.046(2)	–0.004(2)	0.020(2)	–0.004(2)
C(21)	4*e*	0.3528(3)	0.3758(3)	0.3612(2)	0.047(2)	0.072(3)	0.037(2)	0.009(2)	0.017(2)	0.020(2)
C(22)	4*e*	–0.0857(3)	0.5158(3)	0.1564(2)	0.032(2)	0.067(3)	0.033(2)	–0.003(2)	0.010(2)	0.000(2)
C(23)	4*e*	–0.1743(3)	0.5656(3)	0.1786(2)	0.031(2)	0.073(3)	0.051(3)	0.010(2)	0.016(2)	0.009(2)
C(24)	4*e*	0.3551(3)	0.4547(4)	0.4218(3)	0.072(3)	0.092(4)	0.034(3)	0.020(3)	0.016(2)	0.004(2)
C(25)	4*e*	0.4455(4)	0.3903(4)	0.4334(3)	0.066(3)	0.137(5)	0.042(3)	0.031(3)	0.013(2)	0.020(3)
C(26)	4*e*	–0.2632(3)	0.5852(3)	0.2877(3)	0.049(2)	0.074(3)	0.070(3)	0.020(2)	0.033(2)	0.006(3)
C(27)	4*e*	–0.2804(4)	0.5440(4)	0.3657(3)	0.067(3)	0.092(4)	0.073(3)	0.018(3)	0.044(3)	0.007(3)
F(1)	4*e*	0.0432(2)	0.6112(2)	0.0696(1)	0.043(1)	0.090(2)	0.062(2)	0.028(1)	0.023(1)	0.038(1)
Mn(1)	2*b*	½	½	0	0.0352(4)	0.0557(6)	0.0399(5)	0.0063(4)	0.0189(4)	0.0052(4)
N(1)	4*e*	0.3575(2)	0.4020(2)	0.2784(2)	0.033(2)	0.051(2)	0.034(2)	0.006(1)	0.011(1)	0.008(2)
N(2)	4*e*	0.0136(2)	0.5432(2)	0.2162(2)	0.030(2)	0.054(2)	0.033(2)	0.004(1)	0.014(1)	0.004(2)
N(3)	4*e*	–0.1742(2)	0.5392(2)	0.2655(2)	0.031(2)	0.049(2)	0.047(2)	0.004(1)	0.019(1)	0.001(2)
O(1)	4*e*	0.5647(2)	0.6231(2)	0.0856(2)	0.058(2)	0.061(2)	0.059(2)	–0.008(1)	0.031(2)	–0.009(2)
O(2)	4*e*	0.3778(2)	0.4914(2)	0.0507(2)	0.039(1)	0.068(2)	0.038(2)	0.011(1)	0.019(1)	0.012(1)
O(3)	4*e*	0.5774(2)	0.4036(2)	0.1006(2)	0.041(1)	0.067(2)	0.050(2)	0.019(1)	0.026(1)	0.016(1)
O(4)	4*e*	0.6112(2)	0.3193(2)	0.2184(2)	0.036(1)	0.071(2)	0.059(2)	0.014(1)	0.016(1)	0.020(2)
O(5)	4*e*	0.2770(2)	0.2780(2)	–0.0295(2)	0.060(2)	0.091(2)	0.053(2)	0.017(2)	0.029(2)	0.028(2)
O(6)	4*e*	0.3792(2)	0.1849(3)	0.0672(2)	0.061(2)	0.098(3)	0.053(2)	0.032(2)	0.030(2)	0.023(2)
O(7)	4*e*	–0.0814(2)	0.2604(2)	0.1980(2)	0.037(2)	0.082(2)	0.055(2)	0.010(2)	0.018(1)	0.008(2)
O(8)	4*e*	0.0362(2)	0.1938(3)	0.3039(2)	0.055(2)	0.111(3)	0.047(2)	0.015(2)	0.027(2)	0.026(2)
O(9)	4*e*	0.8156(2)	0.3428(2)	0.2918(2)	0.047(2)	0.057(2)	0.062(2)	–0.004(1)	0.020(1)	–0.007(2)
O(10)	4*e*	0.4608(2)	0.1357(2)	0.9528(2)	0.069(2)	0.084(2)	0.060(2)	0.007(2)	0.029(2)	–0.003(2)
O(11)	4*e*	0.7484(2)	0.3148(3)	0.0618(2)	0.056(2)	0.122(3)	0.053(2)	0.026(2)	0.013(2)	0.000(2)
O(12)	4*e*	0.1475(2)	0.3078(3)	0.4342(2)	0.073(2)	0.106(3)	0.078(2)	–0.008(2)	0.019(2)	0.014(2)

Acknowledgments. The authors acknowledge financial support of the National Natural Science Foundation of China (grant No. 31470405) and Guangdong University of Petrochemical Technology.

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