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Crystal structure of *catena-poly*-[(1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-ium-1-yl)-1,4-dihydroquinoline-3-carboxylate- $\kappa^2 O, O'$)-(μ_2 -4,4'-sulfonyldibenzoato- $\kappa^4 O, O': O'', O'''$)zinc(II)] hemihydrate, $C_{31}H_{27}ZnFN_3O_{9.5}S$

CCDC no.: 1500897

Table 1: Data collection and handling.

Crystal:	Colourless blocks
Wavelength:	Size $0.18 \times 0.17 \times 0.17$ mm
μ :	Mo $K\alpha$ radiation ($0.71073 \text{ \AA}$)
Diffractometer, scan mode:	9.8 cm^{-1}
$2\theta_{\max}$, completeness:	Brucker FRAMBO, φ and ω
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	56.8° , $>99\%$
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	10610 , 5155 , 0.022
$N(\text{param})_{\text{refined}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4443
Programs:	424
	SHELX [5], Bruker programs [6], OLEX2 [7]

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.20 mmol), ciprofloxacin (0.40 mmol), 4,4'-sulfonyldibenzoic acid (0.20 mmol), sodium hydroxide (1.0 mmol), and water (15 mL) was stirred for 15 min in air. The mixture was then transferred to a 25 mL Teflon-lined hydrothermal autoclave. The autoclave was heated to 448 K for 96 h under autogenous pressure. After cooling, colorless single crystals of title compound suitable for X-ray analysis were obtained from the reaction mixture.

Experimental details

The H on nitrogen atoms were located in difference Fourier maps and refined in the riding model approximation, with N–H and distances restrained ($(0.86(1)$ or $0.85(1) \text{ \AA}$) and

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Abstract

$C_{31}H_{27}ZnFN_3O_{9.5}S$, triclinic, $P\bar{1}$ (no. 2), $a = 10.6434(4) \text{ \AA}$, $b = 12.6191(4) \text{ \AA}$, $c = 12.8532(5) \text{ \AA}$, $\alpha = 93.998(3)^\circ$, $\beta = 109.121(3)^\circ$, $\gamma = 112.773(3)^\circ$, $V = 1465.16(9) \text{ \AA}^3$, $Z = 2$, $R_{\text{gt}}(F) = 0.0354$, $wR_{\text{ref}}(F^2) = 0.1012$, $T = 293 \text{ K}$.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Zn1	0.58187(3)	0.69208(3)	0.27263(3)	0.02572(11)
C1	1.0199(3)	0.6662(2)	0.3479(2)	0.0239(6)
H1	1.1073	0.7343	0.3854	0.029*
C2	0.8918(3)	0.6787(2)	0.3076(2)	0.0220(5)
C3	0.7561(3)	0.5751(2)	0.2474(2)	0.0215(5)
C4	0.7699(3)	0.4673(2)	0.2246(2)	0.0218(5)
C5	0.6458(3)	0.3641(2)	0.1559(2)	0.0270(6)
H5	0.5562	0.3666	0.1189	0.032*
C6	0.6560(3)	0.2607(2)	0.1432(2)	0.0275(6)
C7	0.7868(3)	0.2482(2)	0.1987(2)	0.0253(6)
C8	0.9113(3)	0.3516(2)	0.2593(2)	0.0237(6)
H8	1.0017	0.3491	0.2921	0.028*
C9	0.9045(3)	0.4604(2)	0.2726(2)	0.0216(5)
C10	0.9052(3)	0.8014(2)	0.3324(2)	0.0244(6)
C11	1.1723(3)	0.5618(2)	0.3936(2)	0.0287(6)
H11	1.2280	0.5608	0.3464	0.034*
C12	1.2604(3)	0.6289(3)	0.5130(3)	0.0438(8)
H12A	1.3669	0.6688	0.5370	0.053*
H12B	1.2184	0.6695	0.5481	0.053*
C13	1.1895(3)	0.4981(3)	0.4868(3)	0.0371(7)
H13A	1.1044	0.4589	0.5059	0.044*
H13B	1.2529	0.4583	0.4948	0.044*
C14	0.9250(3)	0.1296(3)	0.2468(3)	0.0323(7)
H14A	1.0068	0.1953	0.2411	0.039*
H14B	0.9203	0.0573	0.2105	0.039*
C15	0.9535(3)	0.1302(2)	0.3699(3)	0.0335(7)
H15A	1.0411	0.1178	0.4043	0.040*
H15B	0.9715	0.2065	0.4088	0.040*
C16	0.6831(3)	0.0385(3)	0.3168(3)	0.0378(7)
H16A	0.6804	0.1091	0.3489	0.045*
H16B	0.6022	−0.0295	0.3206	0.045*
C17	0.6657(3)	0.0362(3)	0.1950(3)	0.0396(8)
H17A	0.6645	−0.0360	0.1623	0.048*
H17B	0.5724	0.0372	0.1523	0.048*
C18	0.6235(3)	0.7554(3)	0.4892(3)	0.0344(7)
C19	0.6630(3)	0.7586(2)	0.6134(2)	0.0261(6)
C20	0.7280(3)	0.8669(3)	0.6884(3)	0.0365(7)
H20	0.7422	0.9353	0.6612	0.044*
C21	0.7716(3)	0.8734(3)	0.8031(3)	0.0371(7)
H21	0.8174	0.9461	0.8537	0.044*
C22	0.7466(3)	0.7714(2)	0.8419(2)	0.0242(6)
C23	0.6805(3)	0.6623(2)	0.7689(2)	0.0288(6)
H23	0.6637	0.5939	0.7963	0.035*
C24	0.6396(3)	0.6567(3)	0.6540(2)	0.0296(6)
H24	0.5962	0.5841	0.6037	0.036*
C25	0.9572(3)	0.7461(2)	1.0251(2)	0.0244(6)
C26	1.0911(3)	0.8276(2)	1.0286(2)	0.0287(6)
H26	1.0983	0.8963	1.0034	0.034*
C27	1.2144(3)	0.8064(2)	1.0699(2)	0.0292(6)
H27	1.3052	0.8609	1.0731	0.035*
C28	1.2018(3)	0.7031(2)	1.1065(2)	0.0258(6)
C29	1.0654(3)	0.6191(2)	1.0963(2)	0.0289(6)
H29	1.0568	0.5483	1.1171	0.035*
C30	0.9415(3)	0.6399(2)	1.0551(2)	0.0285(6)
H30	0.8495	0.5836	1.0478	0.034*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C31	1.3369(3)	0.6835(3)	1.1618(2)	0.0294(6)
O1	0.62815(19)	0.56972(16)	0.21410(16)	0.0274(4)
O1W ^a	0.3642(6)	0.8897(5)	0.4404(6)	0.0766(19)
H1WA ^a	0.4227	0.9590	0.4417	0.115*
H1WB ^a	0.3893	0.8402	0.4153	0.115*
O2	0.7869(2)	0.81559(16)	0.30430(17)	0.0313(5)
O3	1.0290(2)	0.88487(16)	0.38041(18)	0.0347(5)
O4	0.5990(2)	0.6627(2)	0.42671(18)	0.0436(5)
O5	0.6196(3)	0.8443(2)	0.4545(2)	0.0557(7)
O6	0.8585(2)	0.90190(19)	1.04393(17)	0.0403(5)
O7	0.6910(2)	0.6908(2)	1.01129(17)	0.0402(5)
O8	1.4614(2)	0.76548(19)	1.17832(19)	0.0397(5)
O9	1.3246(2)	0.5913(2)	1.1941(2)	0.0460(6)
N1	1.0294(2)	0.56339(18)	0.33774(19)	0.0226(5)
N2	0.8264(3)	0.0369(2)	0.3828(2)	0.0331(6)
H2A	0.8403	0.0463	0.4564	0.040*
H2B	0.8221	−0.0339	0.3598	0.040*
N3	0.7874(3)	0.13834(19)	0.1872(2)	0.0282(5)
F1	0.53431(19)	0.16519(14)	0.07082(16)	0.0451(5)
S2	0.80440(7)	0.78075(6)	0.98937(6)	0.02726(17)

^aOccupancy: 0.50.

U(H) = 1.5*U*_{eq} (N, O). All other hydrogen atoms were added using geometrical constraints of the SHELX program system [5]. During the refinement, the occupancies of the O1W have been fixed at 0.5.

Discussion

Ciprofloxacin (Hcf), C₁₇H₁₈FN₃O₃ (systematic name 1-cyclopropyl-6-fluoro-4-oxo-7-(1-piperazinyl)-1,4-dihydroquinoline-3-carboxylic acid), is a member of the fluoroquinolone (flu) family of antibiotics, widely used in veterinary clinical practice because of its wide antibiotic spectrum and its excellent bactericidal activity [1]. Our interest in ciprofloxacin and related fluoroquinolones is focused on their potential as multidentate/bridging ligands in coordination chemistry. The cadmium, manganese, copper, nickel and cobalt complexes of ciprofloxacin anion have been reported [2–4].

In the title compound, the Zn^{II} atom (site symmetry 1) exhibits 4+1 coordination with four Zn–O bond lengths in the range 1.97–2.01 Å and one Zn–O distance of 2.33 Å to give a distorted ZnO₅ square-pyramidal geometry. Two O atoms come from a bidentate O,O' coordinated ciprofloxacin (Hcf) zwitterion. Three coordination oxygen atoms belong to two adjacent 4,4'-sulfonyldibenzoato ligands. In the title zinc(II) complex a one-dimensional coordination polymer is present as the 4,4'-sulfonyldibenzoato ligand acts in a bridging mode. All geometrical and structural parameters are in the expected ranges. N–H···O hydrogen bonds connect the coordinations polymers to form a layered structure parallel to the *bc* plane.

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