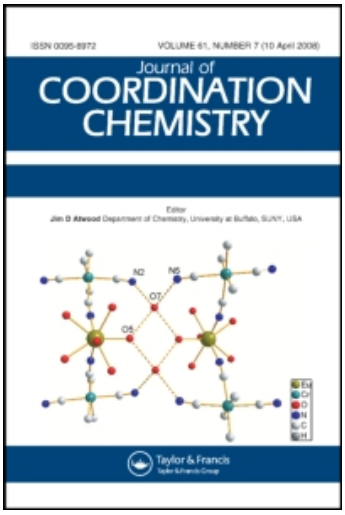

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Syntheses and crystal structure studies of two compounds of quinolones

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Syntheses and crystal structure studies of two compounds of quinolones

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Two complexes with enoxacin and ciprofloxacin were synthesized and the crystal structures are reported. Compound **1**, $[Cu(H\text{-}Eno)\cdot Cl_2]\cdot 3H_2O$ (H-Eno = Enoxacin), crystallizes in the triclinic system, space group $P\bar{1}$, with lattice parameters $a = 8.7731(12)$ Å, $b = 9.4976(14)$ Å, $c = 13.2033(19)$ Å, $\alpha = 86.319(7)^\circ$, $\beta = 71.912(7)^\circ$, $\gamma = 80.604(7)^\circ$, $V = 1031.6(3)$ Å^3, $Z = 2$, $D_c = 1.625$ mgm^{-3}. **2**, $[Mn(Cip)_2]\cdot 2H_2O$ (Cip = mono-anion of ciprofloxacin), crystallizes in the monoclinic, space group $P2(1)/c$, with lattice parameters $a = 5.85690(10)$, $b = 21.9490(6)$, $c = 13.4443(3)$ Å, $\beta = 100.9700(10)^\circ$, $V = 1696.72(7)$ Å^3, $Z = 2$, $D_c = 1.459$ mgm^{-3}.

Keywords: Crystal structure; enoxacin; zwitterion; ciprofloxacin

1. Introduction

Fluoroquinolones, an important class of antibacterial compounds, have a fluorine atom at position 6 and piperazine at position 7 of a quinoline-3-carboxylic acid. Ciprofloxacin (H-Cip) and enoxacin (H-Ex), synthetic antibacterial agents belonging to this family, have a broad spectrum of activity against Gram-negative bacteria but are less active against Gram-positive microorganisms [1]. Many drugs possess modified pharmacological and toxicological properties when administered in the form of metal complexes. In recent years, metal complexes with quinolones have been extensively reported [2–14]; some transition metal ions are effective in induction of the cyotoxicity of quinolones against leukemia *in vitro*. In our previous papers, we described the syntheses and crystal structures of four metal complexes of the fluoroquinolone class [15–17]. In order to continue our work, we report here the syntheses and crystal structures of $[Cu(H\text{-}Eno)\cdot Cl_2]\cdot 3H_2O$ (**1**) and $[Mn(Cip)_2]\cdot 2H_2O$ (**2**).

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2. Experimental

2.1. *Materials and physical measurements*

Ciprofloxacin and enoxacin were purchased from Fluka; all other chemicals were of reagent grade and used as purchased. C, H, and N data were obtained using American PE 2400 II CHNS/O elemental analyzer. Infrared spectra were measured from KBr pellets using a Nicolet 5DXB system. Single-crystal structure data were collected on Smart apex CCD with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 296(2) K.

2.2. *Preparation of (1) and (2)*

2.2.1. [Cu(H-Eno)·Cl$_2$]·3H$_2$O (1). An aqueous mixture (10 mL) containing enoxacin (1 mmol) and $CuCl_2 \cdot 2H_2O$ (1 mmol) was placed in a teflon-lined stainless steel vessel (25 mL). Ethanol (10 mL) was added to the mixture and the pH of the solution was adjusted to 7.0. The vessel was sealed and heated to 110°C for 4 days, cooled to room temperature, and yellow block-shaped crystals of **1** were obtained. Anal. Calcd for $C_{15}H_{19}Cl_2CuFN_4O_6$: C, 32.78; H, 4.00; N, 10.20. Found: C, 32.92; H, 4.03; N, 9.89. IR data: (KBr pellet, cm^{-1}), 3416(s), 1633(s), 1556(s), 1477(s), 1455(s), 1391(m), 1347(w), 1369(m), 1276(s), 1189(w), 970(w), 950(w), 932(w), 907(w), 853(w), 817(w), 765(w), 635(m).

2.2.2. [Mn(Cip)$_2$]·2H$_2$O (2). The procedure is similar to that for **1**, except that ciprofloxacin and $Mn(OH)_2$ were used. Anal. Calcd for $C_{34}H_{32}F_2MnN_6O_8$: C, 54.72; H, 4.30; N, 11.26. Found: C, 54.70; H, 4.32; N, 11.24. IR data: (KBr pellet, cm^{-1}), 3419(s), 2972(w), 2850(w), 2536(w), 1628(s), 1576(s), 1554(s), 1524(s), 1489(s), 1385(m), 1354(m), 1338(m), 1306(s), 1272(s), 1226(m), 1184(w), 1114(m), 1031(w), 949(m), 897(m), 866(m), 842(m), 816(m), 787(w), 715(w), 627(s), 585(w), 557(w), 544(w), 513(w).

2.3. *Crystal structure determination*

X-ray single crystal data collections for **1** and **2** were performed on a Bruker Smart CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Multi-scan absorption correction was applied using SADABS [18]. The structures were solved by direct methods using the SHELXS-97 program [19]. Refinements on F^2 were performed using SHELXL-97 [20] by full-matrix least-squares with anisotropic parameters for all non-hydrogen atoms. The hydrogens of ciprofloxacin and enoxacin were generated geometrically. H atoms of lattice water molecules of **1** and **2** were not located. The crystal data are given in table 1.

3. Results and discussion

3.1. *Spectroscopic properties*

The IR spectra show two very strong peaks at 1633 and 1477 cm^{-1} for **1**, indicating that carboxylic acids of quinolone are deprotonated and coordinated to copper due

Table 1. Summary of crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{15}H_{19}Cl_2CuFN_4O_6$	$C_{34}H_{32}F_2MnN_6O_8$
Formula weight	504.78	745.60
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
Crystal size (mm^3)	$0.50 \times 0.28 \times 0.26$	$0.20 \times 0.15 \times 0.12$
Units of Dimensions (Å, °)		
a	8.7731(12)	5.85690(10)
b	9.4976(14)	21.9490(6)
c	13.2033(19)	13.4443(3)
α	86.319(7)	90
β	71.912(7)	100.9700(10)
γ	80.604(7)	90
V (Å^3)	1031.6(3)	1696.72(7)
Z	2	2
D_{Calcd} ($mg\,m^{-3}$)	1.625	1.459
$F(000)$	514	770
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Completeness	99.4	97.7
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0382$, $wR_2 = 0.1031$	$R_1 = 0.0503$, $wR_2 = 0.1637$
R indices (all data)	$R_1 = 0.0434$, $wR_2 = 0.1068$	$R_1 = 0.0729$, $wR_2 = 0.1835$
Goodness-of-fit on F^2	1.056	1.076

to the absence of a strong ν(COOH) band about 1725 cm^{-1} for enoxacin. The ketonic group participates in the bonding to the metal ion and its stretching band shifts to lower wavenumber at 1556 cm^{-1}. The IR spectrum shows two very strong peaks at 1628 and 1489 cm^{-1} for **2**, indicating that the carboxylic acids of quinolones are deprotonated and coordinated to the metal ions due to the absence of ν(COOH) above 1704 cm^{-1} for ciprofloxacin.

3.2. *Crystal structures*

Figure 1 shows an ORTEP drawing of **1** with the atomic numbering scheme. Selected bond distances and angles are given in table 2. In **1**, the crystal is composed of [Cu(H-Eno) · Cl_2] and uncoordinated water. Enoxacin (H-Eno) shows a zwitterion configuration. The carboxylic acid of quinolones are deprotonated and coordinated to the metal ions, while the terminal N(1) of the piperazyl ring of enoxacin is protonated and loses coordination ability. Cu^{2+} is coordinated by two oxygens and two chlorides, forming a rather distorted tetrahedron. Two oxygens (O_{keto} and $O_{carboxylic}$) from one enoxacin ligand coordinate to Cu(1), forming a six-membered ring (Cu1/O1/C3/C2/C1/O2), with bond distances Cu(1)–O(1) = 1.9563(18) Å, Cu(1)–O(2) = 1.942(2) Å; the Cu–O_{keto} bond length is longer than the Cu–$O_{carboxylic}$. The difference between the carboxylate distances of O(2)–C(1) and O(3)–C(1) [1.274(3) and 1.220(4) Å] confirms the formation of a bond between the anionic carboxylate oxygen and Cu^{2+}; these bond distances are virtually identical in the uncoordinated quinolone. The Cu–Cl bond distances range from 2.2246(8) Å to 2.2304(9) Å. The C1–Cu–C1 and O–Cu–C1 bond angles are 93.84(8)° and 114.51(6)° (table 2). The lattice water, the terminal N of the piperazyl ring of enoxacin,

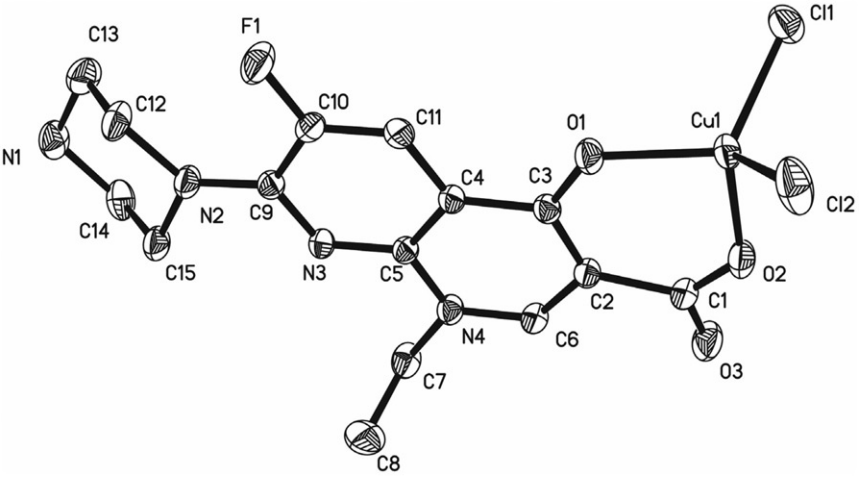

Figure 1. Crystallographically independent structure fragment in **1**. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 30% probability level.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Cu(1)–O(2)	1.942(2)	Cu(1)–O(1)	1.9563(18)
Cu(1)–Cl(1)	2.2246(8)	Cu(1)–Cl(2)	2.2304(9)
O(1)–C(3)	1.282(3)	O(2)–C(1)	1.274(3)
O(3)–C(1)	1.220(4)		
O(2)–Cu(1)–O(1)	93.84(8)	O(2)–Cu(1)–Cl(1)	113.74(8)
O(1)–Cu(1)–Cl(1)	112.87(6)	O(2)–Cu(1)–Cl(2)	107.63(8)
O(1)–Cu(1)–Cl(2)	114.51(6)	Cl(1)–Cu(1)–Cl(2)	112.78(3)
2			
Mn(1)–O(2)	2.139(2)	Mn(1)–O(1)	2.1578(18)
Mn(1)–N(1) #1	2.347(2)	O(2)–C(1)	1.260(3)
O(3)–C(1)	1.246(4)		
O(2)–Mn(1)–O(1)	83.39(7)	O(2) #1–Mn(1)–O(1)	96.61(7)
O(2)–Mn(1)–N(1)#2	91.41(8)	O(2)#1–Mn(1)–N(1)#2	88.59(8)
O(1)–Mn(1)–N(1)#2	86.96(8)	O(1)#1–Mn(1)–N(1)#2	93.04(8)
O(2)–Mn(1)–N(1)#3	88.59(8)	O(2)#1–Mn(1)–N(1)#3	91.41(8)
O(1)–Mn(1)–N(1)#3	93.04(8)	O(1)#1–Mn(1)–N(1)#3	86.96(8)

Note: Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y+1, -z+2$; #2: $-x, y-1/2, -z+3/2$; #3: $x+1, -y+3/2, z+1/2$ for **2**.

uncoordinated carboxylate O atoms, and coordinated Cl^- anions participate in intermolecular hydrogen bonds, such as O(5)–H(5B)···O(3) (2.666(4) Å), O(5)–H(5A)···Cl(1)#1 (3.175(3) Å) (symmetry code: $x, y-1, z$), N(1)–H(1B)···Cl(2)#2 (3.330(3) Å) (symmetry code: $-x+2, -y+2, -z+1$), N(1)–H(1A)···O(5)#3 (2.776(4) Å) (symmetry code: $x, y, z+1$). These intermolecular hydrogen bonds and weak aromatic π–π stacking interactions (3.481 Å) link the complex to form 3D networks (figure 2).

The X-ray crystal analysis of **2** reveal that Mn(II) is in a distorted octahedral geometry with an equatorial plane composed of four oxygens [O(1), O(2), O(1C), and O(2C)], as shown in figure 3. Two oxygens are from the quinolone ring and the

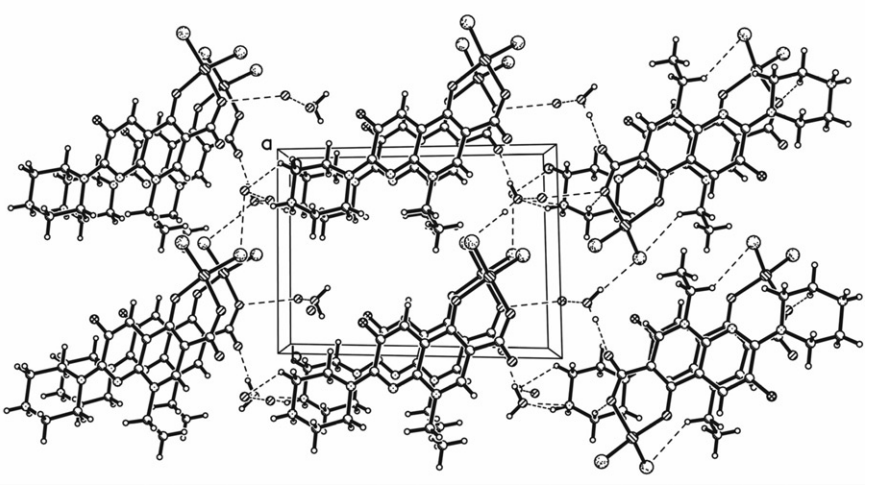

Figure 2. Crystal packing perspective view of **1** showing supramolecular weak aromatic π–π stacking interactions and hydrogen bonds.

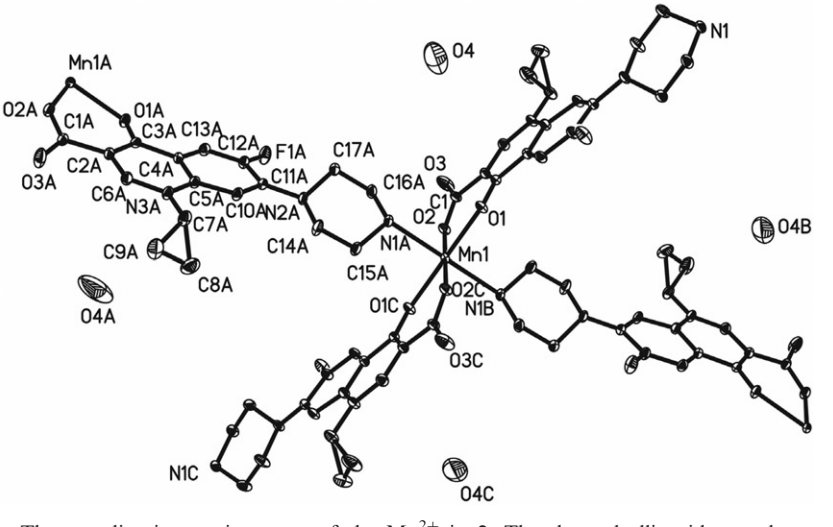

Figure 3. The coordination environment of the Mn^{2+} in **2**. The thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms were deleted for clarity.

others from the carboxylate, forming two stable six-membered chelating rings. The Mn–O bond distances are in the range 2.139(2)–2.1578(18) Å and O–Mn–O bond angles are in the range of 83.39(7)–96.61(7)°, as shown in table 2. The carboxylate of ciprofloxacin in **2** acts as a monodentate ligand with one oxygen of the carboxylate uncoordinated. The apical positions are occupied by two N atoms [N(1A) and N(1B)] of the piperazyl rings, resulting in formation of a 2-D neutral square grid with a cavity dimension of 16.063–16.063 $Å^2$ (the distances of Mn1–Mn1A and Mn1–Mn1D equal to 16.063 Å) (figure 4).

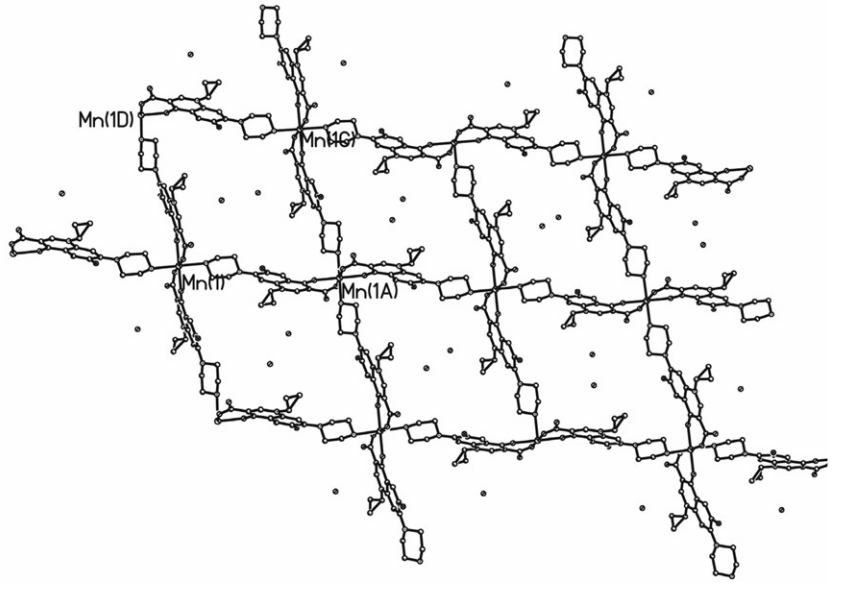

Figure 4. An extended 2-D network perspective view of **2**.

Supplementary material

Crystallographic data for **1** and **2** are deposited with the Cambridge Crystallographic Data Center with deposition numbers CCDC 702856 and 703317, respectively.

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