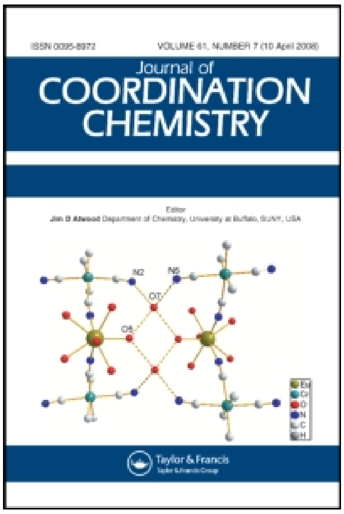

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Syntheses and crystal structures of Zn(II) and Co(II) complexes with ofloxacin and enoxacin

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Syntheses and crystal structures of Zn(II) and Co(II) complexes with ofloxacin and enoxacin

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$[Zn(Ofl)\cdot(H_2O)]\cdot 2H_2O$ (**1**) and $[Co(Enox)_2]\cdot 4H_2O$ (**2**) were obtained by hydrothermal reactions. The solid-state structures have been characterized by IR spectroscopy and single crystal X-ray diffraction analyses. Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$, with lattice parameters $a = 9.2923(5)$, $b = 11.3432(6)$, $c = 17.7722(10)$ Å, $\alpha = 92.839(3)$, $\beta = 94.826(3)$, $\gamma = 91.909(3)^\circ$, $V = 1863.01(18)$ Å^3, $Z = 2$, $D_{\mathrm{Calcd}} = 1.494\ \mathrm{mg\,m^{-3}}$. The coordination environment around Zn^{2+} is a slightly distorted square pyramid. Complex **2** crystallizes in the triclinic system, space group $P2(1)/c$, with lattice parameters $a = 5.97980(10)$, $b = 21.4183(3)$, $c = 13.1539(2)$ Å, $V = 100.2810(10)$, $Z = 2$, $D_{\mathrm{Calcd}} = 1.526\ \mathrm{mg\,m^{-3}}$, Co(II) ion is a distorted octahedral geometry.

Keywords: Crystal structure; Hydrothermal syntheses; Zn; Co

1. Introduction

Many drugs possess modified pharmacological and toxicological properties when administered in the form of transition metal complexes. Metal complexes with quinolones have been extensively reported [1–8] and some transition metal ions are effective in induction of cyotoxicity of quinolones against *leukemia in vitro*. In a previous paper, we described the syntheses and crystal structures of five metal complexes with the quinolone ligands [9–13]. Among them, the bio-activity of $[Mn(H\text{-}Cip)_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$ [9] was similar to that of ciprofloxacin, exhibiting almost the same antibacterial abilities as ciprofloxacin against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* and stronger activity than ciprofloxacin against *Pseudomonas aeruginosa* at lower concentration. $[Ni(H\text{-}Cip)_2(H_2O)_2](NO_3)_2\cdot 2H_2O$ [9] was significantly less active than ciprofloxacin and even inactive against *S. aureus* and *P. aeruginosa*. The two-dimensional complexes $[Mn(Enox)_2]\cdot 4H_2O$ [10], $[Sm(Cip)(Ox)1.5]\cdot H_2O$ [11], $\{[Ag_4(H\text{-}Cip)_2(Cip)_2(NO_3)_2]\cdot 4H_2O\}_n$ [12], and $[M(Enox)_2]\cdot C_2H_5OH$ (M = Zn and Co) [13] lose bio-activity being insoluble in many solvents. Only a few crystal structures of ofloxacin-related compounds have been reported [14–19] with the antimicrobial activity

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of the complexes [17] against various microorganisms established as similar to that of free quinolone drugs. Here, we report the syntheses and crystal structures of Zn(II) and Co(II) complexes with quinolone family members, ofloxacin and enoxacin.

2. Experimental

2.1. *Materials and physical measurements*

$Zn(ClO_4)_2 \cdot 6H_2O$ was prepared by reaction of ZnO with $HClO_4$, and all other chemicals were of reagent grade and used as purchased. Infrared spectra were measured from KBr pellets using a Nicolet 5DXB system. Single-crystal structural data were collected on a Smart Apex CCD with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 296(2) K.

2.2. *Preparation of complexes*

2.2.1. $[Zn(Ofl)_2 \cdot H_2O] \cdot 2H_2O$ (1). A mixture containing ofloxacin (1 mmol) and $Zn(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol) was placed in a Teflon-lined stainless steel vessel (25 mL). CH_3CH_2OH (10 mL) and 10 mL distilled water were added to the mixture. The vessel was sealed and heated to 110°C for 4 days, giving blue, block-shaped crystals of **1**. Anal. calcd for $C_{36}H_{42}F_2N_6O_{11}Zn$: C, 51.54; H, 5.01; N, 10.02. Found: C, 51.58; H, 5.04; N, 10.05. IR data: (KBr pellet, cm^{-1}), 3398(s), 3077(w), 3005(w), 2845(w), 2427(w), 1615(s), 1578(s), 1460(s), 1384(s), 1289(s), 1214(m), 1181(w), 1097(w), 1065(s), 958(m), 818(m), 779(w), 654(m), 548(m), 519(m).

2.2.2. $[Co(Enox)_2] \cdot 4H_2O$ (2). A mixture (15 mL) containing enoxacin (1 mmol) and $Co(OH)_2$ (0.5 mmol) was placed in a Teflon-lined stainless steel vessel (25 mL). Ethanol (5.0 mL) was added to the mixture. The vessel was sealed and heated to 110°C for 5 days. Upon cooling to room temperature, yellow block-shaped crystals of **2** were obtained. Anal. calcd for $C_{30}H_{32}F_2N_8O_{10}Co$: C, 47.27; H, 4.20; N, 14.71. Found: C, 47.31; H, 4.30; N, 14.62. IR data: (KBr pellet, cm^{-1}), 3588(s), 3425(s), 3128(m), 2845(m), 2474(w), 1642(s), 1556(s), 1476(s), 1447(s), 1370(m), 1349(m), 1325(m), 1261(m), 1220(w), 1114(w), 1093(w), 1034(m), 972(w), 943(w), 906(w), 813(m), 765(w), 680(w), 650(w), 558(w), 516(w), 471(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 a graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Multi-scan absorption correction was applied using the SADABS program [20]. The structures were solved by direct methods using SHELXS-97 [21]. Refinements on F^2 were performed using SHELXL-97 [22] by full-matrix least squares with anisotropic parameters for all non-hydrogen atoms; C29 and C30 of **1** are disordered and were refined with restraints. The H atoms of ofloxacin and enoxacin were generated geometrically, while the H atoms of coordinated water were located from the Fourier difference map and refined subject to an O–H = 0.85(1) Å. The H atoms of lattice water molecules in **1** and **2** were not located for high values of temperature factors. The crystal data are given in table 1.

3. Results and discussion

3.1. *Infrared spectra*

The IR spectra show very strong peaks at 1615 and 1460 cm^{-1} for **1**, indicating that the carboxylic acid of the quinolone is deprotonated and coordinated to the metal due to the absence of a strong ν(COOH) band 1716 cm^{-1} for ofloxacin. If the ketonic group participates in bonding to the metal, we expect a shift of its stretching band to lower wavenumber, thus corresponding to the band at 1578 cm^{-1}. The IR spectra show very strong peaks at 1642 and 1476 cm^{-1} for **2**, indicating that the carboxylic acid of quinolone is deprotonated and coordinated to the metal due to the absence of a strong ν(COOH) band at 1725 cm^{-1} for enoxacin. The ketonic group participates in bonding to the metal ion and shifts to 1556 cm^{-1}.

3.2. *Crystal structure of $[Zn(Ofl)_2 \cdot H_2O] \cdot 2H_2O$ (1)*

Figure 1 shows an ORTEP drawing of **1** with the atom numbering scheme. Selected bond distances and angles are given in table 2. In **1**, the crystal is composed of $[Zn(Ofl)_2 \cdot H_2O]$ and uncoordinated water. The coordination environment around Zn^{2+} in the structure is slightly distorted square pyramidal. The Zn^{2+} is 0.3608 Å above the

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

	1	**2**
Formula	$C_{36}H_{42}F_2N_6O_{11}Zn$	$C_{30}H_{32}F_2N_8O_{10}Co$
Formula weight	838.13	761.57
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
Unit cell dimensions (Å, °)		
a	9.2923(5)	5.97980(10)
b	11.3432(6)	21.4183(3)
c	17.7722(10)	13.1539(2)
α	92.839(3)	
β	94.826(3)	100.2810(10)
γ	91.909(3)	
V	1863.01(18)	1657.66(4)
Z	2	2
F(000)	872	786
D_{Calcd} ($Mg\,m^{-3}$)	1.494	1.526
T (K)	296(2)	296(2)
Reflections collected	16,106	15,951
Independent reflections	7286	3268
Goodness-of-fit on F^2	1.057	1.055
Final *R* index [$I > 2\sigma(I)$]	$R_1 = 0.0521$ $wR_2 = 0.1365$	$R_1 = 0.0404$ $wR_2 = 0.1054$
Final *R* index (all data)	$R_1 = 0.0611$ $wR_2 = 0.1440$	$R_1 = 0.0500$ $wR_2 = 0.1123$
Largest diff. peak and hole ($e\,Å^{-1}$)	0.855 and −0.738	0.456 and −0.348

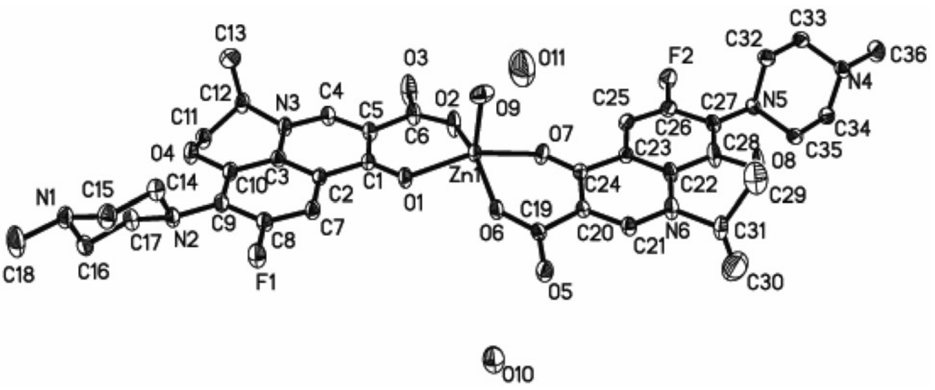

Figure 1. The coordination environment of Zn^{2+} in **1**. The thermal ellipsoids are drawn at 30% probability level.

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

Zn(1)–O(2)	1.976(2)	Zn(1)–O(1)	2.035(2)
Zn(1)–O(6)	1.994(2)	Zn(1)–O(7)	2.073(2)
Zn(1)–O(9)	1.984(2)	O(2)–C(6)	1.274(4)
O(3)–C(6)	1.222(4)	O(1)–C(1)	1.263(3)
O(5)–C(19)	1.228(4)	O(6)–C(19)	1.279(4)
O(7)–C(24)	1.259(3)		
O(2)–Zn(1)–O(1)	88.91(9)	O(6)–Zn(1)–O(7)	87.76(8)
O(2)–Zn(1)–O(9)	103.01(12)	O(9)–Zn(1)–O(7)	100.11(12)
O(9)–Zn(1)–O(6)	102.66(10)	O(9)–Zn(1)–O(1)	105.75(12)
O(6)–Zn(1)–O(1)	86.62(9)	O(2)–Zn(1)–O(7)	85.26(9)

average plane defined by oxygens O1, O2, O6, and O7, which deviate from such average plane 0.1007 Å above (O1), 0.0820 Å above (O2), 0.0813 Å above (O6), and 0.0918 Å above (O7). In the equatorial plane, the Zn^{2+} is coordinated by four oxygens (O$_{\text{keto}}$ and O$_{\text{carboxylic}}$) of two ofloxacin ligands to form two six-membered rings (ring 1: Zn1/O2/C6/C5/C1O1; ring 2: Zn1/O7/C24/C20/C19/O6), with bond distances Zn(1)–O(1) = 2.035(2) Å, Zn(1)–O(2) = 1.976(2) Å, Zn(1)–O(6) = 1.996(2) Å, and Zn(1)–O(7) = 2.073(2) Å; obviously the Zn–O$_{\text{keto}}$ bond length is longer than the Zn–O$_{\text{carboxylic}}$. The apical water is at 1.984(2) Å (Zn(1)–O(9)). The difference in the carboxylate distances of O(2)–C(6) and O(3)–C(6), O(5)–C(19) and O(6)–C(19) [1.274(4), 1.222(4), 1.228(4), and 1.279(4) Å] confirms the formation of a bond between the anionic carboxylate oxygen and Zn^{2+}; these bond lengths are virtually identical in uncoordinated quinolone. The O–Zn(1)–O bond angles vary from 85.26(9) to 105.75(12)°, deviating from the normal angle of 90°. The bicyclical rings A: C1/C2/C3/N3/C4/C5 and B: C2/C3/C7/C8/C9/C10 are essentially coplanar with corresponding dihedral angles of 0.8°. Ring C: C10/O4/C11/C12/N3/C3 is not coplanar with rings A and B, with the torsion angles 147.4 and −158.4° for C(4)–N(3)–C(12)–C(11) and C(11)–O(4)–C(10)–C(9), respectively. O4 and N3 are coplanar with rings A and B, whose equation of least squares plane is $8.539X + 0.615Y - 8.263Z = 3.1032$, with the largest deviation of 0.147 Å below the base plane. O4, C11, and C12 form a least squares plane *D*, $7.016X - 7.714Y - 0.099Z = -7.9353$. The dihedral angle between plane D(O4/C11/C12) and ring A is 49.7°, while the dihedral angle between plane D(O4/C11/C12) and

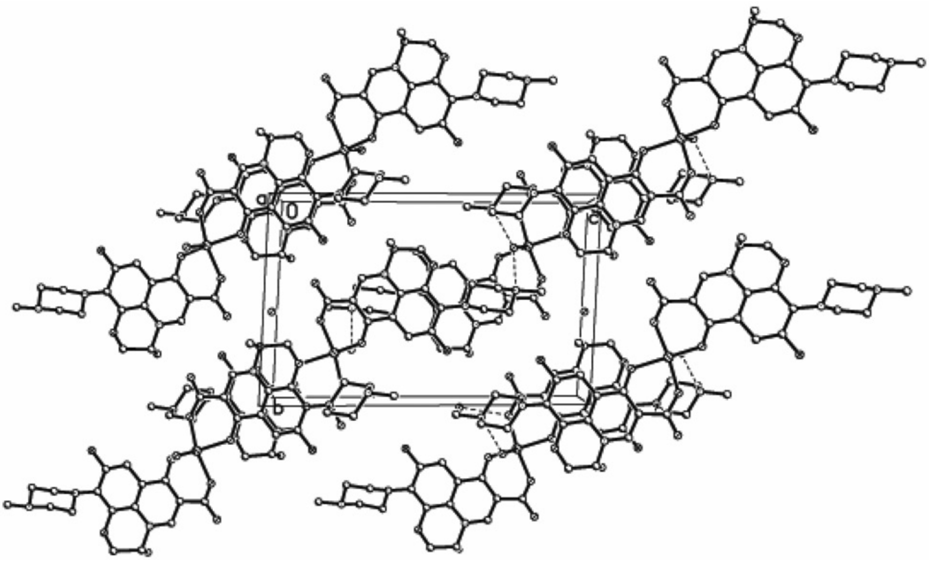

Figure 2. Three-dimensional network of **1**.

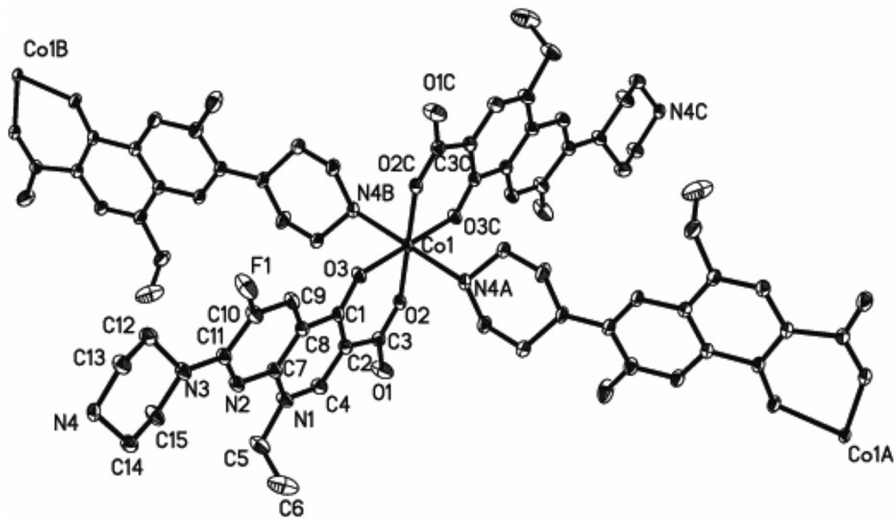

Figure 3. The coordination environment of Co^{2+} in **2**. The thermal ellipsoids are drawn at 30% probability level.

ring B is 49.8°. Two 3-methyl-piperazinyl rings adopt a normal chair conformation, with similar torsion angles: N(4)–C(33)–C(32)–N(5) [−56.8(4)°], N(1)–C(15)–C(14)–N(2) [−57.9(4)°], N(4)–C(34)–C(35)–N(5) [60.9(3)°], N(1)–C(16)–C(17)–N(2) [59.7(4)°]. Lattice water, coordinated and uncoordinated carboxylate oxygens form H bonds, thus forming a three-dimensional network (figure 2).

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Co(1)–O(2)	2.0472(17)	Co(1)–O(3)	2.0693(15)
Co(1)–N(4A)	2.2597(19)	O(1)–C(3)	1.243(3)
O(2)–C(3)	1.260(3)	O(3)–C(1)	1.257(3)
O(2)–Co(1)–O(3C)	92.95(6)	O(2C)–Co(1)–O(3C)	87.05(6)
O(2)–Co(1)–O(3)	87.05(6)	O(2C)–Co(1)–O(3)	92.95(6)
O(2)–Co(1)–N(4A)	90.46(7)	O(2C)–Co(1)–N(4A)	89.54(7)
O(3C)–Co(1)–N(4A)	92.43(7)	O(3)–Co(1)–N(4A)	87.57(7)
O(2)–Co(1)–N(4B)	89.54(7)	O(2C)–Co(1)–N(4B)	90.46(7)
O(3C)–Co(1)–N(4B)	87.57(7)	O(3)–Co(1)–N(4B)	92.43(7)

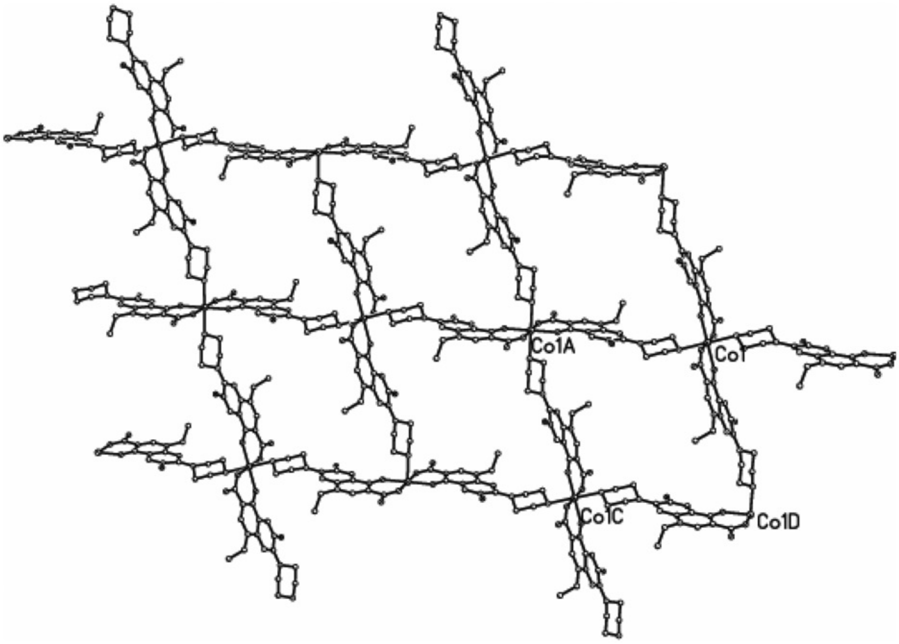

Figure 4. An extended two-dimensional network perspective of **2**.

3.3. *Crystal structure of [Co(Enox)$_2$]·4H$_2$O (2)*

Figure 3 shows an ORTEP drawing of **2** with the atom numbering scheme. Selected bond distances and angles are given in table 3. In **2**, the crystal is composed of [Co(Enox)$_2$] and uncoordinated water molecules, different from that of [Co(HEnox)$_2$(Enox)]Cl · 2CH$_3$OH · 12H$_2$O) [23]. The X-ray crystal analysis of **2** reveals that Co(II) is coordinated in a distorted octahedral geometry with an equatorial plane composed of four oxygens [O(2), O(3), O(2C), and O(3C)], two [O(3) and O(3C)] from the quinolone rings and the other two [O(2) and O(2C)] from carboxylate, forming two six-membered chelating rings. The bond distances Co(1)–O(2) and Co(1)–O(3) are 2.0472(17) and 2.0693(15) Å, respectively. Apical positions are occupied by two N atoms [N(4A)] and N(4B)] of the piperazine rings at 2.2597(19) Å. The difference in the carboxylate distances O(2)–C(3) and O(1)–C(3) [1.260(3) and 1.243(3) Å] confirms the bond between carboxylate and Co^{2+}. The O–Co(1)–O and O–Co–N bond angles vary from 87.05(6) to 92.95(6)°, deviating from 90°. The planes containing the ethyl group carbons are almost perpendicular to the enoxacin ring systems with torsion angles of C(7)–N(1)–C(5)–C(6), C(7A)–N(1A)–C(5A)–C(6A), C(7B)–N(1B)–C(5B)–C(6B), and C(7C)–N(1C)–C(5C)–C(6C) −86.6°. The piperazine rings are noncoplanar with the quinolone rings and adopt a normal chair conformation. The bridging enoxacins link Co^{2+} to form a two-dimensional neutral square grid with a cavity of 13.404−13.404 Å^2 (distances of Co1–Co1A and Co1–Co1D are 13.404 Å) (figure 4).

Supplementary material

Crystallographic data for **1** and **2** was deposited to the Cambridge Crystallographic Data Centre with deposition numbers CCDC 670264 and 692345, respectively.

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