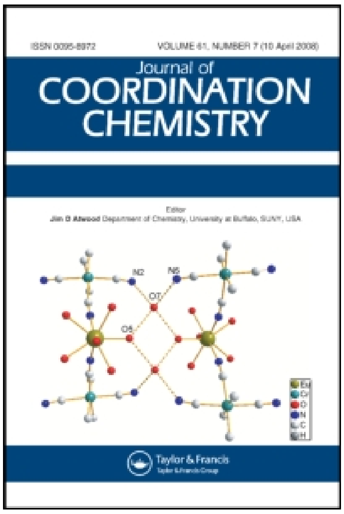

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# A two dimensional coordination polymer based on drug ligand enoxacin and transition metal ion

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A two-dimensional coordination polymer, $[Mn(Enox)_2] \cdot 4H_2O$, **1** (H-Enox = 1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-pierazinyl)-1,8-naphtyridine-3-carboxylic acid), has been rationally designed and synthesized under hydrothermal conditions. Compound **1** is self-assembled from bifunctional drug ligand enoxacin and transition metal ion Mn(II) through covalent coordination bonds and hydrogen bondings.

*Keywords:* Manganese (II); Enoxacin; Coordination polymer; Crystal structure

## 1. Introduction

In the last decade, researchers have undertaken a number of approaches towards the design and synthesis of metal-organic coordination polymers based on the concept of crystal engineering [1], resulting in offering many novel functional materials with various fascinated structural features and properties [2]. The design of solid-state architectures based on "node-and-spacer" type methodology has become an accepted practice [3, 4]. The designed and predictable coordination polymer framework may be exemplified by selection of metal coordination geometry and organic "spacer" ligands [5]. During the past few years a large number of coordination

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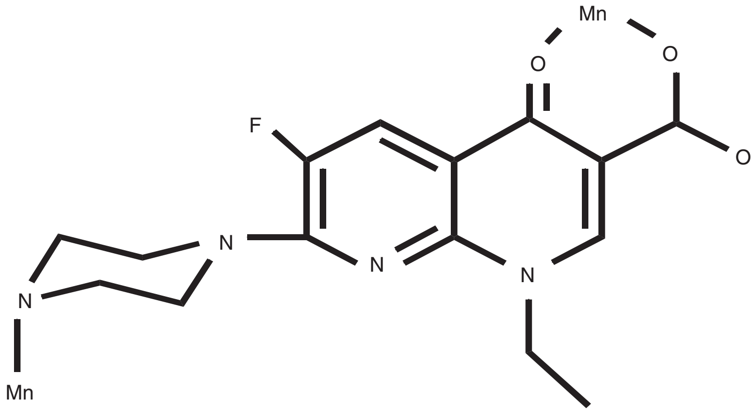

Scheme 1. The coordination mode of Enox$^-$ in **1**.

polymers have been synthesized using these methods. Typically the "spacers" used are bifunctional rod-like ligands such as 4,4′-bipyridine or pyrazine, chosen to function as linear building blocks. Our interests in exploring new coordination framework focus on the bifunctional organic drug ligands, such as norfloxacin, enoxacin with three dentate sites. Enoxacin [H-Enox, 1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-pierazinyl)-1,8-naphtyridine-3-carboxylic acid], a quinolone derivative, is used in the therapy of infections and shows great activity against Gram-positive and Gram-negative bacteria [6]. Several metal complexes such as Zn(II) [7], Mg(II) and Ca(II) [8], Tb(III) [9] with enoxacin have been synthesized and used to electroanalytical applications or fluorimetric analysis, but up to now, their crystal structures have never been reported. In the past 3 years, the authors have designed successfully several transition metal coordination polymers based on drug ligand norfloxacin as building blocks [10–13]. As the continuation work, herein, the first metal-organic coordination polymer with drug ligand enoxacin, $[Mn(Enox)_2]\cdot 4H_2O$ (**1**), in which enoxacin exhibits typical three dentate bridging coordination mode, is reported (scheme 1).

## 2. Experimental

### 2.1. *Synthesis*

$Mn(OH)_2$ (0.2 mmol) and enoxacin (H-Enox) (0.4 mmol) were thoroughly mixed in a pestle and mortar, then placed in a thick-walled Pyrex tube (ca 20 cm long). After 0.5 mL and 1 mL $H_2O$ were added, the tube was frozen with liquid $N_2$, evacuated under vacuum, and flame sealed. The tube was heated at 110°C for 2 days to give golden-yellow block crystals (only one phase) in 60% yield based on H-Enox. Anal. Calcd for $C_{30}H_{38}F_2MnN_8O_{10}$ (%): C, 47.19; H, 5.02; N, 14.67. Found: C, 47.33; H, 5.08; N, 14.59. IR (KBr, cm$^{-1}$): 3418(m), 3219(m), 2980(w), 2937(w), 2862(w), 1634(s, $\nu_{coo-}$), 1621(s), 1575((s), 1557(m), 1480(s, $\nu_{coo-}$), 1455(s), 1446(s), 1392(m), 1369(m), 1347(m), 1292(m), 1190(w), 1157(w), 1114(w), 1095(w), 1050(w),

Table 1. Crystal data and structure refinements for **1**.

| Parameter | |
|---|---|
| Empirical formula | $C_{30}H_{38}F_2MnN_8O_{10}$ |
| $M$ | 763.61 |
| Crystal system | Monoclinic |
| Space group | $P2(1)/c$ |
| $a$ (Å) | 5.8519(2) |
| $b$ (Å) | 21.6843(7) |
| $c$ (Å) | 13.3438(3) |
| $\beta$ (°) | 99.3890(18) |
| $V$ (Å$^3$) | 1670.57(9) |
| $Z$ | 2 |
| $T$ (K) | 293(2) |
| $\lambda$ (Å) | 0.71073 |
| $D_c$ (g cm$^{-3}$) | 1.510 |
| $\mu$ (mm$^{-1}$) | 0.475 |
| Reflections collected | 3487 |
| Independent reflections | 3487 ($R_{int} = 0.0000$) |
| Goodness-of-fit on $F^2$ | 1.048 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0451$, $wR_2 = 0.1251$ |
| $R$ indices (all data) | $R_1 = 0.0604$, $wR_2 = 0.1310$ |

1011(m), 970(w), 949(m), 931(m), 907(w), 853(w), 818(m), 789(w), 764(w), 743(w), 693(w), 633(m), 590(w), 553(w), 509(w).

### 2.2. *Materials and physical measurements*

Enoxacin was provided by Fluka. All reagents used were of analytical grade. C, H, N elemental analyses were carried out with a Perkin-Elmer analyzer model 240II. IR spectra were recorded as KBr discs on a Perkin-Elmer Spectrum One FT-IR spectrophotometer in the 4000–400 cm$^{-1}$ region.

### 2.3. *Crystal structure determination*

A golden-yellow crystal with dimensions $0.51 \times 0.28 \times 0.21$ mm$^3$ was mounted on a Rigaku R-AXIS RAPID IP diffractometer equipped with a graphite monochromator and Mo-$K\alpha$ ($\lambda = 0.71073$ Å) radiation. Intensity data were collected at 293(2) K using $\psi$-scan technique. The structure was solved by the direct methods and refined by the full-matrix least-squares method against $F^2$ [14]. Details of the crystal structure solutions and refinements are listed in table 1. Crystallographic data for compound **1** is deposited at the Cambridge Crystallographic Data Center CCDC, the deposition number is CCDC 246466.

## 3. Results and discussion

The X-ray crystal analysis of **1** revealed that the Mn(II) ion is coordinated in a distorted octahedral geometry (figure 1), with an equatorial plane composed of four oxygen atoms [O(1), O(2), O(1A), and O(2A)]. Two of the oxygen atoms are from

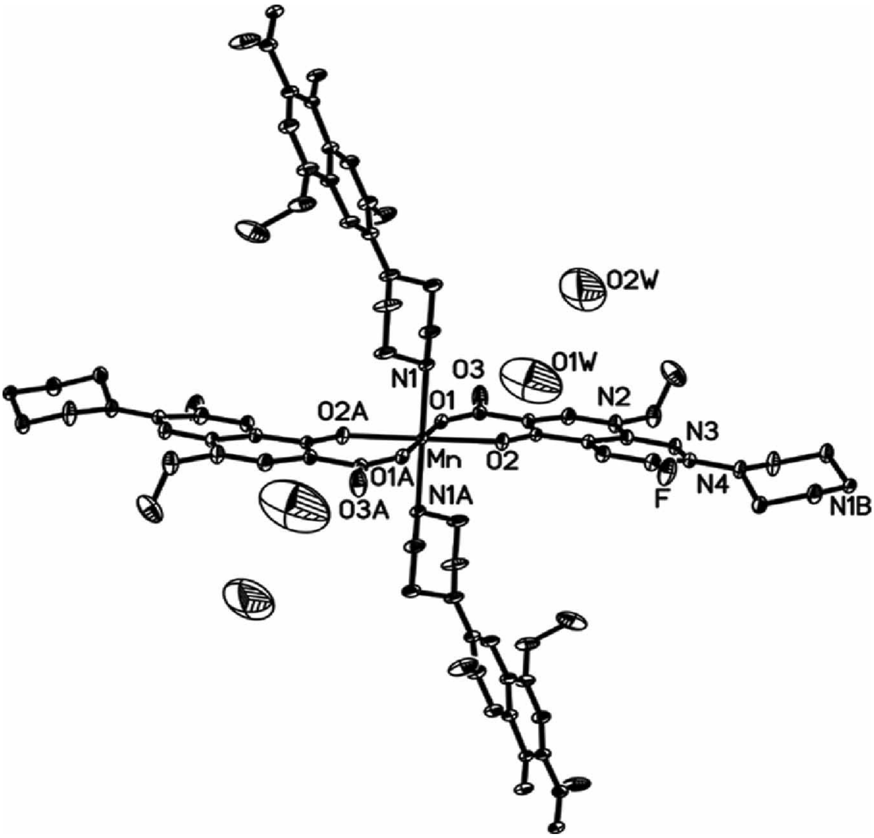

Figure 1. ORTEP view of **1**. The thermal ellipsoids are drawn at the 30% probability level. Important geometry parameters: Mn–O(1) 2.1259(7), Mn–O(2) 2.1488(6), Mn–N(1) 2.3534(7) Å; O(1)–Mn–O(1A) 180.0, O(1)–Mn–O(2) 83.44(2), O(1A)–Mn–O(2) 96.56(2), O(1)–Mn–O(2A) 96.56(2), O(1)–Mn–O(2A) 83.44(2), O(2)–Mn–O(2A) 180.000(19), O(1)–Mn–N(1A) 89.53(2), O(1A)–Mn–N(1A) 90.47(2), O(2)–Mn–N(1A) 92.45(2), O(2A)–Mn–N(1A) 87.55(2), O(1)–Mn–N(1) 90.47(2), O(1A)–Mn–N(1) 89.53(2), O(2)–Mn–N(1) 87.55(2), O(2A)–Mn–N(1) 92.45(2), N(1A)–Mn–N(1) 180.0°.

the quinolone ring and the other from the carboxylate, which forms a stable six-membered chelating ring. The apical positions are occupied by two N atoms [N(1) and N(1A)] of the piperidyl rings, resulting in the formation of a two-dimensional neutral square grid with a cavity dimensional of $13.549 \times 13.549\,\text{Å}^2$ (figure 2), which is slightly smaller than that of $[\mathrm{Mn(Norf)_2}]\cdot 4\mathrm{H_2O}$ [11]. The carboxylate group of enoxacin in **1** acts as a monodentate ligand with one oxygen of the carboxylate group uncoordinated. The uncoordinated carbonyl oxygen atom of carboxylate in enoxacin is strongly hydrogen bonded to water molecules [2.803(2) Å]. The position of the uncoordinated carbonyl oxygen atom points up and is almost perpendicular to the molecular square cavity; water molecules are thus not enclathrated in the cavity but intercalated between two adjacent layers. The adjacent layers almost perfectly overlap together so that the cavity looks like a non-interpenetrating

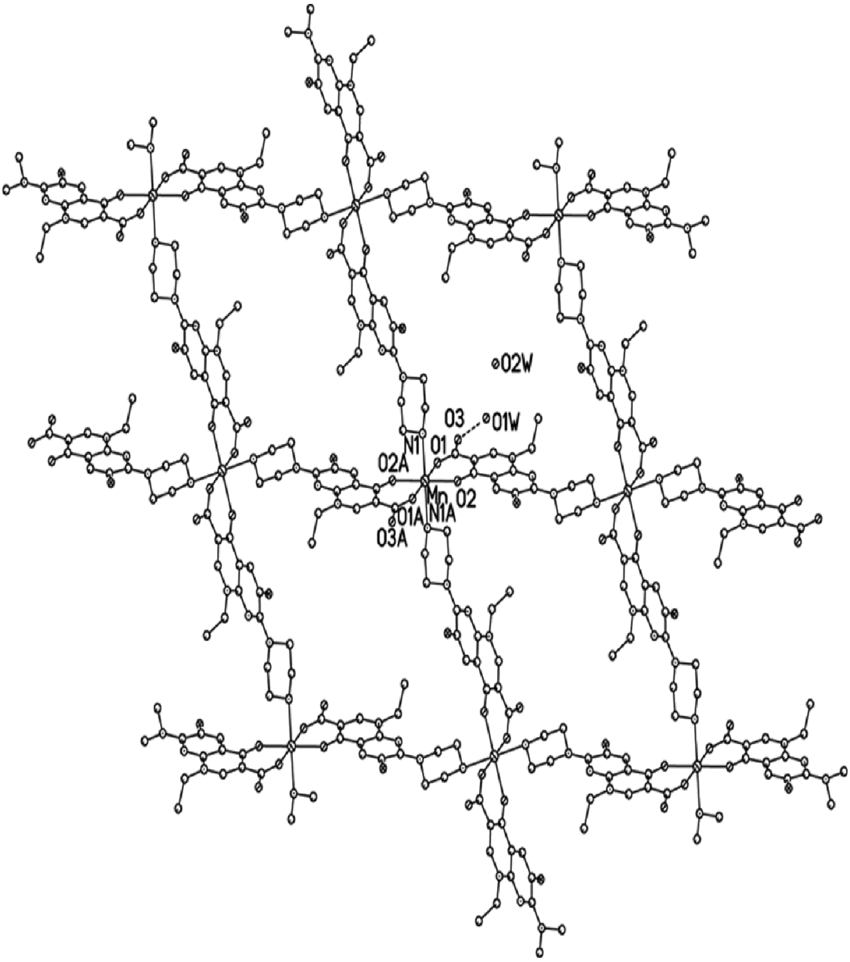

Figure 2. An extended two-dimensional network perspective view of **1**.

open channel. Furthermore, the nanosized square are interlinked together by the intercalated water molecules, which are bonded through hydrogen bonding (O–H ··· O length at 2.603(2) Å), and uncoordinated carbonyl oxygen by a strong hydrogen bonding, resulting in the formation of a nanosized hydrophobic tube (or tunnel) (figure 3). The two-dimensional nanosized neutral cavity without any interpenetrations is to our knowledge rare and appears to be very useful for host-guest chemistry [5]. Similar to $[Mn(Norf)_2]\cdot 4H_2O$ [11], **1** is almost insoluble in most common solvents such as ethanol, chloroform, ethyl acetate, acetone, acetonitrile, benzene, and water.

To study the thermal stability of compound **1**, thermogravimetric analysis (TGA) was performed on the polycrystalline sample. One strikingly clean weight loss step occurred at ca 50–105°C (9.16% loss) and corresponds to the removal of four water molecules per formula unit (9.44%). It is interesting to note that no weight loss was

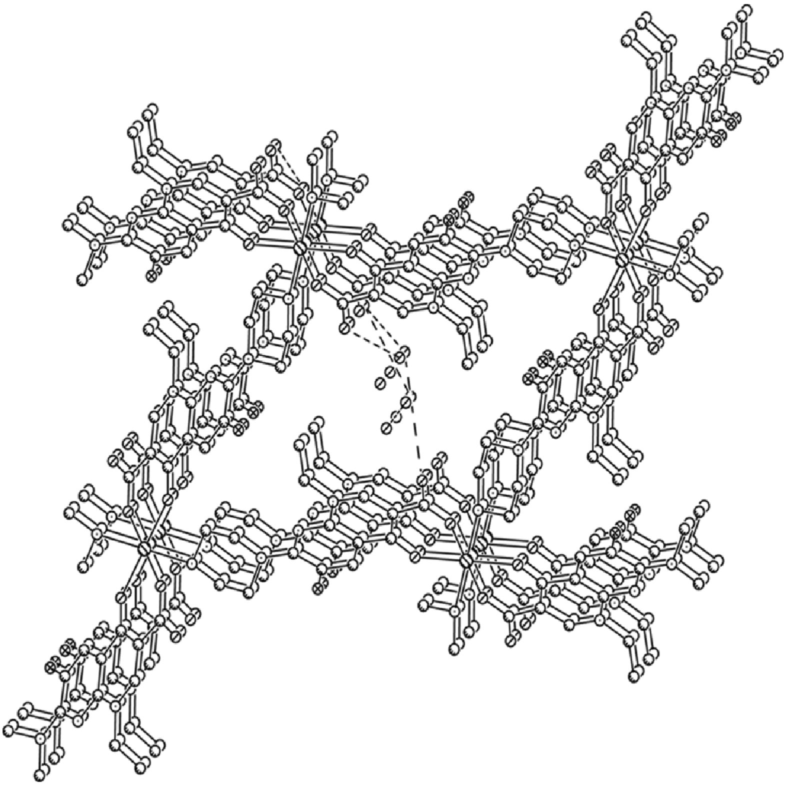

Figure 3. Crystal packing view of **1** along *a*-axis highlighting water molecules intercalated in the nanoporous open channel and no interpenetration occurred in **1**.

recorded between the temperatures 105 and 320°C, probably suggesting the formation of a stable nanosized molecular square.

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