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# 例 研究快报

## 二维纳米空洞方格:诺氟沙星锰(II)配合物

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 关键词:
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### 2D Nanoporous Molecular Square Grid: Manganese (II) Norfloxacin Complex

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The reactions of norfloxacin (H-Norf) with Mn(ClO<sub>4</sub>)  $_{2} \cdot 6H_{2}O$  and Mn(OH)  $_{2}$  yield Mn(H-Norf) (ClO<sub>4</sub>)  $_{2} \cdot 2H_{2}O$  (1) and [Mn(Norf) $_{2} \cdot 4H_{2}O$ ]  $_{n}$  (2), respectively. 1 is monomeric while 2 has a novel 2D neutral square grid with an antibacterial drug as building block. Crystal data for 1: triclinic, space group  $P\overline{1}$  (No. 2), a = 9.0939 (3), b = 9.4395(3), c = 12.7182(3)Å,  $\alpha = 111.447(2)$ ,  $\beta = 90.340(2)$ ,  $\gamma = 112.357(1)^{\circ}$ , V = 926.34(5)Å<sup>3</sup>, Z = 1,  $\rho_{cacl} = 1.664g \cdot cm^{-3}$ . Mo K $\alpha$  radiation ( $\lambda = 0.71073$ Å), T = 293(2) K,  $\mu = 0.595$  mm<sup>-1</sup>.  $R_1 = 0.0692$ , w $R_2 = 0.1482$  for 2320 observed reflections from 4390 independent reflections, GOF = 0.940; Crystal data for 2: Monoclinic,  $P2_1/c$ , a = 5.7530(12), b = 21.865(4), c = 13.343(3)Å,  $\beta = 98.25(3)^{\circ}$ , V = 1661.1(6)Å<sup>3</sup>, Z = 2,  $\rho_{cacl} = 1.527g \cdot cm^{-3}$ , T = 293(2) K,  $\mu = 0.477$  mm<sup>-1</sup>,  $R_1 = 0.0531$ , w $R_2 = 0.1552$  for 2070 observed reflections from 2870 independent reflections, GOF = 1.384. CCDC: 140819; 151063.

Keywords: nanoporous norfloxacin manganese complex

#### 0 Introduction

Norfloxacin H-Norf = 1-ethyl-6-fluoro-1, 4-dihydro -4-oxo-7-(1-piperazinyl) -3- quinoline carboxylic acid), a quinolone type compound, is a widely used antibacterial drug that targets the bacterial type II DNA topoisomerase (gyrase). Suggested modes of action for H-Norf are either inhibition of metalloenzyme DNAgyrase or interaction with the DNA molecule via a metal complex intermediate, and it has been proposed that metal ion complex could be involved in these interactions with DNA<sup>[1]</sup>. It has also been reported that metal complexes of H-Norf possess improved solubility in water and antibacterial activity<sup>[2]</sup>. The sites of bonding of metal ions with quinolones clearly involve the 4-oxo and 3-carboxyl oxygen atoms, which results in the formation of a stable six-membered chelate ring<sup>[3]</sup>. Despite the important role that divalent metal ions may play in this system, there has been no structurally characterized example of a compound containing a di-

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rect coordinate bond between H-Norf and a metal ion, except that we have successfully determined the solid state structure of two dimers of H-Norf with Mg<sup>2+</sup> and Ca<sup>2+</sup> as well as Zn<sup>2+</sup> more recently<sup>[4]</sup>. Recently, Mirkin and co-workers successfully introduced the supramolecular chemistry into biochemistry and constructed novel molecular architectures with DNA<sup>[5a]</sup>. Furthermore, our group have also constructed several supramolecular motifs using organic drug as building blocks<sup>[5b, c]</sup>. Inspired by pioneering self-assembly of molecular square (and other geometry entities) containing metal ions by Lehn, Robson, Stang, and Fujita in the last decade<sup>[6]</sup>, we now describe the construction of a metal-based molecular square grid using H-Norf as building block by self-assembly. The reactions of H- Norf with  $Mn(ClO_4)_2 \cdot 6H_2O$  and  $Mn(OH)_2$  afford  $Mn(H-Norf)(ClO_4)_2 \cdot 2H_2O(1)$  and  $Mn(Norf)_2 \cdot$  $4H_2O$  (2), respectively in which 2 is the novel 2D neutral square grid with anti-bacterial activity and the coordination modes of H-Norf with Mn (II) both in quinolone and H-Norf metal complexes are new (Scheme 1). Here we report their synthesis and crystal structures which provide, new insight into understanding of the fashion of action of quinolone-type antibiotics and are very important not only for coordination chemists but also for biochemists.

#### **1** Results and Discussion

The pale-yellow block powdered 1 and golden-yellow 2 solids were obtained in 65 and 85% yield respectively. The IR spectra of 1 and 2 show two very strong peaks at 1621, 1486cm<sup>-1</sup> and 1621, 1490cm<sup>-1</sup>, respectively; these data indicate that the carboxylic acid groups are deprotonated (for norfloxacin 1710 and 1621cm<sup>-1</sup>). A strong and broad peak at 1094cm<sup>-1</sup> in the IR spectrum of 1 indicates the presence of uncoordinated ClO<sub>4</sub><sup>-</sup> anion.

It is interesting to note that in weakly basic solutions (pH is about 8), the N atom of the piperidyl ring can bind to the metal ion, while in weakly acidic solutions (pH is about 6), the piperidyl N atom is protonated and fails to coordinate to metal ion. This sug-

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gests that the coordination mode of H-Norf with Mn (II) mainly depends upon the pH value of the solution. This finding is fairly good agreement with that found in  $Zn^{2-}$ -H-Norf systems<sup>[4]</sup>.

The crystal structure of  $[Mn(H_2O)_2(H-Norf)_2]$ (ClO<sub>4</sub>)<sub>2</sub> (1), (Fig. 1), is mononuclear, the Mn<sup>2+</sup> center is coordinated in an octahedral environment with an equatorial plane composed of four oxygen atoms (two of them from the quinoline ring and the other from carboxylate groups which form a stable six-membered chelate ring) and two water molecules occupying in the apical positions. The coordination mode of Mn<sup>2-</sup> in weekly acid solution is similar to those found in quinolone antibiotics<sup>13, 41</sup>. The bond lengths and angles are unexceptional, as listed in Table 1. From its packing, there are many H bonds between H<sub>2</sub>O and perchlorate ions (2. 832 ~ 2. 853Å), N cation of piperidyl ring and O of carboxylate (2. 759 ~ 2. 870 Å), as shown in Fig. 2.

 Table 1
 Selected Bond Distances(Å) and Angles(°)

 in 1 and 2

1		2	
	distar	ices/Å	
Mn(1)-O(1)	2.150(3)	Mn(1)-O(1)	2 140(2)
Mn(1)-O(2)	2.106(3)	Mn(1)-O(2)	2.162(2)
Mn(1)-O(1w)	2.182(3)	Mn(1)-N(1B)	2.351(3)
	angle	s/(°)	
O(2)-Mn(1)-O(2A)	180.000(15)	O(1)-Mn(1)-O(1A)	180.000(1)
O(2)-Mn(1)-O(1)	84.52(11)	O(1A)-Mn(1)-O(2A)	83.18(9)
O(1A) - Mn(1) - O(2)	95.48(11)	O(1)-Mn(1)-O(2A)	96.82(9)
O(2A) - Mn(1) - O(1A)	84.52(11)	O(2)-Mn(1)-O(2A)	180.00(8)
O(1)-Mn(1)-O(1A)	180.00(18)	O(1A)-Mn(1)-N(2B)	90.52(9)
O(2)-Mn(1)-O(1w)	91.62(16)	O(1)-Mn(1)-N(2B)	89.48(9)
O(2A)-Mn(1)-O(1w)	88.38(16)	O(2A)-Mn(1)-N(2B)	87.79(10)
O(1wA)-Mn(1)-O(1)	180.0(3)	O(2)-Mn(1)-N(2B)	92.21(10)
O(1)-Mn(1)-O(1w)	89.96(15)	O(1)-Mn(1)-N(2C)	89.48(9)
O(1A) - Mn(1) - O(1w)	90.04(15)	$O(2) \cdot Mn(1) - N(2C)$	87.79(10)
		N(2B) - Mn(1) - N(2C)	180,000(1)

Unlike 1, the structure of 2 (Fig. 3), consists of an equatorial plane defined by O(1), O(2), O(1A) and O(2A) from two different Norf ligands, while the apical positions are occupied by two N atoms [N(2B) and N (2C)] of the piperidyl rings, resulting in the formation of a 2D square grid with a cavity dimension of 13. 642 × 13. 642Å (Fig. 4). Similar to 1, the carboxylate group of Norf in 2 is monodentate while one of the oxygen atom of the carboxylate group is uncoordi-

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Scheme 1



Fig. 1 An ORTEP symmetric unit diagram of [Mn(H-Nor)<sub>2</sub> · 2H<sub>2</sub>O] · (ClO<sub>4</sub>)<sub>2</sub> (1)



Fig. 2 Crystal packing view of [Mn(H-Nor)<sub>2</sub> • 2H<sub>2</sub>O]
• (ClO<sub>4</sub>)<sub>2</sub> (1) in which dotted lines show the presence of H-bonds

nated. The uncoordinated carbonyl oxygen atom is strongly hydrogen-bonded to water molecules  $(2.782\text{\AA})$ . Due to the position of the carbonyl oxygen atom pointing up and perpendicular to the molecular square cav-



- Fig. 3a Mn atom local coordination environment in [Mn(Nor)<sub>2</sub>] • 4H<sub>2</sub>O (2) showing the highlighted water molecules intercalated in the nanoporous open channel
  - The increasing size open circles represent C,  $\,N,\,$  O, F and Mn atoms

ity, water molecules are not enclathrated in the cavity but intercalated between two adjacent layers, as shown in Fig. 5. The adjacent layers almost overlap together so that the cavity looks like a non-interpene- trating nanoporous open channel. Furthermore, the nanosized squares are linked together by intercalated water molecule  $(2.721 \sim 3.253 \text{\AA})$ , and uncoordinated car无机化学学报



Fig. 3b 2-D extended network square grid representation of  $[Mn(Nor)_2] \cdot 4H_2O(2)$  highlighting octahedral Mn atoms



Fig. 4 Crystal packing view of [Mn(Nor)2] • 4H<sub>2</sub>O (2) along a-axis highlighting water molecules(large circles) intercalated in the nanoporous open channel and no interpenetration occurred in 2



Fig. 5 Relationship between two adjacent layers is AA type stacking

The straight lines and open circles represent norfligands and Mn atoms

The intercalated water is omitted for clarity

bonyl oxygen by a strong hydrogen bonding, which results in the formation of a nanosized hydrophobic channel. The 2D nanosized neutral cavity has potenital applications in host-guest chemistry<sup>[7]</sup>. The non-interpenetration is probably due to the introduction of quinoline ring into **2**. Similarly, there are no unexceptional bond lengths and angles found in **2**, as presented in Table 1.

To study the thermal stability of compound 2. thermogravimetric analysis (TGA) was performed on polycrystalline samples which indicated that one weight loss step occurred at ca. 50°C to 140°C (9.25% loss), corresponding to the removal of four water molecules per formula unit (9.43%). Most important is the fact that no weight loss was recorded between the temperature 140 $^{\circ}$ C and 298 $^{\circ}$ C, probably suggesting that the formation of a stable nanosized molecular square architecture. Our experimental results indicate that the host square can intercalated water molecules to regenerate 2 (identical X-ray powder diffraction patterns were obtained for samples of 2 before and after the removal of water guest molecules). It is very interesting to note that the blue fluorescent emission of H-Norf can be quenched after the formation of 1 and 2. Their bioinorganic test is currently under way.

### 2 Conclusions

The binding mode of H-Norf with Mn(II) is mainly dependent upon the pH value of the solution. The isolated two products 1 and 2 definitely provide a new insight not only for biochemists into the understanding of the action fashion of H-Norf with metal ions at different reaction mediums, but also for coordination chemists into the construction of biologically relevant molecular squares.

#### **3** Experimental

Synthesis and characterization of 1 and 2

(a) Compound 1: Samples of 1mmol of Mn(ClO<sub>4</sub>)<sub>2</sub>

•  $6H_2O$  and 2mmol of H-Norf were placed in a thick-walled Pyrex tubes (*ca.* 20cm long). After addition of 0. 5mL of EtOH and 1. 5mL of H<sub>2</sub>O, the tube

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was frozen with liquid N<sub>2</sub>, evacuated under vacuum and sealed with a torch. The tube was heated at 110 °C for one day to give pale yellow block crystals (only one phase) in 65% yield based on H-Norf (Found: C, 41. 51; H, 4. 55; N, 9. 15; Calc.: C, 41. 42; H, 4. 35; N, 9. 06% ) Solid reflectance UV-vis 339. 6 nm. IR (KBr, cm<sup>-1</sup>): 3405(m), 1621(s), 1566(s), 1486(s), 1405(m), 1385(m), 1345(m), 1265(s), 1094(vs), 921(w), 818(w), 756(m) and 624(w).

(b) Compound 2: The procedures are identical to those of 1 using  $Mn(OH)_2$  as starting material. The golden-yellow block crystals (one phase) were harvested, with a yield of 85% based on H-Norf (Found: C, 50. 48; H, 5. 45; N, 11. 13; Calc. : C, 50. 33; H, 5. 54; N, 11. 01 % ). IR (KBr, cm<sup>-1</sup>): 3400(m), 3200(m), 2906(w), 1621(s), 1580(m), 1490(s), 1380(m), 1340(m), 1262(s), 1186(w), 1110(w), 1009(m), 935(m), 886(w), 827(w), 790(w), 748 (w), 700(w) and 635(w).

X-Ray Crystallography of 1 and 2.

Crystal data for 1:  $C_{32}H_{40}Cl_2F_2MnN_6O_{16}$ ,  $M_r =$ 928.54, triclinic, space group  $P\overline{1}$  (No.2), a =9.0939(3), b = 9.4395(3), c = 12.7182(3)Å,  $\alpha =$ 111.447(2),  $\beta = 90.340(2)$ ,  $\gamma = 112.357(1)^{\circ}$ , V = 926.34(5)Å<sup>3</sup>, Z = 1,  $\rho_{cacl} = 1.664$ g · cm<sup>-3</sup>. Mo K $\alpha$  radiation ( $\lambda = 0.71073$ Å), T = 293(2)K,  $\mu =$ 0.595 mm<sup>-1</sup>,  $R_1 = 0.0692$ , w $R_2 = 0.1482$  for 2320 observed reflections from 4390 independent reflections, GOF = 0.940.

Crystal data for **2**:  $C_{32}H_{42}F_2MnN_6O_{10}$ ,  $M_r = 763.66$ , Monoclinic,  $P2_1 / c$ , a = 5.7530(12), b = 21.865(4), c = 13.343(3) Å,  $\beta = 98.25(3)^\circ$ , V = 1661.1(6) Å<sup>3</sup>, Z = 2,  $\rho_{cacl} = 1.527g \cdot cm^{-3}$ , T = 293 (2) K,  $\mu = 0.477 mm^{-1}$ ,  $R_1 = 0.0531$ , w $R_2 = 0.1552$  for 2070 observed reflections from 2870 independent reflections, GOF = 1.384. The structures were solved with Direct Methods using the program SHELXTL (Sheldrick, 1997)<sup>[8]</sup>. All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and

allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless.

**Supporting Information Available**: An X-ray crystallographic file (CIF) is requested from Dr. Ren-Gen Xiong at XIONGRG@ netra. nju. edu. cn.

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