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Two novel entangled metal–quinolone complexes with self-threading and polythreaded characters

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ABSTRACT

Reactions of quinolones with metal salts in the presence of aromatic polycarboxylate ligands under hydrothermal conditions yield two novel entangled metal–quinolone complexes, namely $[Cd_2(saraH)_2(bpdc)_2]\cdot 4.5H_2O$ (**1**) and $[Mn(sara)_2]\cdot 2.5H_2O$ (**2**), (saraH = sarafloxacin, bpdc = 4,4′-biphenyldicarboxylate). Their structures were determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, IR spectra, X-ray powder diffraction, and TG analyses. Compound **1** is an uncommon 2D self-threading network, which represents the first entangled network constructed from mixed sarafloxacin and dicarboxylate ligands. Compound **2** exhibits a novel (2D → 3D) polythreaded architecture that is constructed from 2D 4^4-**sql** nets with side arms, which represents the first example of polythreaded metal–sarafloxacin complex. A comparison of the structures of **1** and **2** shows that the pH plays a crucial role in tuning the structures of the metal–quinolone complexes. Furthermore, the luminescent properties of compound **1** are discussed.

1. Introduction

Current interest in crystal engineering of metal–organic frameworks (MOFs) not only stems from their tremendous potential applications in gas storage, chemical separations, microelectronics, nonlinear optics, and heterogeneous catalysis, but also from its intriguing structural diversity, new topologies, and intricate entangled motifs [1]. Entangled systems (catenanes, rotaxanes, and molecular knots), an extremely active subject in the coordination polymer chemistry, have attracted a great deal of attention from chemists owing to their aesthetic and complicated architectures and topologies [2]. As a result, a variety of novel entangled systems, such as polythreading and self-threading, have been discovered up to now [2a,3]. Polythreading, being considered as extended periodic analogues of molecular rotaxanes or *pseudo*-rotaxanes, is characterized by the presence of closed loops as well as of elements that can thread through the loops. Many exotic polythreaded structures are being documented in last decade aided by the rapid growth of network-based crystal engineering, however, most of them are constructed from lower dimensional (0D, 1D) arrays with side arms [2a], and only a limited number of fascinating polythreaded networks assembled from 2D motifs have been reported up to now [4]. Compared with polythreading, self-threading is a new branch of entanglements and a new threading mode, in which closed loops are threaded by components from the network itself. It can also be considered as a structural compromise between polythreading and self-penetrating due to it possesses partially inherent features of these two classes [3]. This new type of entanglement, owing to being recognized very recently, is quite uncommon in coordination polymers, and only five self-threading frameworks have been reported by us and other groups to date [3]. Furthermore, interest in entangled structures is increasingly heightened by their potential applications ranging from sensor devices to drug delivery vehicles [5]. However, the occurrence of entangled metal–drug complexes is surprisingly rare, although many organic drugs have the potential to act as ligands, and the resulting metal–drug complexes are particularly important both in coordination chemistry and biochemistry [6,7]. On the other hand, despite the fact that there are more topological types of entanglements being discovered, the self-threading and higher dimensional polythreaded MOFs are still quite rare. Therefore, further research is necessary to enrich and develop these fields.

Quinolones are a large family of structurally related highly potent broad-spectrum antibacterial agents widely used in clinical practice for the treatment of variety of infections. Sarafloxacin (saraH) (Scheme S1), synthetic broad-spectrum antibacterial agent belonging to this family, is very active against aerobic Gram-negative microorganisms [7–10]. The mechanisms of action of the quinolone antibacterial drugs are either their inhibition of the

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supercoiling of DNA catalyzed by the enzyme DNA gyrase, or their interaction with the DNA molecule *via* a metal complex intermediate [6–12]. Recently new theoretical–experimental studies on the activity of quinolones and their metal complexes have supported the hypothesis that the mechanism of action of quinolones could be mediated by a metal ion [8,12]. Despite the key role that the metal ions may play in this system, however, the structurally characterized metal–quinolone complexes are still rare [8], not to mention the entangled metal–quinolone coordination polymers. Therefore, the exploration of feasible synthetic routes to construct entangled metal–quinolone complexes is still a great challenge for synthetic chemists, and much work is necessary to enrich and develop this branch.

Recently, we reported one interpenetrated metal–quinolone complex [7c] that represents the first entangled metal–ppa complex. As an extension of our previous work [7c,7d], we report herein two entangled metal–saraH complexes. In our synthetic strategy, the quinolone antibacterial drugs and long aromatic dicarboxylate ligands are simultaneously chosen for the following reasons: (i) on the one hand, the quinolone molecules can act as one-end coordinated ligands, which can be considered as side arms, thus providing great possibilities for the formation of polythreading or self-threading. On the other hand, the long quinolone molecules could equally well be used as long bridging ligands, which will lead to larger voids that may result in entangled structures. (ii) Long aromatic dicarboxylate ligands have shown great potential for assembly of uncommon entangled structures [3b,6b,13]. (iii) The combination of quinolones and long aromatic dicarboxylates may offer new opportunities to construct novel entangled frames. However, coordination polymers constructed from the mixed quinolones and long aromatic dicarboxylates are still very rare, which may be attributed to the fact that two carboxyl-containing ligands would yield more negative charges and make the charge balance difficult and, therefore, further research is necessary to enrich and develop this branch. Fortunately, by trial and error we have now isolated two novel entangled metal–quinolone complexes, namely $[Cd_2(saraH)_2(bpdc)_2]\cdot 4.5H_2O$ (**1**) and $[Mn(sara)_2]\cdot 2.5H_2O$ (**2**) (bpdc = 4,4′-biphenyldicarboxylate), which represent the first examples of entangled metal–quinolone complexes. This work may provide new structural information into understanding the mechanisms of action of the quinolone antibacterial agents.

2. Experimental

2.1. Materials and methods

All chemicals were commercially purchased and used without further purification. The elemental analyses (C, H and N) were carried out with a Perkin–Elmer 2400 CHN Elemental Analyzer. Cd and Mn were determined by a tps-7000 Plasma-Spec(I) inductively coupled plasma atomic emission spectrometer (ICP-AES). IR spectra were recorded in the range 400–4000 cm^{-1} on a Bio-Rad FTS-185 FT/IR Spectrophotometer using KBr pellets. TG analyses were performed on a NETZSCH STA 449C instrument in flowing N_2 with a heating rate of 10 °C·min^{-1}. Excitation and emission spectra were performed on an F-4500 fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. XRPD were recorded on a XD-3 diffractometer using Cu Kα (λ = 1.5406 Å) radiation at room temperature.

2.2. The synthesis of $[Cd_2(saraH)_2(bpdc)_2]\cdot 4.5H_2O$ (**1**)

A mixture of $Cd(OAc)_2\cdot 2H_2O$ (0.5 mmol), sarafloxacin hydrochloride (0.25 mmol), H_2bpdc (0.25 mmol), and distilled water (8 mL) was adjusted to pH 6.5 with 2.5 M KOH solution and then sealed in an 18 mL Teflon-lined autoclave, which was heated in an oven at 130 °C for 72 h. After slow cooling to the room temperature, brown block crystals of **1** were filtered, washed with distilled water and dried at ambient temperature (yield: ca. 48% based on Cd). *Anal.* Calc. for $C_{68}H_{59}Cd_2F_4N_6O_{18.50}$ (**1**): C, 52.45; H, 3.82; Cd, 14.44; N, 5.40. Found: C, 52.69; H, 3.64; Cd, 14.23; N, 5.27%. FT-IR data (cm^{-1}): 3420(m), 3214(m), 3097(w), 2982(w), 2939(w), 2851(w), 2698(w), 2359(w), 2338(w), 1919(w), 1868(w), 1843(w), 1827(w), 1773(w), 1731(w), 1627(s), 1574(s), 1537(m), 1505(s), 1492(s), 1460(m), 1378(s), 1332(m), 1296(s), 1260(s), 1229(s), 1182(m), 1162(m), 1140(w), 1107(m), 1037(w), 1011(m), 923(m), 890(w), 853(w), 817(m), 782(w), 766(m), 732(w), 704(w), 687(w), 665(w), 631(m), 549(m), 487(w), 472(w), 434(w).

2.3. The synthesis of $[Mn(sara)_2]\cdot 2.5H_2O$ (**2**)

A mixture of $Mn(OAc)_2\cdot 4H_2O$ (0.4 mmol), sarafloxacin hydrochloride (0.2 mmol), H_2oba (0.2 mmol), and distilled water (8 mL) was adjusted to pH 10.5 with 25% ammonia solution and then sealed in an 18 mL Teflon-lined autoclave, which was heated in an oven at 150 °C for 72 h. After slow cooling to the room temperature, brown block crystals of **2** were filtered, washed with distilled water and dried at ambient temperature (yield: ca. 53% based on Mn). It is noteworthy that the H_2oba ligand is rather important in the formation of **2**; if it was removed, no crystals would be obtained. *Anal.* Calc. for $C_{40}H_{37}F_4MnN_6O_{8.50}$ (**2**): C, 55.30; H, 4.29; Mn, 6.32; N, 9.67. Found: C, 55.47; H, 4.15; Mn, 6.17; N, 9.78%. FT-IR data (cm^{-1}): 3444(s), 3224(m), 2970(w), 2930(w), 2361(w), 2341(w), 1922(w), 1869(w), 1844(w), 1828(w), 1795(w), 1771(w), 1626(s), 1579(m), 1556(m), 1532(m), 1504(s), 1478(s), 1461(m), 1442(m), 1379(s), 1303(w), 1261(s), 1230(m), 1159(m), 1136(m), 1112(s), 1038(w), 1021(w), 999(m), 922(m), 886(w), 855(w), 818(m), 783(w), 747(w), 731(m), 691(w), 661(w), 639(w), 623(m), 550(m), 512(w), 484(w), 458(w), 422(w).

2.4. X-ray crystallography

Suitable single crystals with dimensions of 0.39 × 0.37 × 0.32 mm for **1** and 0.40 × 0.38 × 0.35 mm for **2** were glued on the glass fibers. Diffraction intensity data were collected on a Bruker Smart Apex CCD diffractmeter with Mo Kα monochromated radiation (λ = 0.71073 Å) at 296(2) K. Absorption corrections were applied using the multi-scan technique. The structures of **1** and **2** were solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 software [14]. All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. The aqua hydrogen atoms were located from difference Fourier maps. The crystal data and structure refinement of compounds **1** and **2** are summarized in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Table 2.

3. Results and discussion

3.1. Crystal structure of compound 1

Compound **1** is a peculiar 2D self-threading frame. Single-crystal X-ray diffraction analysis reveals that the asymmetric unit of **1** has two crystallographically independent Cd atoms, as illustrated in Fig. 1. The Cd1 and Cd2 centers exhibit distorted octahedral geometries and have identical coordination environments, both coordinated by two oxygen atoms (Cd(1)–O 2.252(3)–2.270(2) Å and Cd(2)–O2.252(3)–2.276(2) Å) from one saraH ligand and four carboxylate oxygen atoms (Cd(1)–O 2.207(3)–2.444(3) Å and