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Preparation, characterization and spectroscopic properties of difluoroboron complexes with some fluoroquinolones

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ABSTRACT

Six novel difluoroboron complexes with fluoroquinolones were prepared from fluoroquinolones via complexation with boron trifluoride etherate in DMF–CH_2Cl_2 solution. Their spectroscopic properties were investigated by UV–vis absorption, FTIR, ^{1}H NMR and fluorescence spectroscopic techniques. The results showed that these difluoroboron complexes exhibited the intense fluorescence emission at 401–579 nm under UV visible illumination and possessed a relatively high quantum yield in DMSO solution and solid state. Especially, the difluoroboron complex of Levofloxacin displayed the strongest fluorescence and highest quantum yield (Φ_u = 0.63) in these difluoroboron complexes, due to its conjugated rigid plane system via four fused six-membered cyclic structures.

1. Introduction

Fluoroquinolones, a commonly used term for the quinolonecarboxylic acids, are nowadays the most successful synthetic antibacterial agents in clinical applications [1,2]. Their derivatives are of great attention to the medicinal chemists in the pharmaceutical industry due to their broad spectrum of activity against various bacteria, mycobacteria and parasites [3–5]. Over the past decade, many researchers also have reported the preparation, crystal structure and properties of metal complexes with quinolone derivatives [6–8].

However, until now there were few reports on the difluoroboron complexes of quinolonecarboxylate derivatives [9–12]. Recently, we reported synthesis and photoluminescence properties of some new difluoroboron β-diketonates [13–15] because they exhibited high luminescence in the visible spectrum and can be used as fluorescent probes, laser dyes, nonlinear optics and electroluminescent emitters [16–19]. As a continuation of our work, herein we report the preparation and spectroscopic properties of difluoroboron complexes with some fluoroquinolones, in which the bonding of the quinolones to boron atom was through the pyridone oxygen and the carboxylate oxygen. Structures for the obtained complexes were confirmed by means of the elemental analysis, IR, ^{1}H NMR and ESI–MS spectroscopy. Their optical properties were also investigated by UV–vis absorption and fluorescence spectroscopy.

2. Results and discussion

2.1. Synthesis

Difluoroboron complexes with fluoroquinolones were prepared by the chelation reaction of the fluoroquinolones (Norfloxacin, Ciprofloxacin, Enrofloxacin, Tosufloxacin, Sparfloxacin and Levofloxacin) with an excess of boron trifluoride diethyl ether ($BF_3{\cdot}Et_2O$) in DMF–CH_2Cl_2 (1:1) solution. After recrystallization from DMF–$CHCl_3$ (1:1), pure difluoroboron complexes (**1**–**6**) were isolated in moderate to good yields and their chemical structures are shown in Fig. 1.

2.2. IR spectra

The IR spectral comparison between the fluoroquinolones (Their FTIR, ^{1}H NMR spectroscopic data are in the Supplementary information) and their difluoroboron complexes is very helpful in defining the structure of difluoroboron complexes. The characteristic, strong absorption bands and assignments for the fluoroquinolones and their boron complexes are given in Table 1. The proposed interaction between fluoroquinolones and the boron atom was coordinated through the ketonic group (4-oxo) and

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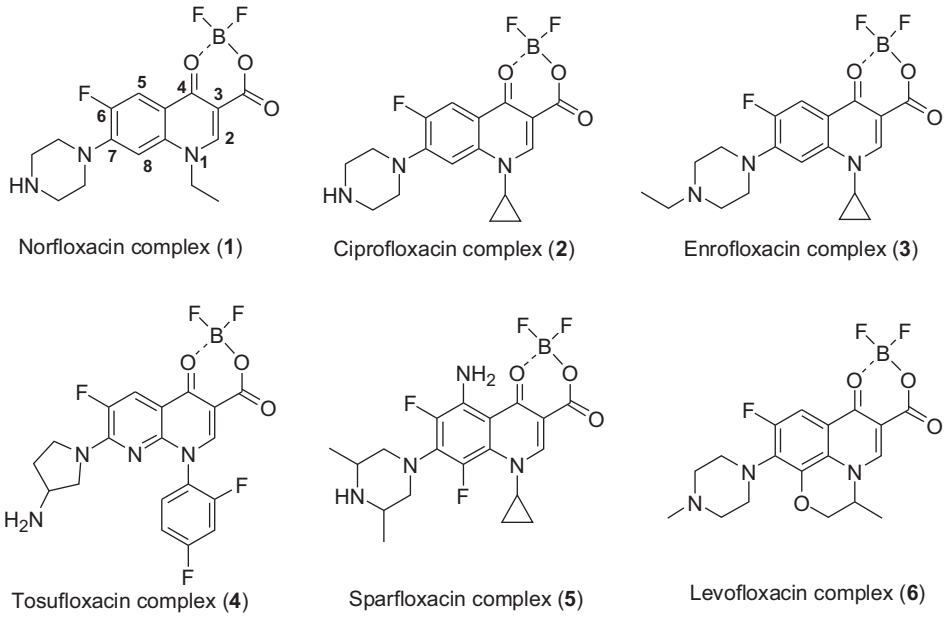

Fig. 1. The chemical structure of difluoroboron complexes with fluoroquinolones.

carboxylic groups; therefore we focus on these group vibrations. The IR spectra of the fluoroquinolones showed broad and strong absorption bands in the 3468–3378 cm^{-1} zones assigned to O–H stretching vibration for carboxylic group. In the boron complexes, the broad bands responsible for the O–H stretching vibration at about 3400 cm^{-1} were not observed; but complexes **4** and **5** exhibited the narrow peaks at 3408 and 3485 cm^{-1}, respectively, which were attributed to the NH_2 stretching vibration. In the free fluoroquinolones, the strong absorption bands in the regions of 1733–1709 cm^{-1} and 1634–1619 cm^{-1} belonged to the C=O stretching vibrations of the carboxylic group and pyridone, respectively [8,20]. However, in the difluoroboron complexes, the carboxylic C=O stretching frequencies were low-frequency shift 8–17 cm^{-1} and the ketonic C=O stretching frequencies were high-frequency shift 11–16 cm^{-1} with respect to those of the corresponding fluoroquinolones. These results indicated that the ketonic C=O and carboxylic groups participated in the formation of difluoroboron complexes. In addition, the strong absorption bands of the difluoroboron complexes in the region of 1191–1148 cm^{-1} were due to the B–F stretching vibrations and rather strong bands in the region of 1062–1042 cm^{-1} were attributed to the B–O stretching vibrations [21,22]. Evidently, there were no strong absorptions in these regions for the fluoroquinolone compounds.

2.3. ^1H NMR spectra

There were three most obvious changes while comparing the ^1H NMR spectra of difluoroboron complexes and fluoroquinolones (Table 2). The first one is that the proton signals at δ = 15.22–15.09 ppm in the fluoroquinolones, which were due to the carboxylic OH protons, disappeared completely in those of difluoroboron complexes. The second is that the proton signals at δ = 8.97–8.50 ppm were attributed to the vinylic protons (C_2–H) in the fluoroquinolones, whereas the vinylic proton signal for difluoroboron complexes was shifted 0.38–0.54 ppm to lower field. The third is that the proton signals at δ = 7.99–7.55 ppm in the fluoroquinolones, which were assigned to the C_5–protons (C_5–H) of quinoline ring, moved 0.17–0.59 ppm to the lower field in difluoroboron complexes. All these are because of difluoroboron complexes formation arising from the electron-withdrawing effect of the chelate ring by the fluorine atoms [21,23]. These results further confirmed the formation of difluoroboron complexes of fluoroquinolones.

2.4. Absorption spectra

The UV–vis absorption spectra for fluoroquinolones and their difluoroboron complexes **1**–**6** in DMSO were presented in

Table 1
Comparison of the characteristic IR data (cm^{-1}) for fluoroquinolones and their difluoroboron complexes.

Compound	ν (COOH)	ν (O–C=O)	ν (C=O, pyridone)	ν (B–F)	ν (B–O)
Norfloxacin	3425 (br, s)	1721 (s)	1624 (s)	–	–
Complex **1**	–	1706 (s)	1635 (s)	1178 (s)	1049 (vs)
Ciprofloxacin	3468 (br, s)	1709 (s)	1622 (s)	–	–
Complex **2**	–	1701 (s)	1634 (s)	1191 (s)	1055 (vs)
Enrofloxacin	3430 (br, s)	1733 (s)	1624 (s)	–	–
Complex **3**	–	1716 (s)	1635 (s)	1148 (s)	1053 (vs)
Tosufloxacin	3378 (br, s)	1725 (s)	1627 (s)	–	–
Complex **4**	3408 (s, ν_{NH_2})	1717 (s)	1643 (s)	1190 (s)	1062 (vs)
Sparfloxacin	3415 (br, s)	1714 (s)	1634 (s)	–	–
Complex **5**	3485 (s, ν_{NH_2})	1697 (s)	1648 (s)	1150 (s)	1042 (vs)
Levofloxacin	3422 (br, s)	1724 (s)	1619 (s)	–	–
Complex **6**	–	1712 (s)	1630 (s)	1162 (s)	1049 (vs)