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研究简报

具有绿色荧光发射效应的氟喹诺酮-铀(Ⅵ)配合物

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关键词:铀(Ⅵ)配合物;水热合成;晶体结构;荧光性质
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Uranium(Ⅵ) Complex Based on a Fluoroquinolone Ligand with Green Fluorescent Emission

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Abstract: A uranium(Ⅵ) complex [UO_2(1-ethyl-6,8-difluoro-7-(3-methyl-piperazinium-1-yl)-4-oxo-1,4-dihydro-quinoline-3-carboxylate)(NO_3)$_2$] was obtained by the hydrothermal treatment of $UO_2(NO_3)_2\cdot 6H_2O$ with lomefloxacin-HCl in water at 80 ℃ in Pyrex tube. The crystal belongs to monoclinic system, space group $P2_1/c$, with a=1.430(3) nm, b=1.032 1(18) nm, c=1.729(3) nm, β=106.67(3)°, V=2.458(6) nm^3, Z=4. This complex is a good green fluorescent material in solid state at room temperature. CCDC: 660959.

Key words: uranium(Ⅵ) complex; hydrothermal synthesis; crystal structure; fluorescence

Fluoroquinolones are broad spectrum antibiotics widely used for the treatment of numerous diseases. Lomefloxacin (LFLX), (1-ethyl-6,8-difluoro-7-(3-methyl-piperazine-1-yl)-4-oxo-1,4-di-hydro-quinoline-3-carboxylic acid), is a widely representative member of this family. It is reported that quinolones can interact with di- and tri-valent metal ions, and some of the metal complexes formed possess improved water solubility and anti-bacterial activity[1], which has been reported to subsequently increase antibacterial activity of these class of compounds[2]. Therefore, many complexes of quinolone and metal ion have been reported recently[3~16]. Herein, we report the synthesis and crystal structure of a new kind of uranium coordination compound with lomefloxacin. [UO_2(1-ethyl-6,8-difluoro-7-(3-methyl-piperazinium-1-yl)-4-oxo-1,4-dihydro-quinoline-3-carboxylate)(NO_3)$_2$] was obtained by the hydrothermal treatment of $UO_2(NO_3)_2\cdot 6H_2O$ with Lomefloxacin-HCl in water at 80 ℃ in Pyrex tube, as shown in Scheme 1. The crystal belongs to monoclinic system, space group $P2_1/c$, with a=1.430(3) nm, b=1.032 1(18) nm, c=1.729(3) nm, β=106.67(3)°, V=2.458(6) nm^3, Z=4. This complex is a good green fluorescent material in solid state at room temperature.

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Compound [UO_2(1-ethyl-6,8-difluoro-7-(3-methyl-piperazinium-1-yl)-4-oxo-1,4-dihydro-quinoline-3-carboxylate)(NO_3)$_2$] is a hydrogen-bonding connected three dimension uranium(Ⅵ) complex. As Fig.1 shows, each uranium ion is coordinated by eight oxygen atoms in a

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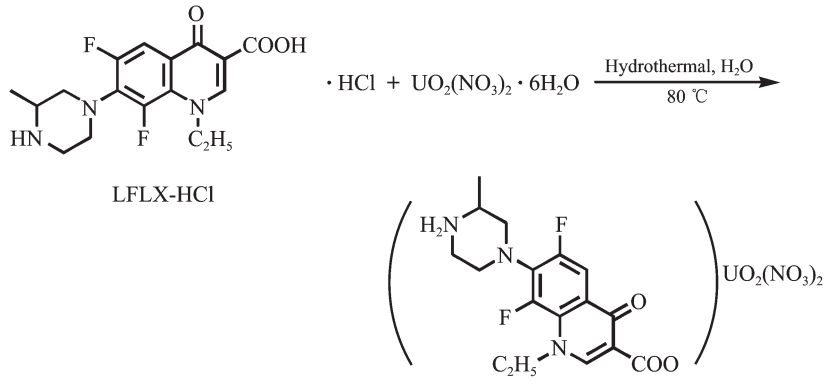

Scheme 1

hexagonal bipyramid arrangement. Every uranium center is bound axially to two oxygen atoms forming a uranyl group and the bond distance of U1-O3 is 0.183 6(17) nm, U1-O9 is 0.175 4(19) nm (O=U=O angle: 176.06(19)°), that is, three atoms (O3, U1, O9) lie almost in one line as shown in Table 1. The six equatorial coordination sites around the uranium center are occupied by four oxygen atoms of two individual nitrate groups and two oxygen atoms from lomefloxacin ligand, the lengths of coordinating bond U-O: 0.240 2 ~0.274 5 nm. On the other hand, every lomefloxacin as a double-dentate ligand coordinate to one uranium center. There is no classic hydrogen bondes in this compound, but many weak intra- and intermolecular hydrogen bonds exist, those are: hydrogen bonds among carbon hydrogens and oxygen atoms of the uranyl group (C19–H19A … O9 0.341 5 nm), uncoordinated oxygen atom of nitro groups (C5–H5A … O10 0.346 6 nm; C18–H18A … O13 0.304 5 nm), oxygen atom of uncoordinated carboxylate group (C5–H5A…O8 0.275 3 nm), and fluoro atoms (C4–H4A … F2 0.290 3 nm; C7–H7B … F2 0.281 0 nm; C18–H18B … F1 0.283 2 nm) to result in the formation of a

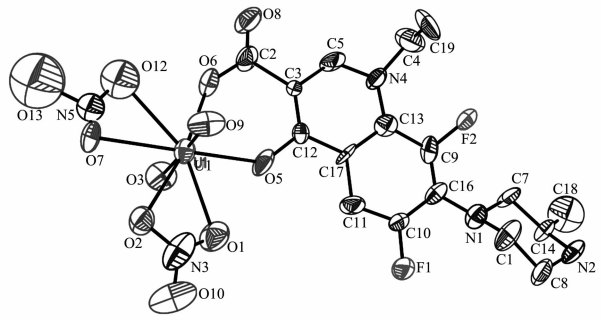

Fig.1　Asymmetric unit of $UO_2(LFLX)(NO_3)_2$, hydrogen atoms are omitted for clarity

Table 1　Selected bond lengths (nm) and angles (°) for compound $UO_2(LFLX)(NO_3)_2$]

U1-O9	0.175 4(19)	U1-O3	0.183 6(17)	U1-O6	0.240(2)
U1-O5	0.241 7(19)	U1-O1	0.259(3)	U1-O7	0.262(2)
U1-O2	0.263(2)	U1-O12	0.274(5)	F2-C9	0.143(3)
F1-C10	0.135(3)				
O9-U1-O3	176.2(12)	O9-U1-O6	89.5(9)	O3-U1-O6	91.4(10)
O9-U1-O5	92.9(11)	O3-U1-O5	90.8(10)	O6-U1-O5	71.7(7)
O9-U1-O1	92.5(10)	O3-U1-O1	89.0(10)	O6-U1-O1	142.1(9)
O5-U1-O1	70.9(9)	O9-U1-O7	94.5(14)	O3-U1-O7	81.7(13)
O6-U1-O7	104.8(10)	O5-U1-O7	171.5(12)	O1-U1-O7	112.8(11)
O9-U1-O2	87.8(10)	O3-U1-O2	90.6(10)	O6-U1-O2	169.1(7)
O5-U1-O2	119.6(7)	O1-U1-O2	48.7(8)	O7-U1-O2	64.9(10)
O9-U1-O12	91.6(13)	O3-U1-O12	85.6(14)	O6-U1-O12	61.8(12)
O5-U1-O12	132.7(12)	O1-U1-O12	155.7(13)	O7-U1-O12	43.0(12)
O2-U1-O12	107.6(12)				

new 3D framework uranium(Ⅵ) complex, as shown in Fig.2.

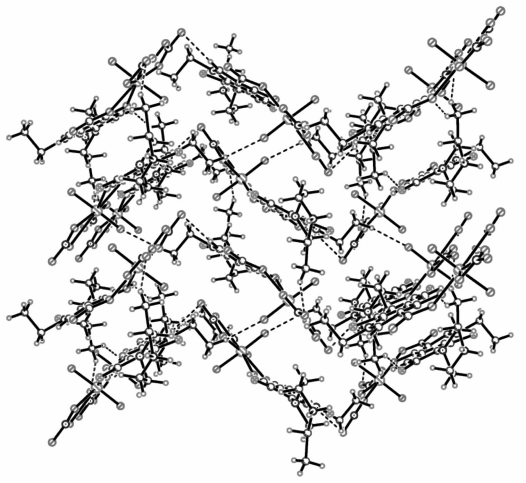

Fig.2 Hydrogen bonding interactions view of the complex (along *a* axis)

The fluorescent emission spectra for the complex wavelengths produced the characteristic vibronic structure of the UO^{2+} moiety which have five characteristic peaks of each spectrum ranged from about 425~500 nm and exhibit strong green fluorescent emission at room temperature in solid state (Fig.3).

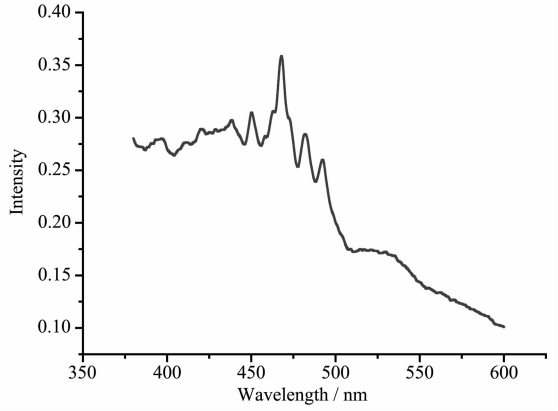

Fig.3 Fluorescence spectra of the complex in the solid state at room temperature

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