研究简报

一种含阻转异构体的二羧酸铀(Ⅵ)有机-金属配合物

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关键词:铀(Ⅵ)配合物;水热合成;晶体结构
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Uranium(Ⅵ) Metal-organic Framework with Atropisomeric Dicarboxylic Ligand

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Abstract: Uranium(Ⅵ) complex [UO_2((*R*,*S*)-1,1′-binaphthylene-2,2′-dicarboxylate)(H_2O)] was obtained by the hydrothermal treatment of $UO_2(NO_3)_2\cdot 6H_2O$ with (*R*,*S*)-1,1′-binaphthylene-2,2′-dicarboxylic acid(BCA) (L) in water at 180 ℃ in Pyrex tube. The crystal belongs to monoclinic system, space group *C*2/*c*, with *a*=1.640 3(3) nm, *b*=1.196 7(2) nm, *c*=1.066 3(17) nm, β=104.412(4)°, *V*=2.027 2(6) nm^3, *Z*=4. CCDC: 659617.

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

Hydrothermal chemistry has been demonstrated to be a highly versatile technique for the synthesis of new materials[1,2]. O′Hare group has synthesized a series of uranium coordination polymers under hydrothermal conditions, results showed those compounds exhibited novel networks, and indict stable porous actinide-organic frameworks can be achieved. However, there are few reports about the uranium coordination polymer with racemic organic ligands[3~11]. Herein, we would like to report the synthesis and crystal structure of a new kind of uranium coordination compound with atropisomeric ligand ((*R*,*S*)-1,1′-binaphthylene-2,2′-dicarboxylic acid. Uranium(Ⅵ) complex [UO_2((*R*,*SS*)-1,1′-binaph-thylene-2,2′-dicarboxylate) (H_2O)] was obtained by the hydrothermal treatment of $UO_2(NO_3)_2\cdot 6H_2O$ with (*R*,*S*)-1,1′-binaphthylene-2,2′-dicarboxylic acid(BCA) (L) in water at 180 ℃ in Pyrex tube, as shown in Scheme 1. The crystal belongs to monoclinic system, space group *C*2/*c*, with *a*=1.640 3(3) nm, *b*=1.196 7(2) nm, *c*=1.066 3(17) nm, β=104.412(4)°, *V*=2.027 2(6) nm^3, *Z*=4.

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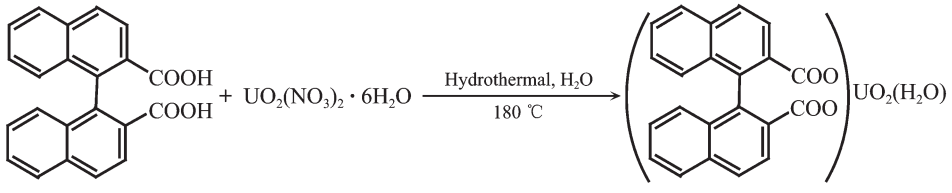
Compound [UO_2((*R*,*S*)-1,1′-binaphthylene-2,2′-di-



Scheme 1

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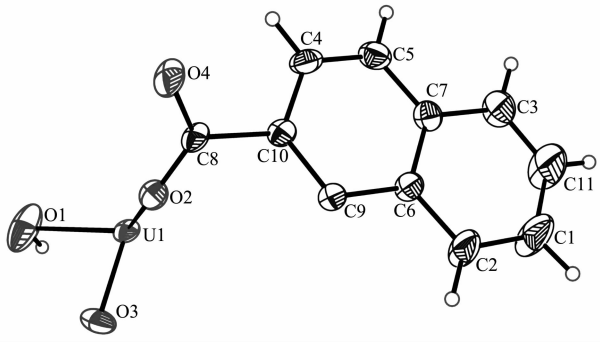
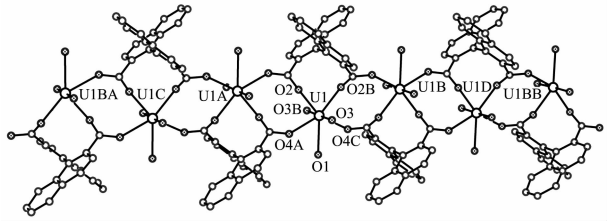
carboxylate)·(H_2O)] exhibits a one-dimension chain structure consisting of continuing dimers in which two uranium centers are linked through carboxylic group of the ligand (*R*,*S*)-1,1′-binaphthylene-2,2′-dicarboxylate (BC). Each uranium is coordinated by seven oxygen atoms in a pentagonal bipyramid arrangement (Fig.1). Every uranium center is bound axially to two oxygen atoms forming a uranyl group and the bond distance of U1-O3 is 0.175 6(6) nm (O=U=O angle: 178.2(3)°), that is, three atoms (O3, U1, O3B) lie almost in one line as shown in Table 1. The five equatorial coordination sites around the uranium center are occupied by one oxygen atom of water and four oxygen atoms from three different atropismeric ligands (BC). On the other hand, every BC as a quadridentate ligand coordinate to three uranium centers to form one-dimension chain as shown in Fig.2. Two naphthylene rings of every organic ligand distribute to two sides of the chain that is formed by the uranyl group, water and the carboxylic group of BC. At the same time, atropisomers are stereoisomers resulting from hindered rotation about single bonds, and the dihedral angle between two naphthalene rings is *ca.* 78.3°.



Drawn with 30% of probability

Fig.1　Asymmetric unit of the title complex



Hydrogen atoms are omitted for clarity

Fig.2　1D chain structure of the title complex

Table 1　Selected bond lengths (nm) and angles (°) for compound [UO_2((*R*,*S*)-1,1′-binaphthylene-2,2′-dicarboxylate)(H_2O)]

U1-O3	0.175 2(6)	O3-U1-O3B	178.2(3)	O4A-U1-O4C	128.4(3)	O3B-U1-O4A	89.6(3)
U1-O2	0.234 2(4)	O3B-U1-O2	89.6(2)	O3A-U1-O1	90.92(16)	O2B-U1-O4A	74.87(16)
U1-O4A	0.237 6(5)	O3B-U1-O2B	89.0(2)	O2A-U1-O1	139.08(11)	O3B-U1-O4C	91.2(3)
U1-O1	0.255 2(9)	O3-U1-O4A	91.2(3)	O4C-U1-O1	64.21(14)	O2B-U1-O4C	156.72(19)
U1-O3B	0.175 2(6)	O2-U1-O4A	156.72(19)	O3-U1-O2	89.0(2)	O3-U1-O1	90.92(16)
U1-O2B	0.234 2(4)	O3-U1-O4C	89.6(3)	O3-U1-O2B	89.6(2)	O2-U1-O1	139.08(11)
U1-O4C	0.237 6(5)	O2-U1-O4C	74.87(16)	O2-U1-O2B	81.8(2)	O4A-U1-O1	64.21(14)

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