研究简报

6,6′-二硝基-2,2′-联苯酸铀(Ⅵ)配聚物

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Uranium(Ⅵ) Coordination Polymer with 6,6′-dinitro-biphenyl-2,2′-dicarboxylic Acid Ligand

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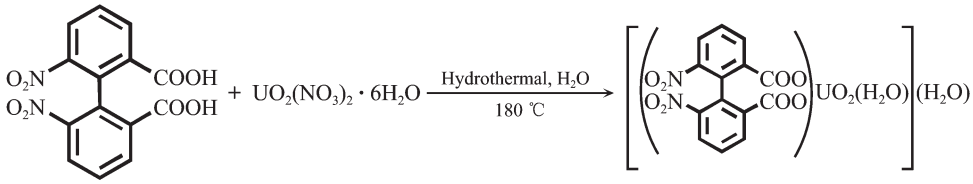
Abstract: Uranium(Ⅵ) complex {[UO_2((*R*,*S*)-1,1′-biphenyl-6,6′-dinitro-2,2′-dicarboxylate)(H_2O)](H_2O)} was obtained by the hydrothermal treatment of $UO_2(NO_3)_2\cdot 6H_2O$ with (*R*,*S*)-6,6′-dinitro-biphenyl-2,2′-dicarboxylic acid(BSNCA) (L) in water at 180 ℃ in Pyrex tube. The crystal belongs to triclinic system, space group $P\bar{1}$, with a=0.903 45(14) nm, b=1.024 43(16) nm, c=1.058 95(16) nm, α=90.411(3)°, β=112.934(3)°, γ=92.554(3)°. CCDC: 659613.

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

There have been extensive studies of metal-organic frameworks (MOFs) containing phenyldicarboxylic or biphenyldicarboylic acids as building block recently[1~4]. In some cases organic ligands are used to control the dimensionality or structures of MOFs, and the choices of the metal and the ligand depend upon the desired properties. And attentions were paid on synthesizing some organically template materials with actinide elements such as uranium, since this kind of compounds bear variety of coordination geometries and a number of stable oxidation states to form novel frameworks and can display catalytic, optical, magnetic, ion-exchange and interaction properties[5~16]. Herein we report a coordination polymer with ligand (*R*,*S*)-6,6′-dinitro-biphenyl-2,2′-dicarboxylic acid (BSNCA). The ligand (*R*,*S*)-6,6′-dinitro-biphenyl-2,2′-dicarboxylic acid is a good candidate of the atropisomeric ligands, uranium(Ⅵ) complex {[UO_2((*R*,*S*)-1,1′-biphenyl-6,6′-dinitro-2,2′-dicarboxylate)(H_2O)](H_2O)} was obtained by the hydrothermal treatment of $UO_2(NO_3)_2\cdot 6H_2O$ with (*R*,*S*)-6,6′-dinitro-biphenyl-2,2′-dicarboxylic acid (BSNCA) (L) in water at 180 ℃ in Pyrex tube (Scheme 1).



Scheme 1

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The crystal belongs to triclinic system, space group $P\bar{1}$, with a=0.903 45(14) nm, b=1.024 43(16) nm, c=1.058 95(16) nm, α=90.411(3)°, β=112.934(3)°, γ=92.554(3)°.

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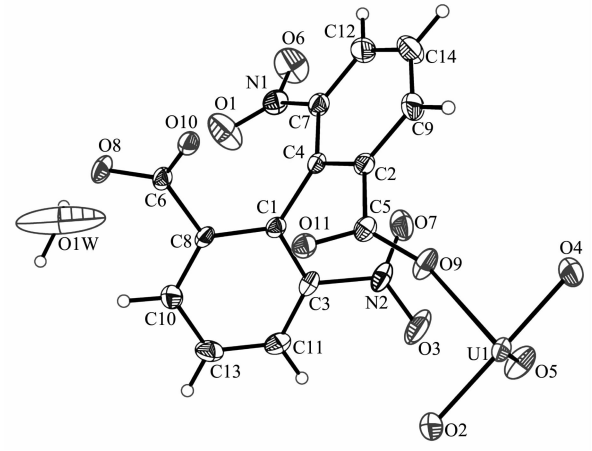
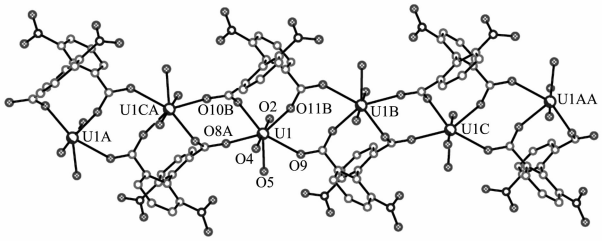
Fig.1 shows the oxygen atoms of nitro groups fail to coordinate to uranium center. Unexceptionally, the coordination environment of each uranium center can be best described as a pentagonal bipyramid defined by one oxygen of water, four oxygen of racemic atropisomeric ligand (*R*,*S*)-1,1′-biphenyl-6,6′-dinitro-2,2′-dicarboxylate (BSNC) and two oxygen belonging to uranyl group (Fig.1).



Drawn with 30% ellipsoids probability

Fig.1 Asymmetric unit of the complex

And identically, four oxygen atoms from three different atropisomeric ligands (BSNC) and one oxygen atom of water coordinate to uranium atom by occupying the five equatorial coordination sites, while the axial sites are occupied by two oxygen atoms to form uranyl group (U1-O4: 0.174 9(4) nm, U1-O2: 0.176 4(4) nm, O4-U1-O2 angle: 178.30(18)°). At the meantime, BSNC as a bridging ligand connects three uranium atoms through its four oxygen atoms of carboxylic group to result in the formation of 1D chain (Fig.2) and the dihedral angle of two phenyl rings is about 76.13°. It is worth noting that there are two kinds of strong hydrogen bonding interactions are observed: one is the hydrogen bonding between the uncoordinated water and coordinated water (O5–H⋯O1W: 0.259 8 nm), the other is hydrogen interactions between oxygen atoms (O2 and O6) of uncoordinated nitro group and uncoordinated water. The key bond distances and angles have been lain in Table 1, the length s of coordinating bond U-O: 0.234 2~0.255 2 nm.



Uncoordinated water and hydrogen atoms are omitted for clarity, operators for generating equivalent atoms: x, y, $z-1$; $-x$, $-y$, $-z+2$ and x, y, $z+1$

Fig.2 One-dimension chain of the complex

Table 1 Selected bond lengths (nm) and angles (°) for the complex

U1-O4	0.174 9(4)	U1-O2	0.176 4(4)	U1-O10B	0.233 5(4)
U1-O8A	0.236 5(4)	U1-O11B	0.236 7(4)	U1-O9	0.241 5(4)
U1-O5	0.247 8(4)				
O4-U1-O2	178.30(18)	O4-U1-O10B	88.42(19)	O2-U1-O10B	90.38(18)
O4-U1-O8A	92.68(19)	O2-U1-O8A	88.20(18)	O10B-U1-O8A	76.34(14)
O4-U1-O11B	90.15(19)	O2-U1-O11B	88.43(18)	O10B-U1-O11B	78.52(14)
O8A-U1-O11B	154.60(15)	O4-U1-O9	86.1(2)	O2-U1-O9	94.32(18)
O10B-U1-O9	150.10(14)	O8B-U1-O9	133.24(14)	O11B-U1-O9	72.13(13)
O4-U1-O5	92.3(2)	O2-U1-O5	89.4(2)	O10B-U1-O5	143.85(14)
O8A-U1-O5	67.52(15)	O11A-U1-O5	137.60(14)		

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