

铀-钾异核配位聚合物的合成及晶体结构

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摘要: 在水热反应条件下合成了 1 种新颖的 U(VI)-K 异核配位聚合物 $[\text{UO}_2\text{K}_2(\text{pdc})_2(\text{H}_2\text{O})_3]_n$ (H_2pdc = 吡啶-2,6-二羧酸), 通过元素分析、红外、紫外光谱及热重对该配合物进行了表征。单晶结构表明: 配合物属于单斜晶系, $C2/c$ 空间群; 晶胞参数分别为 $a=1.888\,5(6)$ nm, $b=1.490\,0(5)$ nm, $c=0.740\,2(2)$ nm, $\beta=111.104(10)^\circ$ 。中心铀及钾原子通过 2 个氮原子和 6 个氧原子与吡啶-2,6-二羧酸配体结合。不同的 $[\text{UO}_2\text{K}_2(\text{pdc})_2] \cdot 3\text{H}_2\text{O}$ 单元通过氧原子桥联组成三维链状配位聚合物。配位聚合物中存在 $\pi \cdots \pi$ 相互作用及氢键作用。CCDC: 727858。

关键词: 铀; 吡啶-2,6-二羧酸; 配位聚合物; 晶体结构

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Synthesis, Crystal Structure of Uranium-Potassium Heteronuclear Coordination Polymer

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Abstract: A novel U(VI)-K heteronuclear coordination polymer $\text{UO}_2\text{K}_2(\text{pdc})_2 \cdot 3\text{H}_2\text{O}$ (H_2pdc = pyridine-2,6-dicarboxylic acid) has been synthesized hydrothermally and determined by means of IR, UV and X-ray single-crystal diffraction methods. The single-crystal X-ray analysis of the complex reveals that the crystal belongs monoclinic, space group $C2/c$ with $a=1.888\,5(6)$ nm, $b=1.490\,0(5)$ nm, $c=0.740\,2(2)$ nm, $\beta=111.104(10)^\circ$. The centered uranium atom and potassium atoms are bonded to two pdc ligands via two nitrogen atoms and six oxygen atoms. Different $[\text{UO}_2\text{K}_2(\text{pdc})_2 \cdot 3\text{H}_2\text{O}]$ units are bridged by oxygen atoms to form three-dimensional chain coordination polymer. In addition, there are $\pi \cdots \pi$ stacking interactions and hydrogen bonds in the coordination polymer. CCDC: 727858.

Key words: uranium; pyridine-2,6-dicarboxylic acid; coordination polymer; crystal structure

The chemistry of metal-organic coordination assemblies has been enriched enormously in the past two decades, and a variety of coordination assembly polymers have been discovered^[1]. Uranium ions have attracted considerable interest because of their reactivity, coordination behavior, bonding interactions between the metal center and ligand and their possible applications^[2].

Recently, the construction of uranyl-organic

assemblies has attracted increasing interest, and a number of coordination compounds formed through the connection of uranyl units with various organic ligands have been prepared and structurally characterized. From a structural point of view, the uranyl ion is likely to form U-O (or U-F, U-N) polyhedra, which may be cross-linked by organic and/or inorganic components into chains, sheets, or three-dimensional frameworks. Furthermore, the U-O (or U-F, U-N) polyhedra have

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strong tendency to polymerize into various polynuclear clusters such as dinuclear, trinuclear, and tetranuclear clusters, infinite chains, or sheets of different local structures. As a result, a very rich structural chemistry may be found for uranyl-organic assembly polymers. Recently the synthesis and crystal structures of mixed uranyl/alkali metal ions complexes with homooxalix-arenes have been published^[3-4]. H₂pdc (pyridine-2,6-dicarboxylic acid) is an efficient ligand which is usually used as a tridentate ligand, as well as a bridging linker in the chemical design of metal-organic molecular assemblies^[5-9].

1 Experimental section

1.1 Materials and physical measurements

All materials and organic solvents were of analytical grade and were used without further purification. Distilled deionized water was used throughout. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 II CHNSO elemental analyzer. The infrared spectrum was recorded as a KBr pellet on a Nicolet 170SXFTIR spectrometer in the range 400 ~4 000 cm⁻¹. Thermogravimetric analyses (TG/DTA) were performed in flowing nitrogen gas on a Perkin-Elmer-7 instrument with a heating rate of 10 °C · min⁻¹ from room temperature to 900 °C. The electronic absorption spectra were taken on a Shimadzu UV-240 spectrophotometer.

1.2 Synthesis of the complexes

UO₂ (0.134 0 g) was solved in hot HCl (38%), H₂pdc was added into this solution. The mixture was stirred for half an hour in air, and the solution pH was

adjusted to 4.8 by the addition of KOH (2 mol · L⁻¹) solution. The mixture was then transferred to a Teflon-lined stainless steel autoclave (25 mL) and kept at 170 °C for 5 d. After the autoclave had cooled to room temperature, giving a blue solution. The resulting solution was evaporated slowly at room-temperature. After several days, crystals of this polymer were formed. Dry crystals disintegrated in air. Anal. Calc. for C₁₄H₁₂K₂N₂O₁₃U(%) : C, 22.94; H, 1.64; N, 3.82. Found (%): C, 23.90; H, 1.56; N, 3.86.

1.3 X-ray crystal structure determination

Single-crystal X-ray crystallographic analyses was performed at 291(2) K on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo K α (λ = 0.071 073 nm) radiation. Data collection, indexing, and initial cell refinements were carried out using SMART software^[10]. Frame integration and final cell refinements were carried out using SAINT software^[11]. Absorption corrections for each data set were applied using SADABS program^[12]. The single Crystal structure of title compound was solved by direct methods using the SHELXS^[13] and refined on F^2 by the full-matrix least-squares methods using the SHELXL program^[13]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located at their ideal positions as a riding mode. A summary of the crystallographic data and structural determination for the title polymer is listed in Table 1. Selected bond lengths and bond angles are provided in Table 2. More details on the crystallographic studies as well as atom displacement parameters are presented in the Supporting Information.

CCDC: 727858.

Table 1 Crystallographic parameters of the title complex

Formula	C ₁₄ H ₁₂ N ₂ O ₁₃ K ₂ U	Z	4
Formula weight	732.49	Absorption coefficient / mm ⁻¹	8.858
Temperature / K	291(2)	$F(000)$	1 376
Wavelength / nm	0.710 73	Index ranges	$-23 \leq h \leq 23, -15 \leq k \leq 18, -6 \leq l \leq 9$
Crystal system	Monoclinic	θ range for data collection / (°)	2.11 to 25.15
Space group	$C2/c$	Reflections collected	5 496
a / nm	1.8885(6)	Unique reflections	2 210
b / nm	1.490 0(5)	Completeness to $\theta=25.99^\circ$ / %	99.70
c / nm	0.740 2(2)	Final R indices ($I > 2\sigma(I)$)	$R_1=0.037\ 2, wR_2=0.091\ 1$
β / (°)	111.104(3)	R indices (all data)	$R_1=0.052\ 5, wR_2=0.093\ 5$
Volume / nm ³	1.943 2(11)	Largest diffraction peak and hole / (e ⁻ · nm ⁻³)	1.247, -1.413

(a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; (b) $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$; (c) $w^{-1} = [s^2(F_o^2)^2 + (0.06P)^2 + 1.99P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2 Main bond length (nm) and bond angles ($^{\circ}$) of the title complex

U1-O1	0.245 6(6)	U1-O3	0.244 1(6)	U1-O5	0.175 9(6)
U1-N1	0.266 5(8)	K1-O1	0.310 0(7)	K1-O2	0.302 3(6)
K1-O3	0.295 6(7)	K1-O4	0.286 3(7)	K1-O5	0.297 6(7)
K1-O6	0.271 3(6)	K1-O7	0.278 2(7)		
U1-O1-K1	88.21(19)	U1-O3-K1	91.86(19)	U1-O5-K1	107.9(3)
O1-K1-O3	48.13(17)	K1-O7-K1	103.6(2)	O2-K1-O4	163.38(19)
K1-O6-K1	97.6(3)	O6-K1-O7	83.23(14)	O4-K1-O6	108.66(18)
O4-K1-O7	70.3(2)	O1-U1-O3	119.4(2)	O3-U1-O5	89.8(3)
O5-U1-O5	180.0(6)	O1-U1-O5	89.3(2)		

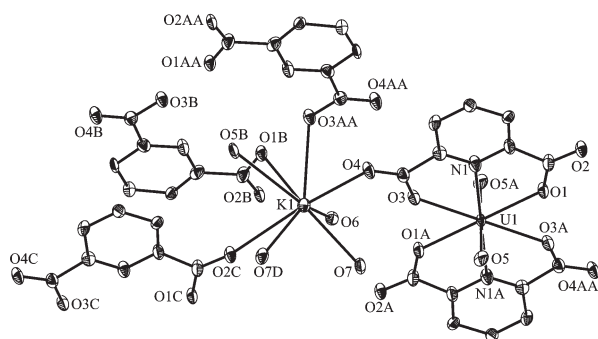
2 Results and discussion

2.1 Description of the crystal structure

Single-crystal X-ray structural analysis reveals that the uranium ion is eight coordinated. The axial positions of the dodecahedron are occupied by O5 atoms. The local coordination environment around U is depicted in Fig.1. Two ligands coordinate to uranium ion through four oxygen atoms and two nitrogen atoms. The U1-O3 (pdc), U1-O1 (pdc) bond distances ranging from 0.244 1(6) to 0.245 6(6) nm. U1-N1 bond distance is 0.266 5(8) nm. Both of uranium ion and two pdc ring are in the same plane, two O5 atoms at “polar” position and two pdc ligands at “equator” position. U1-O5 bond distance is 0.175 9(6) nm. While the O5-U1-O5 angles is $180.0(6)^{\circ}$. K^{+} is eight-coordinated. O1, O3, O5 still connect with K1, K1-O1, K1-O3, K1-O5 bond distances ranging from 0.310 0(7) to 0.295 6(7) nm, the U1-O1-K1, U1-O3-K1, U1-O5-K1 angles are $88.21(19)^{\circ}$, $91.86(19)^{\circ}$, $107.9(3)^{\circ}$. The four O atoms of pdc all ligate different potassium atoms. O1-K1-O3 angles is

$48.13(17)^{\circ}$. K1-O4 (pdc), K1-O2 (pdc) bond distances ranging from 0.286 3 (7) to 0.302 3 (6)nm. O2-K1-O4 angles is $163.38(19)^{\circ}$. Potassium atoms connect with each other through O7, O6. K1-O7 distance is 0.278 2(7) nm, K1-O6 is 0.271 3(6) nm. K1-O6-K1, K1-O7-K1 angles are $97.6(3)^{\circ}$, $103.6(2)^{\circ}$.

One U1 and two K1 atoms are bridged by three oxygen atoms, two free oxygen atoms and an oxygen atom from the pdc. Two potassium atoms are bridged by one oxygen atom from water. The interesting structural feature is to note that different $[UO_2K_2(pdc)_2 \cdot 3H_2O]$ units are linked by O4 from pdc and O6 from water to form a one-dimensional chain coordination polymer down c axis (Fig.2). Meanwhile, different $[UO_2K_2(pdc)_2 \cdot 3H_2O]$ units are also bridged by O7 from water to form another one-dimensional chain coordination polymer down a axis. Furthermore, the two-dimensional chain structures are associated with each other via O6, so that a 3D framework is formed (Fig.3).



Symmetry code: A: $1/2-x, 1/2-y, -z$; AA: $1-x, y, 1/2-z$; B: $1/2+x, 1/2-y, 1/2+z$; C: $1/2+x, 1/2+y, 1+z$; D: $1-x, y, 3/2-z$

Fig.1 Crystal structure of the coordination polymer

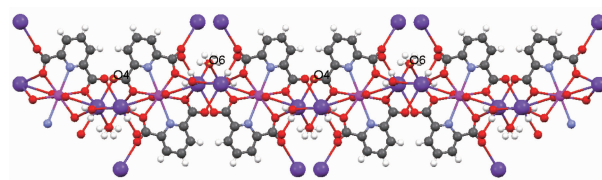


Fig.2 1D chain coordination polymer structure of the coordination polymer down c axis

The important intermolecular interaction is the offset face-to-face $\pi \cdots \pi$ stacking interaction between the benzene rings. The shortest $\pi \cdots \pi$ centroid-to-centroid distance between the offset face-to-face (dihedral angle between the two benzene rings is 5.85°) aromatic rings of neighbouring pdc ring is 0.370 2 nm,

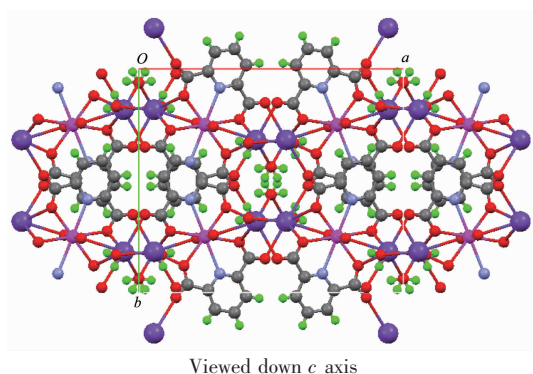


Fig.3 Packing of the molecules in a unit cell of the coordination polymer

Table 3 Hydrogen bonds length and bond angles of the title compound

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
O6-H6A...O2B	0.085 00	0.229 0	0.288 3(7)	127.0
O6-H6C...O2A	0.085 00	0.210 0	0.288 3(7)	153.0
O6-H7A...O2E	0.085 00	0.205 0	0.283 4(9)	154.0
O6-H7B...O3	0.085 00	0.225 0	0.287 4(9)	130.0
O6-H7B...O1A	0.085 00	0.229 0	0.300 9(9)	143.0

Symmetry code: A: $1/2+x, 1/2-y, 1/2+z$; B: $1/2-x, 1/2-y, -z$; E: $1/2-x, 1/2+y, 1/2-z$.

2.2 IR/UV spectra

The FTIR spectrum of the complex is consistent with the structural data. Characteristic bands of the dicarboxylate groups are at 1625 and 1586 cm^{-1} due to the asymmetric stretching. The strong band at 3406 cm^{-1} (O-H stretching vibration) indicates the presence of uncoordinated water molecules. The peak at 1425 cm^{-1} is assigned to the absorption of C=N group of pdc.

The UV spectrum of the complex was obtained in H_2O solution with H_2O as a reference. Two absorption bands at 225 and 267 nm were observed, they are strong and sharp, which may arise from the $\pi \rightarrow \pi^*$ transition of ligands.

2.3 TG analyses

The TGA measure (Fig.4) shows a three-step weight loss: the first loss of 4.48% occurs between room temperature and 71.5°C , corresponding to the loss of two coordinated water molecules, (calc. 4.37%). The second weight loss of 23.43% occurs in the range of $300\sim 413^\circ\text{C}$, resulting from the release of one pdc molecule (calc. 22.26%). The third step was attributed to the removal of another pdc ligand and inorganic components from 448 to 689°C with the lost weight of

hence, the $\pi \cdots \pi$ stacking interactions are very strong, lying in the range of reported distance $0.33\sim 0.38 \text{ nm}^{[14]}$. The hydrogen bonds have also been observed, which is shown in Table 3. The existences of hydrogen bonds increase the stability of the structure.

Observed along a^* axis, polymer showed a network structure, we can see same quadrilateral holes. The hole's area is $0.4229 \text{ nm} \times 0.2441 \text{ nm}$. This structure may have potential application value for the screening of match size of the molecules or molecular recognition.

58.50%.

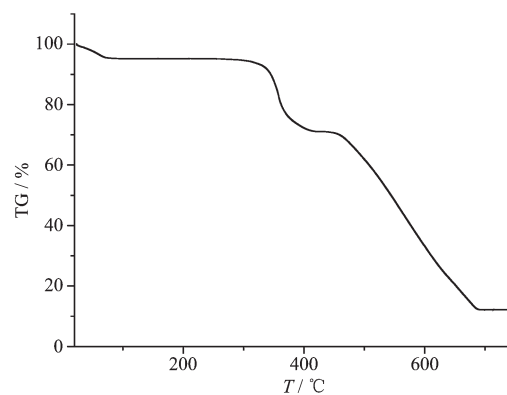


Fig.4 TG curve of the coordination polymer

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