



## 在 Demko-Sharpless 四唑合成反应中的一个意外的 不同配位模式的铀配合物

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### An Unexpected Uranyl(VI) Complex with Different Coordination Mode in Demko-Sharpless' Tetrazole Synthesis Reaction

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**Abstract:** Under hydrothermal conditions, the reaction of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with ligand 4-cyanopyridine *N*-oxide in the presence of  $\text{NaN}_3$  affords one complex,  $\{[(\text{POTZ})_2(\text{H}_2\text{O})_3(\text{UO}_2)](\text{H}_2\text{O})\}$  (**1**) ( $\text{POTZ}$ =4-tetrazolyl pyridine *N*-oxide), which is another example of a pyridine *N*-oxide complex of uranium and exhibit strong green fluorescent emission at room temperature. The structure was determined by single crystal X-ray diffraction. Crystal data:  $P2_1/m$ ,  $a=0.664\ 16(10)$  nm,  $b=2.104\ 1(3)$  nm,  $c=0.683\ 29(10)$  nm,  $\beta=93.295(3)^\circ$ ,  $V=0.953\ 3(2)$  nm<sup>3</sup>,  $Z=2$ ,  $R_1=0.033\ 7$ ,  $wR_2=0.083\ 3$ . CCDC: 241841.

**Key words:** uranium; tetrazole; coordination mode; fluorescent; hydrothermal synthesis

## 0 Introduction

Actinide compounds display unusual structural complexity and variability, concomitant with a wide range of physicochemical properties that may find applications in fabrication of devices with optical, magnetic, and catalytic properties<sup>[1-6]</sup>. The hydrothermal chemistry of uranium has been the subject of attention in recent years owing to the potential structural diversity resulting from the high coordination numbers available to  $\text{U}^{6+}$ <sup>[1-6]</sup>.

The tetrazole functional group has found a wide range of applications in coordination chemistry as lig-

ands, in medicinal chemistry as a metabolically stable surrogate for a carboxylic acid group, and in materials science as high density energy materials<sup>[7]</sup>. Recently, Demko and Sharpless have successfully reported a safe, convenient and environmentally friendly procedure for the synthesis of 5-substituted 1H-tetrazoles in water, this efficient, new synthetic approach offers exciting and fascinating prospects for the simple generation of a variety of new compounds<sup>[8]</sup>. A number of metal complexes have been successfully trapped which were regarded as intermediates during Demko-Sharpless' tetrazole synthesis, the coordination mode of those complexes usually used N atoms from tetra-

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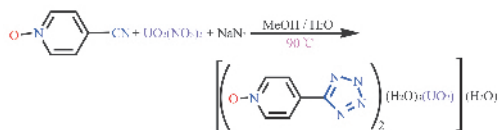
第一作者: 王锡森, 男, 28 岁, 博士生; 研究方向: 烯烃铜配位聚合物。

zoyl group coordination with metal ions<sup>[9]</sup>. Generally, 1H-tetrazoles were prepared by the addition of azide to nitriles in water using zinc salts (as Lewis acid) as catalysts, although the role of the Zn ion in this reaction is unclear. The use of other metal salts (such as  $\text{UO}_2^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  et al.) (as Lewis acid) as catalysts during Demko-Sharpless' tetrazole synthesis are hardly successful, because the cyano groups easily hydrolyze in acid solution<sup>[10]</sup> in the presence of  $\text{NaN}_3$ . Herein we report the first example of 1H-tetrazoles  $\{[(\text{POTZ})_2(\text{H}_2\text{O})_3(\text{UO}_2)](\text{H}_2\text{O})\}$  (**1**) [POTZ=4-tetrazolyl pyridine *N*-oxide] which was prepared by the addition of azide to nitriles in water using uranyl salts (as Lewis acid) as catalysts and the synthesis, solid-state structure, thermal stability and luminescent properties.

## 1 Experimental

### 1.1 Synthesis of $\{[(\text{POTZ})_2(\text{H}_2\text{O})_3(\text{UO}_2)](\text{H}_2\text{O})\}$ **1**

Complex **1** was prepared as shown in scheme 1. Hydrothermal treatment of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.052 0 g, 0.1 mmol) and 4-cyanopyridine oxide (0.012 0 g, 0.1 mmol) with  $\text{NaN}_3$  (0.009 8 g, 0.1 5mmol) and  $\text{H}_2\text{O}$  (1.5 mL), methanol (1 mL) were frozen and sealed under vacuum and placed inside an oven at 90 °C. Kelly block crystals were obtained after 10~12 h of heating which was only one phase. The yield of **1** was 60% based on uranium. (Calc: for **1**: C 22.67, H 3.15, N 35.31; Found for **1**: C 22.54, H 3.10, N 36.10. IR (KBr,  $\text{cm}^{-1}$ ) for **1**: 3 263(br,s), 3 127(w), 3 060(w), 2 080 (s), 1 654(m), 1 627(w), 1 531(m), 1 457(m), 1 439(m), 1 370(m), 1 297(m), 1 213(s), 1 191(s), 1 126(w), 1 066 (w), 956(w), 861(m), 842(m), 762(m), 708(w), 685(w), 654(m), 605(w), 582(w), 527(w), 464(w), 437(w).



Scheme 1

### 1.2 X-ray data collection and structure determination of **1**

A single crystal of **1** with dimensions of 0.20 mm  $\times$  0.20 mm  $\times$  0.10 mm was mounted with epoxy on a Pyrex fiber affixed to a brass pin and transferred to a Siemens SMART CCD area detector diffractometer equipped with Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073$  nm) using  $\omega$ -scan mode. The data collection covered over a

hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different  $\phi$  angle ( $0^\circ$ ,  $88^\circ$  and  $180^\circ$ ) for the crystal and each exposure of 30 s covered  $0.3^\circ$  in  $\omega$ . The crystal-to-detector distance was 4 cm and the detector swing angle was  $-35^\circ$ . Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analyzing the duplicate reflections and was found to be negligible. The unit cell parameters were determined using SMART and refined using SAINT. The three sets of data collected were reduced using SAINT. Empirical absorption correction was performed using SADABS. The structure was solved with direct methods and refined using the program SHELXTL. All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon

Table 1 Crystal data and structure refinement for **1**

Empirical formula	$\text{C}_{12}\text{H}_{16}\text{N}_{10}\text{O}_8\text{U}$
$F_w$	666.38
$T / \text{K}$	296(2)
Wavelength / nm	0.071 073
Crystal system	Monoclinic
Space group	$P2_1/m$
$a / \text{nm}$	0.664 16(10)
$b / \text{nm}$	2.104 1(3)
$c / \text{nm}$	0.683 29(10)
$\beta / ^\circ$	93.295(3)
$V / \text{nm}^3$	0.953 3(2)
$Z$	4
$\rho(\text{calc}) / (\text{g} \cdot \text{cm}^{-3})$	2.322
$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	8.582
$F(000)$	628
Crystal size / mm	$0.2 \times 0.2 \times 0.1$
$\theta$ range for data collection / $^\circ$	$1.94 \sim 26.00$
Index ranges	$-8 \leq h \leq 6, -25 \leq k \leq 22, -8 \leq l \leq 8$
Reflections collected	5 510
Independent reflections	1 926 [ $R(\text{int})=0.037\ 9$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	1 926 / 0 / 151
Goodness-of-fit on $F^2$	1.103
Final $R$ indices [ $I > 2\sigma(I)$ ](6 699)	$R_1=0.033\ 7, wR_2=0.083\ 3$
$R$ indices (all data)	$R_1=0.036\ 5, wR_2=0.084\ 7$

atoms. The final difference Fourier map was found to be almost featureless. Crystallographic data and bond

lengths and angles are summarized in Tables 1 and 2. CCDC: 241841.

**Table 2** Selected bond distances (nm) and angles (°) for **1**

U(1)-O(2)	0.175 4(6)	U(1)-O(1)	0.176 8(6)	U(1)-O(4)#1	0.237 3(4)
U(1)-O(4)	0.237 3(4)	U(1)-O(3)	0.239 3(6)	U(1)-O(5)#1	0.241 8(5)
U(1)-O(5)	0.241 8(5)	O(4)-N(5)	0.133 7(7)	C(6)-N(3)	0.132 1(8)
C(6)-N(4)	0.134 6(8)	N(4)-N(1)	0.134 9(7)	N(3)-N(2)	0.133 0(7)
N(2)-N(1)	0.131 9(8)	C(4)-C(3)	0.138 6(9)		
O(2)-U(1)-O(1)	178.9(2)	O(2)-U(1)-O(4)#1	91.1(2)	O(1)-U(1)-O(4)#1	89.8(2)
O(2)-U(1)-O(4)	91.1(2)	O(1)-U(1)-O(4)	89.8(2)	O(4)#1-U(1)-O(4)	69.7(2)
O(2)-U(1)-O(3)	88.8(3)	O(1)-U(1)-O(3)	90.1(3)	O(4)#1-U(1)-O(3)	145.14(12)
O(4)-U(1)-O(3)	145.14(12)	O(2)-U(1)-O(5)#1	91.81(13)	O(1)-U(1)-O(5)#1	87.86(13)
O(4)#1-U(1)-O(5)#1	72.36(17)	O(4)-U(1)-O(5)#1	142.02(17)	O(3)-U(1)-O(5)#1	72.80(13)
O(2)-U(1)-O(5)	91.81(13)	O(1)-U(1)-O(5)	87.86(13)	O(4)#1-U(1)-O(5)	142.02(17)
O(4)-U(1)-O(5)	72.36(17)	O(3)-U(1)-O(5)	72.80(13)	O(5)#1-U(1)-O(5)	145.3(3)
N(5)-O(4)-U(1)	127.0(3)				

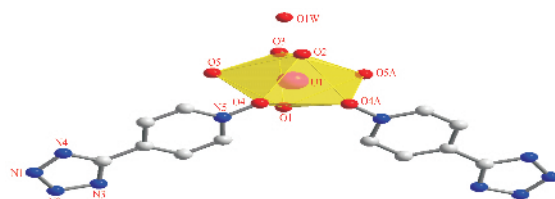
Symmetry transformations used to generate equivalent atoms: #1:  $x, -y+3/2, z$ .

## 2 Results and discussion

The IR spectrum of compound **1** shows the absence of a cyano peak in the  $2100\text{ cm}^{-1}$  region, which supports the proposed reaction between the nitrile and the azide. The formation of a tetrazole group is supported by the emergence of a peak at *ca.*  $1500\text{ cm}^{-1}$ . A peak at  $3400\sim 3500\text{ cm}^{-1}$  is that of water, as **1** contains coordinated water and perhaps uncoordinated water as well.

The monomeric structure of compound **1** was unveiled by an X-ray single-crystal diffraction study as shown in Fig.1. To our surprised, the ligand POTZ was synthesized in the reaction, but the coordination mode of the U ions with the ligand were different with other metal ions in Demko-Sharpless's tetrazole synthesis reaction. In general other metal ions coordinated with N atoms from tetrazoyl group of ligands synthesized in situ during Sharpless's tetrazole synthesis reaction, while only O atoms coordinated with U ions in this compound, which are unprecedented in tetrazole-metal coordination chemistry, as far as we are aware. This may suggest that  $\text{UO}_2^{2+}$  ions can be regard as catalysts (as Lewis acid) during this Demko-Sharpless's tetrazole synthesis reaction and tend to coordinate with oxygen atoms since the water molecules are very strong nucleophilic group during this reaction.

On the other hand, the coordination mode of  $\text{UO}_2^{2+}$  with O atom is normal in complexes containing  $\text{UO}_2^{2+}$  cations<sup>[2-6]</sup>.



**Fig.1** Polyhedral representation of **1** shows the local coordination geometry around U centers has a distorted hexagonal bipyramidal

The local coordination environment around U atom in **1** can best be described as a distorted pentagonal bipyramid with two O atoms from uranyl ion in the axial positions and five oxygen atoms in the plane, two oxygen atoms are from N-oxides and three oxygen atoms are from water. The  $\text{UO}_2^{2+}$  group is linear with usual values (U(1)-O(1) 0.176 8(6), U(1)-O(2) 0.175 4(6) nm) for the  $\text{U}=\text{O}$  distances; The  $\text{U}-\text{O}(\text{H}_2\text{O})$  bond distance (U(1)-O(3) 0.239 3(6); U(1)-O(5) 0.241 8(5) nm) are of the same order. The  $\text{U}-\text{O}(\text{ligand})$  length (U(1)-O(4) 0.237 3(4) nm) compare well with 0.232 1 nm (mean) in  $[\text{UO}_2(\text{pyOS})_2\text{dmsO}]$ , with 0.234 7 nm in  $[\text{UO}_2(\text{pyOO})_2\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$ , with 0.237 8 nm (mean) in  $[\text{UO}_2(\text{bipyOO})(\text{NO}_3)_2]$ , with 0.234 5 nm in  $\text{UO}_2(\text{NO}_3)_2[(\text{EtO})_2\text{P}(\text{O})\text{pyO}]^{[11]}$ , with 0.238 2 nm in  $\text{UO}_2(\text{NO}_3)[\text{Ph}_2\text{P}(\text{O})\text{pyO}]^{[11]}$ ,

with 0.237 6(2) nm in  $[\text{UO}_2(4\text{-CH}_3\text{pyO})_2(\text{NO}_3)_2]^{[12]}$ , and 0.236 1(5) nm in  $[\text{UO}_2(\text{TTA})_2 \cdot p\text{-NO}_2\text{-C}_5\text{H}_4\text{NO}]^{[13]}$ . In this Uranium(VI) dioxo complex, two deprotonated tetrazolyl group of different ligand compensated the charge of the  $\text{UO}_2^{2+}$  unit and no hydroxo ligands involved in the structure.

It is notable that in complex **1** the N atoms of the tetrazolyl group of POTZ are hydrogen bonded to coordinated waters and uncoordinated water, and the coordinated waters and uncoordinated water are also linked by hydrogen bonding (Fig.2). Moreover, there are the stabilizing  $\pi\text{-}\pi$  interactions (about 0.354 nm) of adjacent complexes. Thus the hydrogen bond and  $\pi\text{-}\pi$  interactions among ligands and waters formed three-dimensional network as shown in Fig.2. As far as we are aware, complex **1** is the first examples of uranyl(VI) complex containing tetrazole ligand synthesized *in situ*.

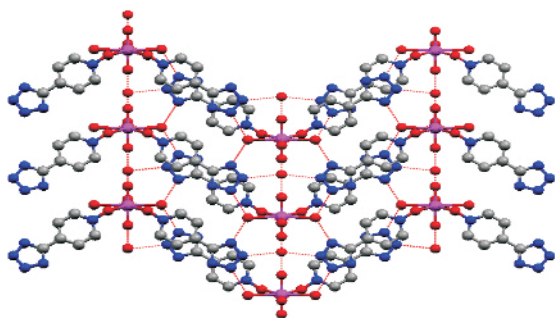


Fig.2 3-D network representation of **1** through H-bonds and  $\pi\text{-}\pi$  interactions

The dot line represent hydrogen bonds.

Hydrogen bonds (nm):

O1W-H1WB $\cdots$ O1, 0.293 96(4);

O1W-H1WB $\cdots$ N1, 0.294 18;

O3-H3C $\cdots$ O4, 0.295 37;

O3-H3D $\cdots$ O1W, 0.260 82(4);

O5-H5A $\cdots$ N4, 0.273 97;

O5-H5B $\cdots$ N2, 0.274 43;

C1-H1A $\cdots$ N3, 0.327 70

Thermogravimetric analysis (TGA) of the polycrystalline sample **1** showed that one discrete weight loss (9.33%) occurred at 120~200  $^{\circ}\text{C}$ , corresponding to the removal of three water molecules per formula unit (10.80% calculated). Beyond 235  $^{\circ}\text{C}$ , the decomposition of the network apparently occurred. On the other hand, complex **1** exhibit strong green fluorescent emission when irradiated with 367 nm light at room temperature (Fig.3), which is typical for the uranyl

fluorescent spectrum<sup>[1-6]</sup>.

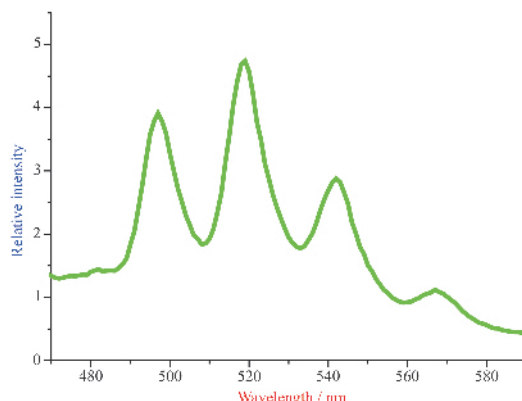


Fig.3 Solid state fluorescent emission spectrum of **1** at room temperature ( $\lambda_{\text{ex}}=367$  nm)

The results presented here demonstrate the value of hydrothermal approaches in the generation of novel complexes. This work described provides strong encouragement that novel metal coordination polymers may be produced by the hydrothermal generation of bridging ligand in the presence of appropriate metal ions.

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