



Synthesis and Characterization of a Layered Uranium Phosphites

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Abstract

A novel layered oxouranium phosphite open-structure $[\text{C}_{10}\text{H}_{24}\text{N}_2] \cdot [(\text{UO}_2)_2(\text{HPO}_3)_3] \cdot \text{H}_2\text{O}$ (denoted as ZZ-1) was hydrothermally synthesized by using isophorondiamine (IPDA) as the template. Single crystal structure refinement discloses that ZZ-1 crystallizes in the monoclinic space group $\text{P}2_1\text{c}$ with the cell parameters of $a = 18.347(4)\text{\AA}$, $b = 6.7341(13)\text{\AA}$, $c = 20.639(4)\text{\AA}$, $\beta = 114.61(3)^\circ$, $V = 2318.2(8)\text{\AA}^3$, $Z = 2$. The structure of ZZ-1 is constructed by UO_7 monomer, U_2O_{12} dimer and HPO_3 groups. The monomeric UO_7 or dimeric U_2O_{12} is connected by HPO_3 groups to form two types of 4-ring chains. An undulating sheet is then generated by connecting these two types of chains via HPO_3 bridges. The layer structure is formed by stacking the sheet along the direction with the organoamine cations and water molecules intercalated in the interlayer spaces with strong H-bonds to the framework oxygen atoms. Although a mixture of cis and trans IPDA is used, only cis PDA serves as the template. A typical green light emission of UO_2^{2+} is observed when excited by 266 nm laser.

Keywords: Hydrothermal synthesis, Open-framework compound, Single crystal structure, Template synthesis, Oxouranium phosphite

1. Introduction

Open-framework materials have been extensively pursued due to their structural diversities and potential applications in catalysis, absorption, separation, ion-exchange and host-guest chemistry. Recently, replacing tetrahedral HOPO_3^{2-} by pseudo pyramidal HPO_3^{2-} has been demonstrated to be an effective approach to generate more open framework structures. The occurrence of HOPO_3 , $\text{O}=\text{PO}_3$ groups in some large pore zeolitic compounds verified its possibility. From this view, replacing tetrahedral phosphate groups by pseudo-pyramidal phosphite units has been considerably explored and resulted in a new family of metal phosphite compounds in the past decade. Metal phosphites with novel structures and compositions have experienced dramatic expansion under the assistance of various organoamines. Crystals with extra-large pores were also achieved, including TJPU-3 with 20-ring apertures, ZnHPO-CJ1 and Cr-NKU-24 with 24-ring openings, and NTHU-5 with the largest 26-ring micropores. As well-known, uranium is fruitful in coordination geometry and valence state, which lead to structural versatility of uranium-containing framework. However, open-framework uranium phosphites are seldom in the documents.

On the other hand, organic isomer separation and recognition have stimulated extensive research into the preparation of separation media. Inorganic matrix for isomer recognition have been considerably pursued but the occurrence is scarce. Successful examples for isomer separation include the ND-1 and a tin phosphate that only use trans-1,2-diaminocyclohexane as the template. Herein, by using isophorondiamine (IPDA) as the template, a layered oxouranium phosphite, $[\text{C}_{10}\text{H}_{24}\text{N}_2] \cdot [(\text{UO}_2)_2(\text{HPO}_3)_3] \cdot \text{H}_2\text{O}$ (ZZ-1) was isolated. Only cis-IPDA served as template.

2. Experimental

ZZ-1 was hydrothermally synthesized by using isophorondiamine (mixtures of cis- and trans- isomers, Aldrich) as the template. All chemicals were used without purification. Typically, 0.107g $\text{UO}_2(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, 0.116g H_3PO_3 and 0.042g IPDA were dispersed into 5ml distilled water. After stirred for 1.5hs, the mixture was sealed in an autoclave and heated at 180 °C for 144hs. The hydrothermal reaction produced yellow stick-like crystals, which were washed by distilled water and dried at room temperature. The experimental and simulated XRD patterns are well matched,

indicating the monophasic feature of the products. EDAX measurement gave the U:P ratio of 2:3. XPS gave the binding energy of U4f7/2 of 381.2 eV that very close to the value of UO_3 , indicating the hexavalent state of U.

3. Results and discussion

ZZ-1 crystallizes in the monoclinic space group $\text{P}2_1\text{c}$. The asymmetric unit contains 31 non-hydrogen atoms (Figure 1A). The uranium atoms are all in pentagonal bipyramid geometry. Two vertex of the pentagonal bipyramid are occupied by acyl-oxygen atoms. While U(1) is a monomeric UO_7 , two adjacent U(2) O_7 groups are edge shared to form dimeric U_2O_{12} (Figure 1B and 1C). All the phosphorous atoms are pseudo pyramidal HPO_3 groups. A strong IR adsorption at 2378.1 cm^{-1} verifies the presence of P-H bonds.

Insert Figure 1 Here

Insert Figure 2 Here

The extended structure is built by UO_7 , U_2O_{12} , and HPO_3 groups. The connection of these groups generate two types of 4-ring chains running along b axis. These two types of chains alternatively align along ab plane with a cut angle of about 104° . Connecting these two types of chains generates an undulating sheet that extended along ab plane. Stacking these sheets along c axis gives rise to a layer structure. The interlayer spaces are occupied by diprotonated IPDA cations and water molecules with complex H-bond to the framework oxygen. Interestingly, all the IPDA cations are in cis- form (Figure 1C). The means isolation ZZ-1 lead to the separation of cis-IPDA from the isomer mixtures.

UV light excited green light emission is a well-known character for uranyl-containing compounds, which is usually used to determine the presence of U(VI) in minerals. The fine structures of photoluminescence spectra of ZZ-1 show typical emission features upon irradiation with 266 nm UV light (Figure 2B). A strong peak at 525 nm accompanied by four weaker peaks at 504, 549, 575, and 604 nm is observed as a typical phenomenon for UO_2^{2+} .

4. Summary

A new open-framework oxouranium phosphite, ZZ-1, has been synthesized under the hydrothermal condition by using isophorondiamine as the templates. It has a layered structure with the isophorondiamine cations and water molecules intercalated in the interlayer spaces. The connection of the UO_6 pentagonal bipyramids and HPO_3 pseudo pyramids generates two kinds of chain structures. These two types of chains fuse to form a 4,8-network sheet that are stacking to generate the layer structure. As well, separation of IPDA isomers is achieved by isolating ZZ-1 crystals. Fluorescent spectroscopy analysis reveals that the uranium phosphite exhibits interesting intense photoluminescence upon photoexcitation at 266 nm.

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Table 1. Details of data collection and structure refinement of ZZ-1

Empirical formula	[C ₁₀ H ₂₄ N ₂].[(UO ₂) ₂ (HPO ₃) ₃].H ₂ O
Formula weight	1940.64
Temperature	293(2) K
Wavelength	0.71073
Unit cell dimensions	<i>a</i> (Å)
	<i>b</i> (Å)
	<i>c</i> (Å)
	β (°)
Volume (Å ³)	2318.2(8)
Z, calculated density	2, 2.78g/cm ³
Absorption coefficient	14.228 mm ⁻¹
F(000)	1776
Crystal size	0.2 x 0.2 x 0.2 mm
Theta range for data collection	2.44 - 25.02 °
Limiting indices	-21 ≤ h ≤ 21, -8 ≤ k ≤ 7, -23 ≤ l ≤ 24
Reflections collected / unique	19331 / 4054 [R(int) = 0.0579]
Completeness to theta = 24.99	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.2849
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.018
Final R indices [I > 2sigma(I)]	R1 = 0.0275, wR2 = 0.648
R indices (all data)	R1 = 0.0325, wR2 = 0.658
Largest diff. peak and hole	1.068 and -1.352 e.Å ⁻³

Table 2. Selected bonds and angles for ZZ-1

Bond lengths			
U1–O4	1.772(5)	U2–O10	1.756(5)
U1–O6	1.775(5)	U2–O11	1.773(5)
U1–O1 ^{#2}	2.314(5)	U2–O8	2.272(5)
U1–O5	2.315(5)	U2–O9	2.318(5)
U1–O2	2.340(4)	U2–O13 ^{#2}	2.378(5)
U1–O7	2.470(5)	U2–O12	2.472(4)
U1–O3	2.538(5)	U2–O13	2.594(5)
P1–O1	1.508(5)	P2–O8	1.518(5)
P1–O2	1.513(5)	P2–O7	1.531(5)
P1–O5 ^{#1}	1.533(5)	P2–O3	1.533(5)
P3–O9 ^{#1}	1.509(5)	O5–P1 ^{#1}	1.533(5)
P3–O12	1.527(5)	O9–P3 ^{#1}	1.509(5)
P3–O13	1.534(5)	O13–U2 ^{#2}	2.378(5)
O1–U1 ^{#2}	2.314(5)		
Bond angles			
O4–U1–O6	177.6(2)	O10–U2–O11	179.8(2)
O4–U1–O1 ^{#2}	89.2(2)	O10–U2–O8	86.0(2)
O6–U1–O1 ^{#2}	93.2(2)	O11–U2–O8	93.8(2)
O4–U1–O5	90.98(19)	O10–U2–O9	92.1(2)
O6–U1–O5	89.40(18)	O11–U2–O9	87.85(19)
O1 ^{#2} –U1–O5	79.71(16)	O8–U2–O9	82.02(16)
O4–U1–O2	91.76(19)	O10–U2–O13 ^{#2}	88.6(2)
O6–U1–O2	88.77(18)	O11–U2–O13 ^{#2}	91.6(2)
O1 ^{#2} –U1–O2	78.27(16)	O8–U2–O13 ^{#2}	161.45(16)
O5–U1–O2	157.76(17)	O9–U2–O13 ^{#2}	80.44(16)
O4–U1–O7	86.5(2)	O10–U2–O12	92.63(19)
O6–U1–O7	91.3(2)	O11–U2–O12	87.35(18)
O1 ^{#2} –U1–O7	154.22(15)	O8–U2–O12	77.23(16)
O5–U1–O7	74.97(16)	O9–U2–O12	158.34(16)
O2–U1–O7	127.22(16)	O13 ^{#2} –U2–O12	120.80(15)
O4–U1–O3	91.88(19)	O10–U2–O13	83.1(2)
O6–U1–O3	86.15(19)	O11–U2–O13	97.0(2)
O1 ^{#2} –U1–O3	147.06(15)	O8–U2–O13	131.69(16)
O5–U1–O3	133.16(16)	O9–U2–O13	145.11(15)
O2–U1–O3	68.79(16)	O13 ^{#2} –U2–O13	64.95(18)
O7–U1–O3	58.58(15)	O12–U2–O13	56.53(14)
O1–P1–O2	112.0(3)	O8–P2–O7	114.6(3)
O1–P1–O5 ^{#1}	113.4(3)	O8–P2–O3	114.3(3)
O2–P1–O5 ^{#1}	109.4(3)	O7–P2–O3	106.2(3)
O9 ^{#1} –P3–O12	115.2(3)	P1–O1–U1 ^{#2}	138.6(3)
O9 ^{#1} –P3–O13	113.2(3)	P1–O2–U1	136.9(3)
O12–P3–O13	103.3(3)	P2–O3–U1	96.0(2)
P1 ^{#1} –O5–U1	141.4(3)	P3–O12–U2	101.7(2)
P2–O7–U1	98.8(2)	P3–O13–U2 ^{#2}	148.5(3)
P2–O8–U2	147.5(3)	P3–O13–U2	96.4(2)
P3 ^{#1} –O9–U2	144.8(3)	U2 ^{#2} –O13–U2	115.05(17)

Symmetry transformation used to generate equivalent atoms: 1: -x+1, -y, -z+1; 2: x, y+1, z.

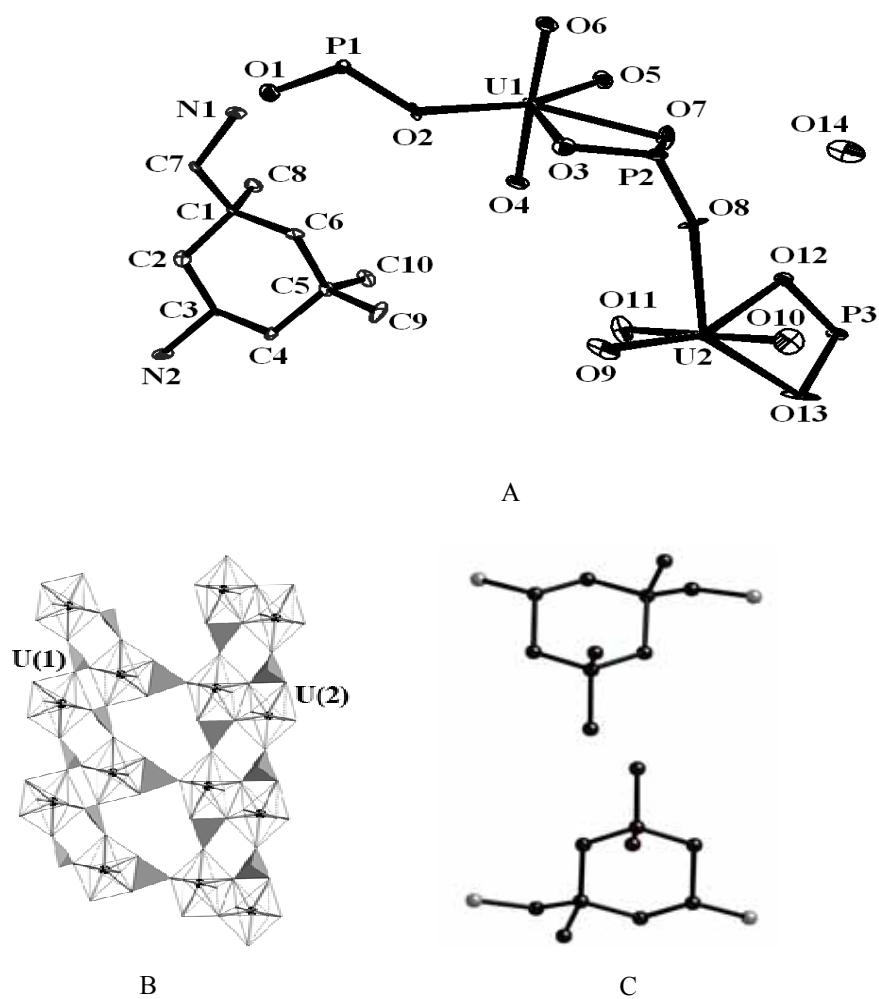


Figure 1. ORTEP plot of ZZ-1 showing the labeling scheme(A); Polyhedral representations of the two types of four-ring chains in ZZ-1(B): HPO_3 linked $\text{U}(1)\text{O}_7$ monomer and HPO_3 connected $\text{U}(2)_2\text{O}_{12}$, and (C) ball and stick model of the IPDA cations in cis- conformation.

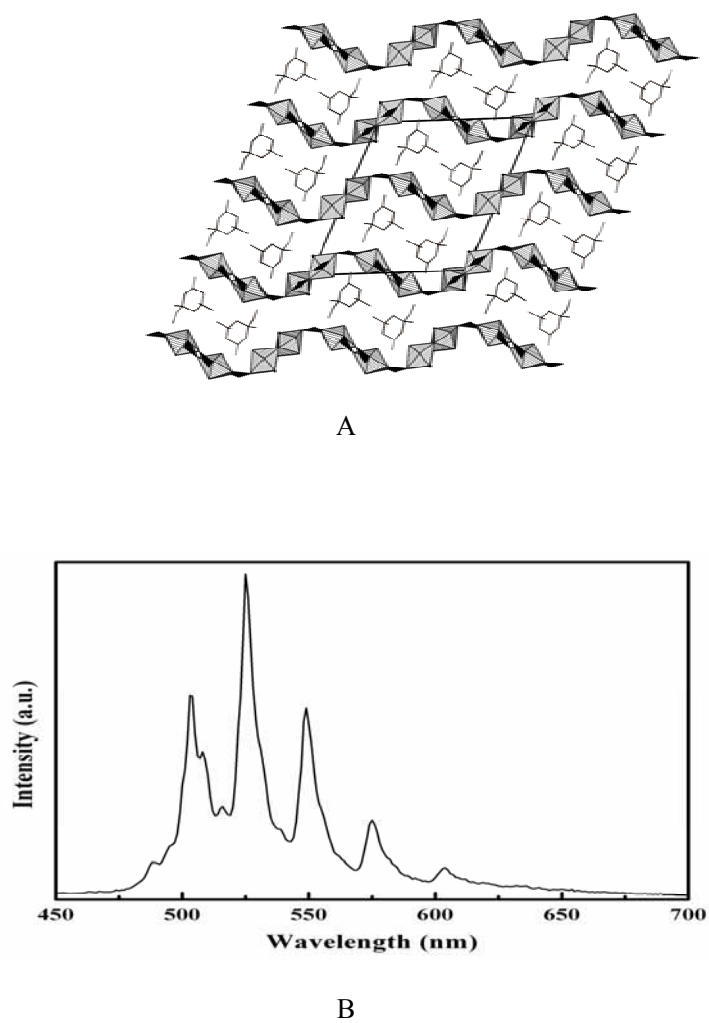


Figure 2. The layer structure with the intercalated H_2IPDA cations of ZZ-1 viewed along the b direction

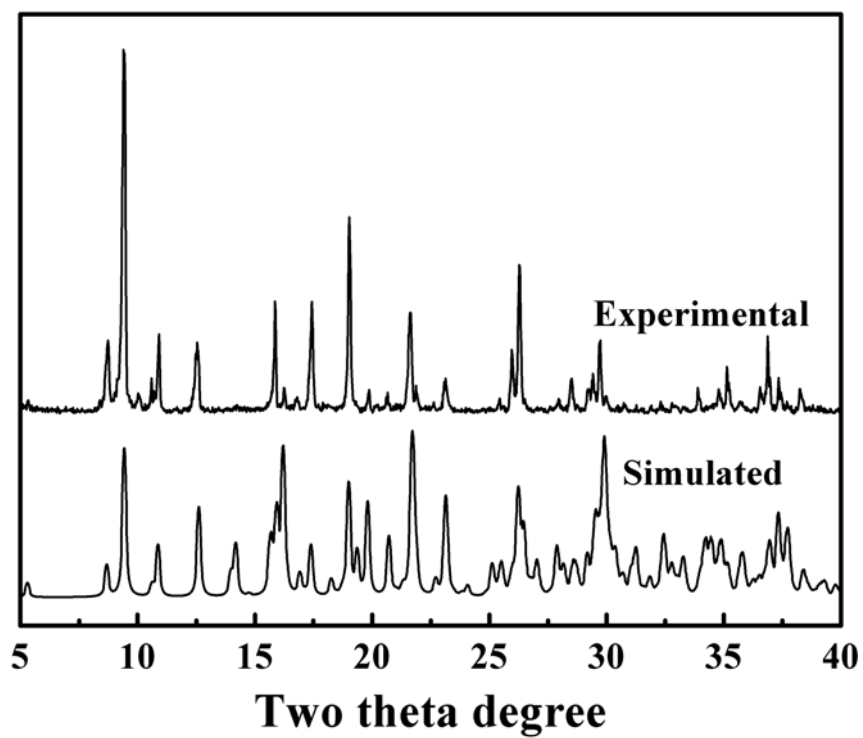


Figure 3. Simulated and experimental XRD patterns for ZZ-1

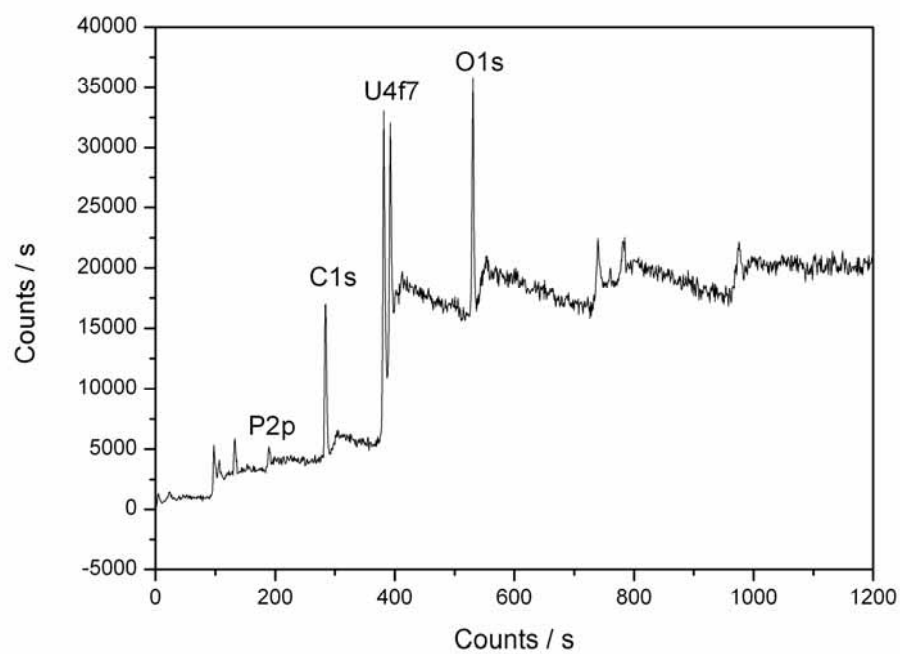


Figure 4. XPS curve for ZZ-1