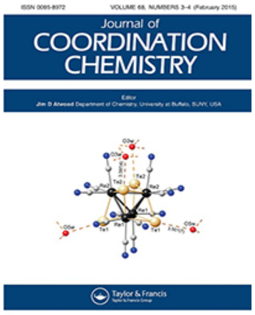

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Design, synthesis and structure of uranyl coordination polymers from 2-D layer to 3-D network structure

SI YUE WEI†, FENG YING BAI‡, YA NAN HOU†, XIAO XI ZHANG†, XUE TING XU†, JI XIAO WANG†, HUAN ZHI ZHANG§ and YONG HENG XING*†

†College of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, PR China
‡College of Life Sciences, Liaoning Normal University, Dalian, PR China
§Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin, PR China

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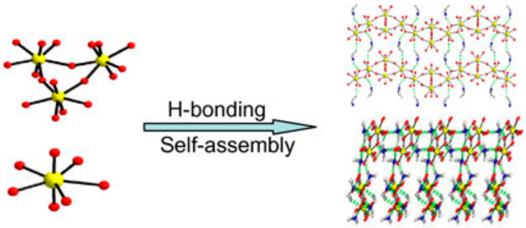

Solvothermal reaction of uranyl acetate and succinic acid in DMF resulted in formation of three uranyl coordination polymers, $[(UO_2)_4(\mu_2\text{-}OH)_7(OH)_6]\cdot 2(H_2O)\cdot(H_3O)\cdot 4NH_2(CH_3)_2$ (**1**), $[(UO_2)(\mu_2\text{-}OH)(OH)_3]\cdot 2NH_2(CH_3)_2]$ (**2**), and $[(DMF)_2(UO_2)(\mu_2\text{-}OH)_4(UO_2))]$ (**3**). The products were characterized by elemental analysis, IR spectroscopy, X-ray single crystal, and powder diffraction. Structural analysis shows that **1** is a layer, **2** and **3** are 3-D network structures.

Keywords: Coordination polymer; Solvothermal reaction; Crystal structure; DMF hydrolysis

1. Introduction

Uranyl compounds have attracted attention for potential applications in ion exchange [1, 2], proton conductivity [3], photochemistry [4, 5], nonlinear optical materials [6, 7], catalysis [8], and especially in energy and the military. The directed assembly of discrete molecules to build polymeric arrays is a topic of interest, and crystal engineering provides a tool for realization of such targets. The predictable self-assembly of low-dimensional molecules into high-dimensional frameworks through weak intermolecular interactions such as hydrogen bonds, weak van der Waals interactions, and π–π stacking is an important strategy in crystal

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*Corresponding author. Email: xingyongheng@lnnu.edu.cn engineering [9]. Oxygen and nitrogen-containing organic compounds are often used to construct diverse structures and functional uranyl compounds, providing the possibility of forming hydrogen-bonded network structures. In some cases, hydrogen bonds link uranyl discrete clusters to form chains, layers, or even 3-D network structures.

Design, synthesis, and structures of uranyl compounds composed of uranyl carboxylates such as $[UO_2)_3(Hcit)_2(H_2O)_3]\cdot 2H_2O$ [10], uranyl phosphonates and carboxyphosphonates such as $Co_2[(UO_2)_6(PO_3CH_2CO_2)_6(H_2O)_{13}]\cdot 6H_2O$ [11], and uranyl curbit[n]urils such as $[UO_2(CB_5)](ReO_4)_2\cdot 2H_2O$ and $[s_2(CB_5)(H_2O)_2][(UO_2)_2(HCOO)(OH)_4]_2\cdot 3H_2O$ [12] have been described. However, studies of uranyl coordination polymers with solvents as ligands are rare. The $UO_2{}^{2+}$ species with inactive U=O double bonds generally is coordinated only through equatorial ligands, yielding infinite chains or sheets, while 3-D framework structures are formed occasionally . In this work, three uranyl coordination polymers have been synthesized. We employ a common ligand (DMF) to connect UO_2^{2+} to form uranyl polymers from 2-D layer to 3-D network structures. DMF can be used as a solvent and a coordinated ligand. DMF is easily hydrolyzed, producing $NH_2(CH_3)_2{}^+$ in strong acid, strong base, or high temperature [13]. In this paper, we use these properties of DMF hydrolysis and coordination to construct three uranyl coordination polymers, $[(UO_2)_4(\mu_2\text{-}OH)_7(OH)_6]\cdot 2(H_2O)\cdot(H_3O)\cdot 4NH_2(CH_3)_2$ (**1**), $[(UO_2)(\mu_2\text{-}OH)(OH)_3]\cdot 2NH_2(CH_3)_2]$ (**2**), and $[(DMF)_2(UO_2)(\mu_2\text{-}OH)_4(UO_2))]$ (**3**).

2. Experimental

2.1. *Materials and methods*

IR spectra were recorded on a JASCO FT/IR-480 PLUS Fourier transform spectrometer with pressed KBr pellets from 200 to 4000 cm^{-1} and a Bruker AXS TENSOR−27 FTIR spectrometer with KBr pellets from 4000 to 400 cm^{-1}. Elemental analyses for C, H, and N were carried out on a PerkinElmer 240C automatic analyzer. X-ray powder diffraction (PXRD) patterns were obtained on a Bruker Avance-D8 equipped with Cu Kα radiation ($\lambda = 1.54183$ Å), in the range $5° < 2\theta < 50°$, with a stepsize of 0.02° (2θ) and a count time of 2 s per step.

2.2. *Synthesis*

All chemicals purchased were of reagent grade or better and used without purification. *Caution*! While the uranium compound used in these studies contained depleted uranium, precautions are needed for handling radioactive materials, and all studies should be conducted in a laboratory dedicated to studies of radioactive materials.

2.2.1. Synthesis of $[(UO_2)_4(\mu_2\text{-}OH)_7(OH)_6]\cdot 2(H_2O)\cdot(H_3O)\cdot 4NH_2(CH_3)_2$ (1). A mixture of $UO_2(CH_3COO)_2\cdot 2H_2O$ (0.0326 g, 0.0769 mM) and succinic acid (0.0290 g, 0.25 mM) in DMF (4 mL) was stirred for 1 h at room temperature, then the pH adjusted to 7 by solution of sodium hydroxide (1 M). The mixture was introduced into a reaction kettle and heated statically at 160 °C for three days. Resulting light yellow product was then filtered off, washed with water, and dried in air. Anal. Calcd for $C_8H_{52}N_4O_{24}U_4$ (%): C, 6.23; H, 3.36; and N, 3.64. Found (%): C, 6.20; H, 3.29; and N, 3.69.

2.2.2. Synthesis of $[(UO_2)(\mu_2\text{-}OH)(OH)_3]\cdot 2NH_2(CH_3)_2]$ (2).

The preparation is similar to that of **1** except that the temperature was changed to 100 °C and pH adjusted to 2 by solution of nitric acid (1 M). Yellow crystals of **2** were obtained after washing by water several times. Anal. Calcd for $C_4H_{20}N_2O_6U$ (%): C, 11.2; H, 4.65; and N, 6.51. Found (%): C, 11.0; H, 4.61; and N, 6.42.

2.2.3. Synthesis of $[(DMF)_2(UO_2)(\mu_2\text{-}OH)_4(UO_2))]$ (3).

The preparation is similar to that of **1** except that the temperature was changed to 80 °C. Yellow crystals of **3** were obtained after washing by water several times. Anal. Calcd for $C_6H_{18}N_2O_{10}U_2$ (%): C, 9.55; H, 2.39; and N, 3.71. Found (%): C, 9.44; H, 1.94; and N, 3.60.

2.3. *X-ray crystallographic determination*

A single crystal with dimensions 0.58 mm × 0.34 mm × 0.18 mm for **1** was selected for structure determination. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) from $1.87 < \theta < 25.00°$. A total of 20,048 (4303 unique, $R_{\text{int}} = 0.0456$) reflections were measured. The structure of **2** was determined by single crystal X-ray diffraction. A yellow single crystal of **2** with dimensions 0.50 mm × 0.34 mm × 0.18 mm was mounted on a glass fiber. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) from $2.17 < \theta < 25.00°$. A total of 4612 (1941 unique, $R_{\text{int}} = 0.0575$) reflections were measured. In **2**, the largest diff. peak and hole are 7.418 and −4.975 e $Å^{-3}$ and the major residual peaks appear around U (U1–Q1 and U1–Q2 bond lengths are 0.883 and 0.902 Å).

The structure of **3** was determined by single crystal X-ray diffraction. A yellow single crystal of **3** with dimensions 0.44 mm × 0.38 mm × 0.13 mm was mounted on a glass fiber. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) from $2.17 < \theta < 25.00°$. A total of 9043 (3637 unique, $R_{\text{int}} = 0.0362$) reflections were measured. In **3**, the largest diff. peak and hole are 7.133 and −1.398 e $Å^{-3}$ and the major peaks appear around U (U1–Q1 and U2–Q2 bond lengths are 0.829 and 0.811 Å). Empirical absorption corrections were applied using multi-scan technique. All absorption corrections were performed using SADABS [14]. Crystal structures were solved by direct methods. All nonhydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using SHELXL-97 [15]. Hydrogens on carbon and nitrogen were fixed at calculated positions and refined using a riding model, but the hydrogens of lattice water molecule in **1** were found in the difference Fourier map. The hydrogens of the μ_2-O (O3, O5, O6, O10 for **1**; O3 for **2**; O3, O4, O5, O8 for **3**) and the U–Ot from terminal hydroxo ions (O4, O9, O14 for **1**; O4, O5, O6 for **2**) were not located. Crystal data and details of the data collection and the structure refinement are given in table 1. Selected bond distances and angles are given in table 2. Figures and drawings were made with Diamond 3.2.

Table 1. Crystal data of **1–3**.

Complexes	**1**	**2**	**3**
Formula	$C_8H_{52}N_4O_{24}U_4$	$C_4H_{20}N_2O_6U$	$C_6H_{18}N_2O_{10}U_2$
Formula weight	1540.66	430.25	754.28
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pnma*	*C2/c*	*C2/c*
a (Å)	17.0296(13)	13.620(4)	23.848(2)
b (Å)	22.1116(17)	8.709(2)	7.3947(7)
c (Å)	9.0134(7)	19.604(5)	17.0358(16)
α (°)	90	90	90
β (°)	90	100.957(4)	97.690(2)
γ (°)	90	90	90
V (Å^3)	3394.0(5)	2283.0(10)	2977.3(5)
Z	4	8	8
D_{Calcd} (g cm^{-3})	3.015	2.503	3.366
Crystal size/mm	0.58 × 0.34 × 0.18	0.50 × 0.34 × 0.18	0.44 × 0.38 × 0.13
F(0 0 0)	2752	1584	2656
μ (Mo-Kα)/mm^{-1}	19.114	14.224	21.777
θ (°)	1.84–28.34	2.79–24.99	1.72–28.37
Reflections collected	20,048	4612	9043
Independent reflections [$I > 2\sigma(I)$]	4303(3615)	1941(1687)	3637(2856)
Parameters	198	123	185
Goodness of fit	1.030	1.1	1.045
R^a	0.0427 (0.0535)^b	0.0877 (0.0950)^b	0.0390 (0.0565)^b
$wR_2{}^a$	0.1079 (0.1134)^b	0.2461 (0.2546)^b	0.0948 (0.1021)^b

$^a R = \Sigma$êêF_oê − êF_c êê/ΣêF_oê, $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$; [$F_o > 4\sigma(F_o)$].
^{b}Based on all data.

3. Results and discussion

3.1. *Synthesis*

$UO_2(CH_3COO)_2 \cdot 2H_2O$ and succinic acid were used as starting materials while a solvothermal synthesis assisted by DMF was adopted to prepare the uranyl complexes. Originally, we added succinic acid to the system to obtain a uranium coordination polymer with carboxylic acids [16], unfortunately, reaction results show that the succinic acid is not coordinated with uranyl, and protonated $NH_2(CH_3)_2{}^+$ cation, which is produced by DMF hydrolysis that connects with uranyl by hydrogen bonds or DMF directly coordinated with uranyl. When succinic acid was not added in the synthetic system, we do not obtain **1–3**. Thus, the addition of the succinic acid is necessary in the reaction. In the reactions, similarly, pH is also essential to the polymerization of uranyl. Isolated $UO_2{}^{2+}$ cations exist in aqueous solution (pH < 2.5). However, in less acidic media, the identity of uranyl species varies with the concentration of OH^-(aq) ions [17]. When pH > 2.5, $UO_2{}^{2+}$ tends to hydrolyze and polymerize, forming a number of polynuclear uranyl species, and then generate complex precipitates, such as $U_2O_5{}^{2+}$ and $U_3O_8{}^{2+}$ [17]. The main factors which influence the hydrolysis are temperature and the concentration of $UO_2{}^{2+}$. The process of UO_2^{2+} hydrolysis is shown below:

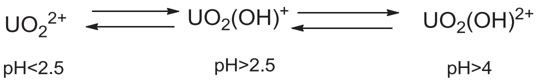

Table 2. Selected bond distances (Å) and angles (°) for **1–3.***

Complex **1**					
O(1)–U(1)	1.774(7)	O(2)–U(1)	1.767(7)	O(3)–U(1)	2.298(5)
O(4)–U(1)	2.251(5)	O(6)–U(1)	2.289(5)	O(7)–U(2)	1.767(9)
O(8)–U(2)	1.772(9)	O(9)–U(2)	2.258(5)	O(10)–U(2)	2.296(7)
O(11)–U(3)	1.774(9)	O(12)–U(3)	1.769(9)	O(10)–U(3)	2.313(7)
O(13)–U(3)	2.256(5)				
U(1)–O(3)–U(2)	157.1(2)	U(1)–O(6)–U(3)	161.4(3)	U(2)–O(10)–U(3)	146.9(4)
O(2)–U(1)–O(1)	178.3(4)	O(1)–U(1)–O(6)	90.3(3)	O(4)–U(1)–O(3)	76.17(19)
O(2)–U(1)–O(4)	91.1(3)	O(2)–U(1)–O(6)	90.3(3)	O(4)–U(1)–O(6)	154.87(19)
O(2)–U(1)–O(5)	89.7(3)	O(7)–U(2)–O(9)$^{\#2}$	90.8(3)	O(7)–U(2)–O(8)	178.7(4)
O(8)–U(2)–O(9)	90.3(3)	O(8)–U(2)–O(10)	89.8(4)	O(9)–U(2)–O(10)	143.38(14)
O(12)–U(3)–O(11)	179.1(4)	O(11)–U(3)–O(13)$^{\#2}$	91.2(3)	O(13)–U(3)–O(10)	141.76(14)
O(11)–U(3)–O(13)	91.2(3)	O(12)–U(3)–O(10)	88.1(4)	O(10)–U(3)–O(6)	68.98(13)
Complex **2**					
U(1)–O(1)	1.793(13)	U(1)–O(2)	1.792(12)	U(1)–O(4)	2.235(12)
U(1)–O(3)	2.364(11)	U(1)–O(5)	2.244(11)	U(1)–O(6)	2.323(10)
O(1)–U(1)–O(2)	177.3(7)	O(2)–U(1)–O(4)	92.4(6)	O(4)–U(1)–O(5)	77.7(5)
O(4)–U(1)–O(6)	151.5(5)	O(1)–U(1)–O(3)	90.5(6)	U(1)–O(3)–U(1)$^{\#1}$	115.5(4)
O(5)–U(1)–U(1)$^{\#1}$	178.2(4)	O(6)–U(1)–O(3)$^{\#1}$	136.8(4)	O(1)–U(1)–O(4)	92.4(6)
O(2)–U(1)–O(5)	89.7(7)	O(5)–U(1)–O(6)	73.9(4)	O(4)–U(1)–O(3)	136.1(5)
O(5)–U(1)–O(3)	146.1(4)	O(6)–U(1)–O(3)	72.3(4)	O(5)–U(1)–U(1)$^{\#1}$	178.2(4)
Complex **3**					
U(1)–O(1)	1.747(7)	U(1)–O(2)	1.755(8)	U(1)–O(4)	2.290(6)
U(1)–O(3)	2.324(6)	U(1)–O(5)$^{\#1}$	2.325(5)	U(1)–O(5)	2.327(5)
U(1)–O(3)$^{\#2}$	2.332(5)	U(1)–U(1)$^{\#1}$	3.9199(4)	U(1)–U(1)$^{\#2}$	3.9199(4)
U(2)–O(6)	1.746(7)	U(2)–O(7)	1.752(7)	U(2)–O(4)	2.291(6)
U(2)–O(8)	2.323(6)	U(2)–O(8)$^{\#3}$	2.331(6)	U(2)–O(10)	2.377(7)
U(2)–O(9)	2.382(8)	U(1)–U(1)$^{\#2}$	3.9199(4)	U(2)–U(2)$^{\#3}$	3.8961(8)
O(1)–U(1)–O(2)	179.2(4)	O(1)–U(1)–O(4)	87.8(3)	O(2)–U(1)–O(4)	91.5(3)
O(1)–U(1)–O(3)	92.6(3)	O(1)–U(1)–O(5)$^{\#1}$	89.1(3)	O(4)–U(1)–O(5)$^{\#1}$	140.9(2)
O(1)–U(1)–O(5)	90.4(3)	O(4)–U(1)–O(5)	77.7(2)	O(2)–U(1)–O(3)$^{\#2}$	90.7(3)
O(3)–U(1)–O(3)$^{\#2}$	141.33(15)	O(4)–U(1)–U(1)$^{\#2}$	109.96(16)	O(3)–U(1)–U(1)$^{\#2}$	173.89(13)
O(8)–U(2)–U(2)$^{\#3}$	33.24(15)	O(10)–U(2)–U(2)$^{\#3}$	104.07(19)	O(6)–U(2)–O(7)	178.7(4)
O(6)–U(2)–O(4)	91.2(3)	O(7)–U(2)–O(4)	89.7(3)	O(6)–U(2)–O(8)	90.4(3)
O(7)–U(2)–O(8)	88.3(3)	O(4)–U(2)–O(8)	138.6(2)	O(6)–U(2)–O(10)	88.2(3)
O(7)–U(2)–O(10)	91.5(3)	O(4)–U(2)–O(10)	150.5(2)	O(8)–U(2)–O(10)	70.9(2)
O(6)–U(2)–O(9)	91.5(3)	O(7)–U(2)–O(9)	89.6(3)	O(8)–U(2)–O(9)	145.7(3)

*Symmetry codes: #1: $-x$, $1-y$, $2-z$; #2: x, $1.5-y$, z for **1**; #1: $1.5-x$, $0.5-y$, $1-z$ for **2**; #1: $-x+y$, $0.5-y$, $1-z$; #2: $0.5-x$, $0.5+y$, $0.5-z$; #3: $0.5-x$, $-0.5+y$, $0.5-z$ for **3**.

Under highly acidic conditions, the monomeric UO_2^{2+} cation directly takes part in crystal growth (such as **2**). A binuclear model of uranyl complex was composed under pH 7 and solvothermal conditions, and the binuclear species with uranium coordination to DMF (such as **3**). For trinuclear $(UO_2)_3(\mu_2\text{-}OH)_5^+$, the species may lose a water to form a oxo-hydroxo-uranium polyhedral cation, $(UO_2)_3O(\mu_2\text{-}OH)_3^+$ [18]. In the relatively high pH values, oligomeric uranyl species are formed and subsequently involved in crystallization of uranyl complex.

3.2. *Crystal structure analysis*

3.2.1. Crystal structure of 1. Complex **1** crystallizes in the orthorhombic system with *Pnma* space group. Selected bond distances and angles of **1** are given in table 2. X-ray single crystal analysis indicates that the asymmetric unit of **1** is made up of two UO_2^{2+}

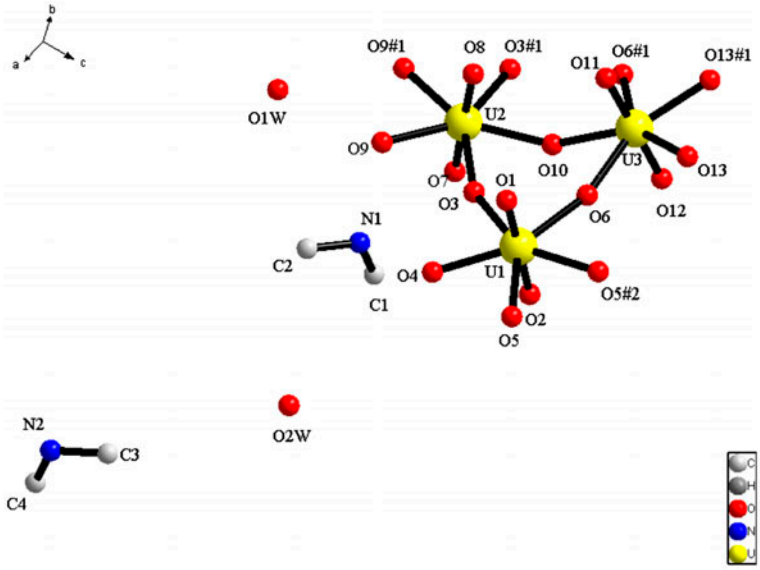

Figure 1. The coordination environment of U in **1** (hydrogens omitted for clarity). Symmetry codes: #1: $-x$, $1-y$, $2-z$; #2: x, $1.5-y$, z.

cations, three and a half hydroxo bridge groups, three terminal hydroxo ions, two free protonated $NH_2(CH_3)_2^+$ cations, a free water, and a half protonated water (H_3O^+). O1W is protonated water and O2W is water molecule. From the coordination environment of U (figure 1), the three uranium ions are all seven-coordinate. The U1 center is coordinated with seven oxygens (O1, O2, O3, O4, O5, O5$^{\#2}$, and O6; #2: $-x$, $1-y$, $1-z$) to form a pentagonal bipyramid geometry, O1 and O2 are terminal oxygens, O4 is from terminal hydroxo ions, and O3, O5, O5$^{\#2}$ (#2: $-x$, $1-y$, $1-z$), and O6 are hydroxo bridge atoms. Through hydroxo bridge atoms (O3 and O6), U1 is further connected with U2 and U3, respectively. U2 and U3 are connected by hydroxo bridge (O10). U1, U2, U3, O3, O6, and O10 are self-assembled to form a twisty six-member ring. U2 is bonded with seven oxygens (O3, O7, O8, O9, O10, O3$^{\#1}$, O9$^{\#1}$, #1: x, $1.5-y$, z) with O7 and O8 terminal, O9 and O9$^{\#1}$ are from terminal hydroxo ions, and O3 and O3$^{\#1}$ (#1: x, $1.5-y$, z) are hydroxo bridges to generate a pentagonal bipyramid geometry. The coordination environments of U2 and U3 are quite similar, except that the pair of terminal hydroxo groups on each U center (adjacent in the pentagonal plane) is different. The O9···O9$^{\#1}$ separation on U2 is 2.69 Å, whereas the corresponding separation between terminal hydroxo groups on U3

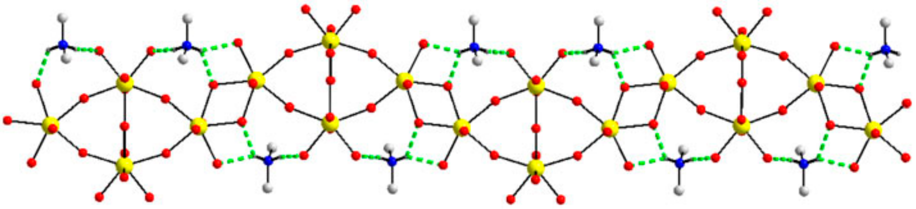

Figure 2. A 1-D chain network structure of **1**.

(O13···O13$^{\#1}$) is 2.79 Å. The U=O bond lengths range from 1.756(10) to 1.789(12) Å, the bond lengths of U–O$_t$ from terminal hydroxo ions vary from 2.251(5) to 2.258(5) Å, and the bond lengths of U–O$_b$ from hydroxo bridges vary from 2.248(5) to 2.385(5) Å. The average bond length of U–O$_b$ is 2.325(5) Å which matches that of 2.33(3) Å from the CSD, and is close to that reported [19] (2.35(4) Å), but is much shorter than the corresponding bond length of U–O$_W$ from coordination water (2.406 Å) [20]. The bond angles of O=U=O range from 178.0(6) to 179.6(6)° and the bond angles of O–U–O vary from 63.9(3) to 157.0(4)°.

In the packing of **1**, four adjacent O=U=O are connected by hydroxo bridges to form a building block of $(UO_2)_4(\mu_2\text{-}OH)_9(OH)_4$. These two adjacent building blocks further share two hydroxo bridges and expanded along the *b* axis to form a 1-D chain. There are strong H-bonds between the protons on nitrogen of the dimethylammonium cations and oxygen of the chain (figure 2). The hydrogen bonds are N2–H2D···O13, 2.7244 Å, 167.00°; N2–H2E···O4, 2.8667 Å, 148.00°; N2–H2E···O5, 2.7943 Å, 133.00°, while H2E is the hydrogen of a bifurcated hydrogen bond. Furthermore, the chain is more stable in the presence of these hydrogen bonds. Adjacent chains are further connected by C3–H3B···O1 (3.2531 Å, 140.00°) to form a 2-D layer structure (figure 3).

3.2.2. Crystal structure of 2

Complex **2** crystallizes in the monoclinic system with *C2/c* space group. Selected bond distances and angles of **2** are given in table 2. X-ray single crystal analysis indicates that **2** is made up of one crystallographically independent UO_2^{2+}, one hydroxo bridge, three terminal hydroxo ions, and two protonated $NH_2(CH_3)_2^+$ cations.

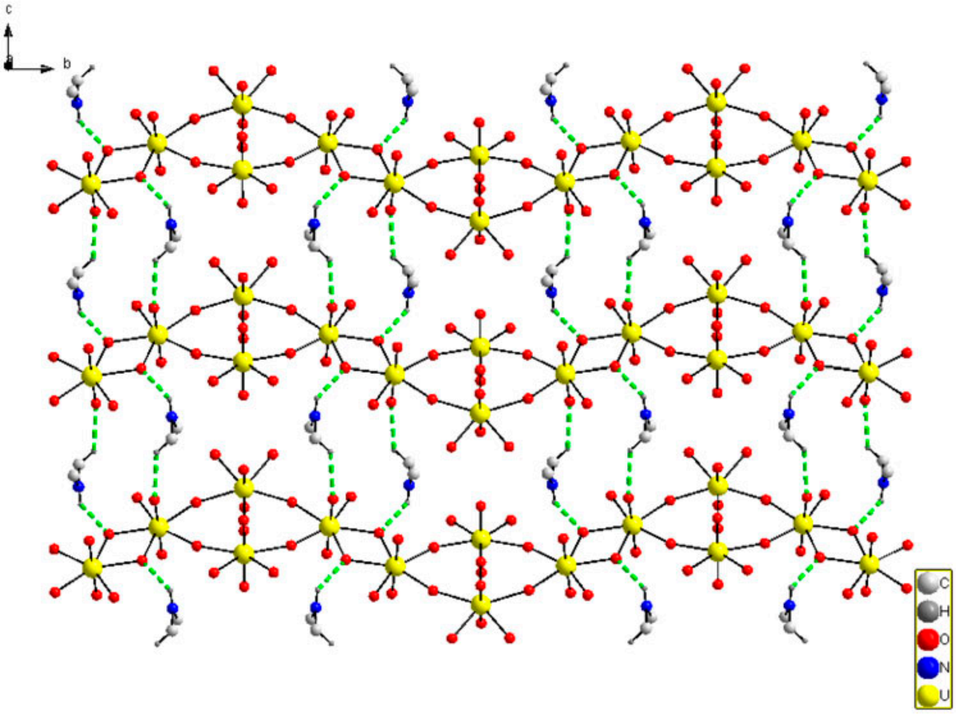

Figure 3. A view of hydrogen-bonding interactions of **1**.

U(VI) is seven-coordinate (figure 4), O1 and O2 are terminal oxos, O4, O5, and O6 originate from terminal hydroxo ions, and O3 and O3$^{\#1}$ (#1: $1.5-x$, $0.5-y$, $1-z$) are hydroxo bridges in a pentagonal bipyramid. The U=O bond lengths range from 1.792(13) to 1.793(13) Å. The bond lengths of U–O$_t$ from terminal hydroxo ions vary from 2.235(12) to 2.323(10) Å and the bond lengths of U–O$_b$ from bridging hydroxo groups range from 2.235(12) to 2.383(11) Å. The average U–O$_b$ bond length is 2.374(11) Å, matching that of 2.33(3) Å from the CSD, and close to that reported [19] (2.35(4) Å), but shorter than the bond length of U–O$_W$ (2.406 Å) reported [20]. The bond angle of O=U=O is 177.3(7)° and the bond angles of O–U–O vary from 64.5(4) to 151.5(5)°.

In the molecular packing, a cluster unit $[(UO_2)_2(\mu_2\text{-}OH)_2(OH)_6]$ is connected by two types of hydrogen bonds, N–H···O and C–H···O. They are N1–H1NA···O5, N1–H1NB···O6, N2–H2NA···O3, N2–H2NA···O4, N2–H2NB···O6, and C3–H3B···O6. The hydrogen bond connecting mode is illustrated in figure 5. Two adjacent cluster units $[(UO_2)_2(\mu_2\text{-}OH)_2(OH)_6]$ are connected by hydrogen bonds (N2–H2NA···O4, 2.9698 Å, 139.58°; N2–H2NB···O6, 2.7317 Å, 169.98°) and expanded to form an infinite chain along the *b* axis. Adjacent chains are further connected by the cluster units with intermolecular hydrogen bonds (N1–H1NA···O5, 2.5820 Å, 169.95°; N1–H1NB···O6, 2.7679 Å, 169.34°) to form a 3-D network structure (figure 6).

3.2.3. Crystal structure of 3

Complex **3** crystallizes in the monoclinic system with *C2/c* space group. Selected bond distances and angles of **3** are given in table 2. X-ray single crystal analysis indicates that **3** is made up of two UO_2^{2+} cations, four hydroxo bridges, and two DMF molecules. U1 and U2 are seven-coordinate. The two distinct uranyl ions, U1 and U2, have nearly linear $[O{=}U{=}O]^{2+}$ bond angles of 179.3(4) and 178.7(4)°, respectively. U1(VI) is coordinated by O1 and O2 (U(1)–O(1), 1.748(7) Å; U(1)–O(2), 1.755(8) Å) from terminal oxo groups, O3, O3$^{\#3}$, O4, O5, and O5$^{\#2}$ (#2: $0.5-x$, $0.5+y$, $0.5-z$; #3: $0.5-x$, $-0.5+y$, $0.5-z$) from hydroxo bridges to form a pentagonal bipyramid. Similarly, U2(VI) is coordinated by O6 and O7 (U(2)–O(6), 1.749(7) Å; U(2)–O(7), 1.751(7) Å) from terminal oxos, O8 and O8$^{\#1}$ (#1: $-x$, y, $0.5-z$) from hydroxo bridges, and O9 and O10 from DMF (U(2)–O(9), 2.382(8) Å; U(2)–O(10), 2.377(7) Å) to form a pentagonal

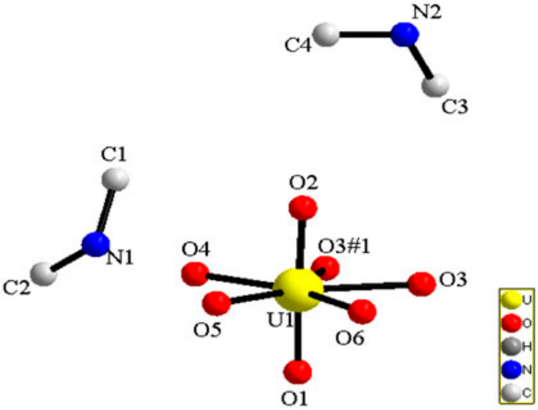

Figure 4. The coordination environment of U in **2** (hydrogens omitted for clarity). Symmetry codes: #1: $1.5-x$, $0.5-y$, $1-z$.

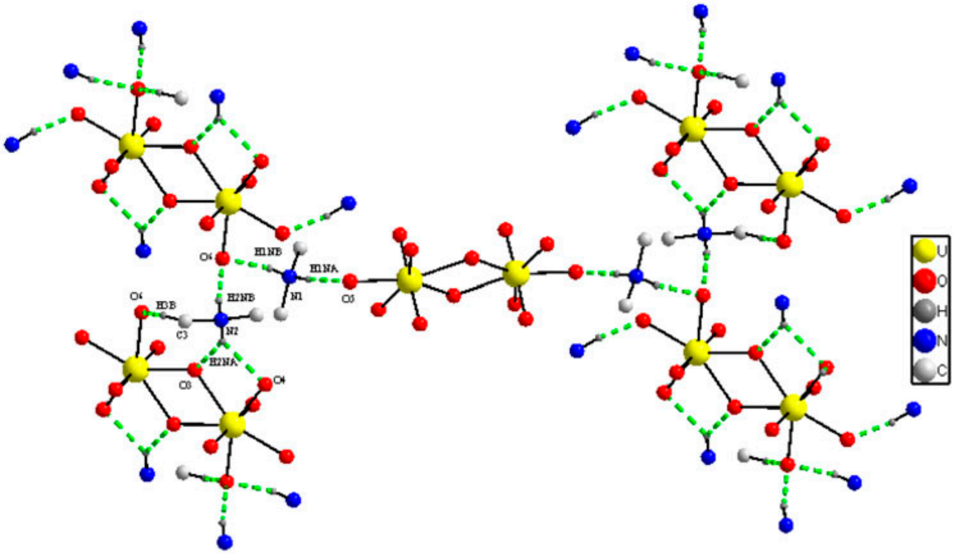

Figure 5. Hydrogen bonds connecting of **2**.

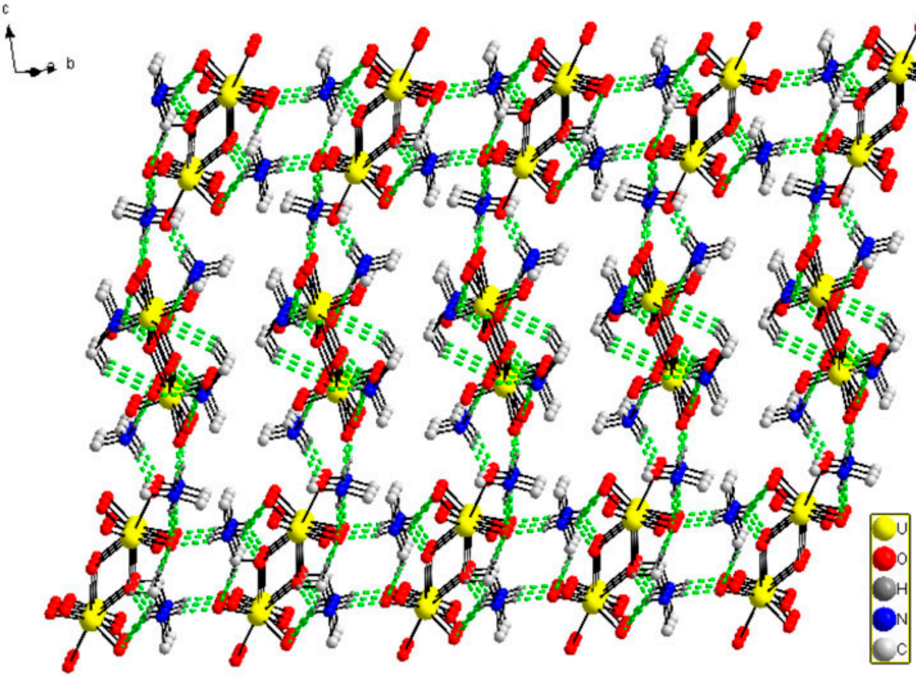

Figure 6. A view of hydrogen-bonding interactions of **2**.

bipyramid (figure 7). The average bond length of U–O_{DMF} is 2.380(8) Å, close to 2.401(4) Å reported [16]. Bond lengths of U–O_b from bridging hydroxo groups vary from 2.290(6) to 2.332(5) Å and bond angles O−U−O vary from 119.0(10) to 121.4(10)°.

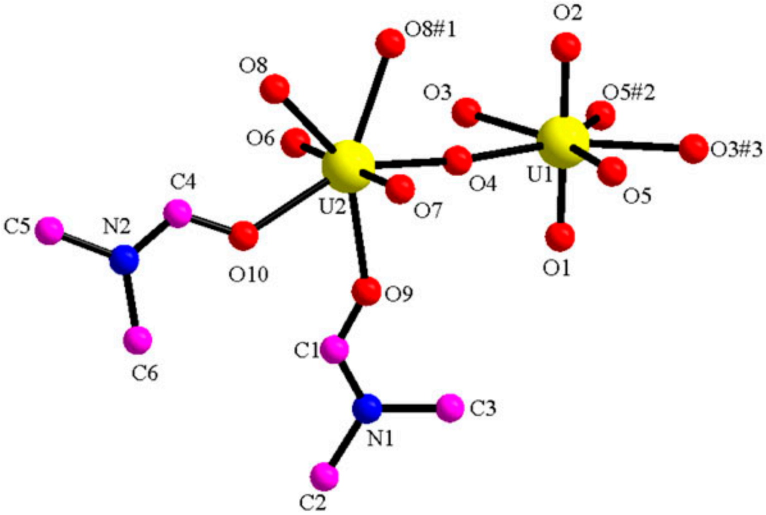

Figure 7. The coordination environment of U in **3** (hydrogens omitted for clarity). Symmetry codes: #1: $-x+y$, $0.5-y$, $1-z$; #2: $0.5-x$, $0.5+y$, $0.5-z$; #3: $0.5-x$, $-0.5+y$, $0.5-z$.

There is a hydrogen bond based on C–H···O in the framework structure, including C3–H3B···O1, C6–H6A···O3, and C6–H6C···O7. Two adjacent units $UO_2(\mu_2\text{-}OH))$ are connected by two hydroxo bridges and expanded along the *b* axis to form a 1-D chain. Parallel chains are further bridged by building blocks of $[(OH)(DMF)_2(UO_2)(OH)_2(UO_2)(DMF)_2(OH)]$ to form a 2-D network structure with the coordinated DMF oriented above and below the mean plane of the network (figure 8). The 2-D network structure is further connected by hydrogen bonds (C3–H3B···O1, 3.3869 Å, 170.86°; C6–H6A···O3, 3.2948 Å, 144.60°; C6–H6C···O7, 3.2677 Å, 138.78°) to form a 3-D network structure (figure 9).

3.3. *IR spectroscopy*

In IR spectra [figure S1(a)–(c), see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.992341] of the complexes, the broad absorptions at 3456, 3376, and 3442 cm^{-1} indicate the presence of N–H stretching of DMF. The bands at 2920, 2912, and 2943 cm^{-1} are attributed to the presence of asymmetrical C–H (CH_3) stretches. The bands at 1642, 1633, and 1655 cm^{-1} are attributed to bending of N–H. The bands at 1469–1363 cm^{-1} are assigned to C–H bending. Bands at 918, 929, and 923 cm^{-1} are assigned to the U=O stretch. The FTIR spectra of the complexes are consistent with the structural analyses; detailed assignment of the IR spectra for **1–3** is shown in table 3.

3.4. *X-ray powder diffraction study*

The simulated and experimental PXRD spectra of **1–3** are shown in Supplementary material (figures S2–S4). The experimental PXRD spectra accord with the simulated PXRD spectrum, indicating that **1–3** are pure phase, without impurities.

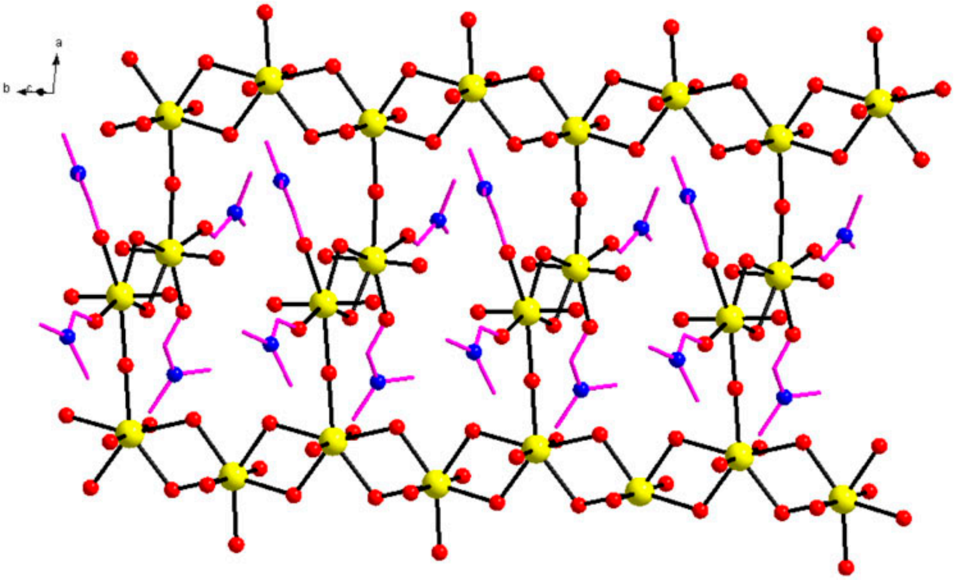

Figure 8. A 2-D layer network structure of **3** viewed from the *a*–*b* plane.

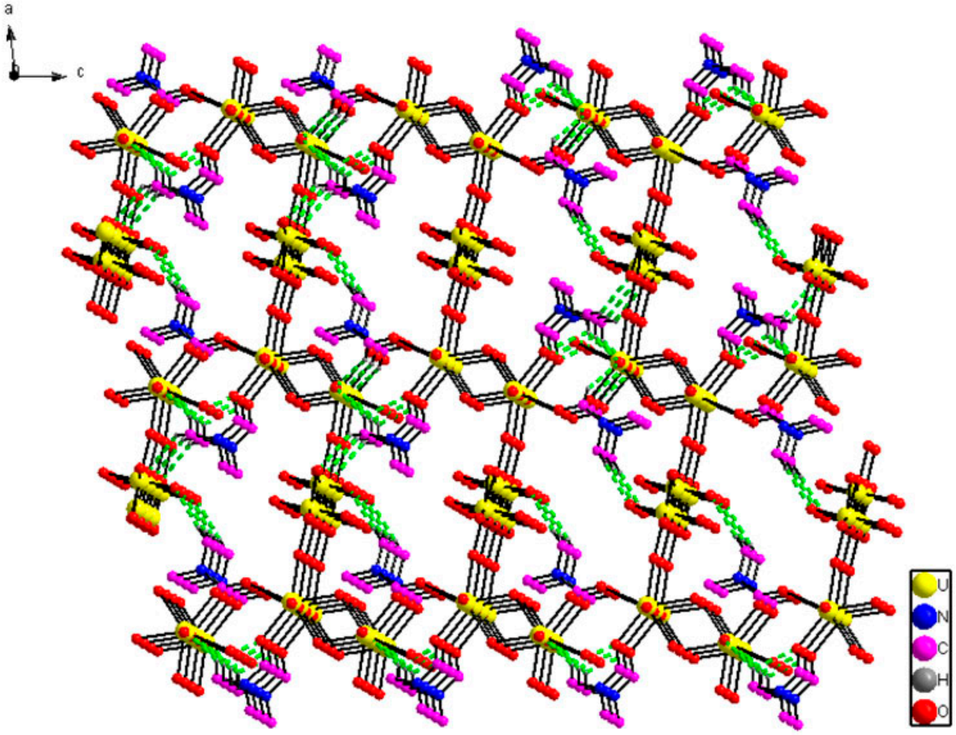

Figure 9. A view of hydrogen-bonding interactions of **3**.

Table 3. IR spectra of **1–3**.

Complexes	**1**	**2**	**3**
ν_{NH}	3456	3376	3442
$\nu_{(CH3)}$	2920	2912	2943
δ_{NH}	1642	1633	1655
$\delta_{C–H}$	1469, 1396	1401	1435, 1363
$\nu_{U=O}$	918	929	923

4. Conclusion

We have reported three uranyl complexes, $[(UO_2)_4(\mu_2\text{-}OH)_7(OH)_6]\cdot 2(H_2O)\cdot(H_3O)\cdot 4NH_2(CH_3)_2$ (**1**), $[(UO_2)(\mu_2\text{-}OH)(OH)_3]\cdot 2NH_2(CH_3)_2]$ (**2**), and $[(DMF)_2(UO_2)(\mu_2\text{-}OH)_4(UO_2))]$ (**3**). For **1**, the building block $((UO_2)_4(\mu_2\text{-}OH)_9(OH)_4)$ is shared by two hydroxo bridges and further expanded along the *b* axis to form a 1-D chain; adjacent chains are further connected by hydrogen bonds (N–H···O and C–H···O) to form a 2-D layer. For **2**, $[(UO_2)_2(\mu_2\text{-}OH)_2(OH)_6]$ is connected by hydrogen bonds (N–H···O and C–H···O) to form a 3-D network structure. For **3**, DMF is monodentate and connected by hydrogen bonds (C–H···O) to form a 3-D network structure. Research is in progress with the aim of exploring the uranium coordination chemistry with different ligands and further study of their properties.

Supplementary material

Tables of atomic coordinates, isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge by quoting the publication citation and deposition numbers CCDC for **1–3**: 979412, 979413 and 979414, respectively, from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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