



Research paper

Construction of uranyl phosphonates from multifunctional zwitterionic ligands

Xiaomin Hou^b, Si-Fu Tang^{a,*}^a College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Changcheng Road 700, Chengyang District, Qingdao 266109, China^b College of Life Science, Qingdao Agricultural University, Changcheng Road 700, Chengyang District, Qingdao 266109, China

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ABSTRACT

Two new uranyl diphosphonates, namely, $[\text{UO}_2(\text{H}_3\text{L}^1)_2(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ (**1**) and $[\text{UO}_2(\text{H}_3\text{L}^2)(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ (**2**), $\text{H}_4\text{L}^1 = \text{PyNHCH}(\text{PO}_3\text{H}_2)_2$, $\text{H}_5\text{L}^2 = \text{Py}(\text{COOH})\text{NHCH}(\text{PO}_3\text{H}_2)_2$, have been hydrothermally synthesized from the reactions of two diphosphonate ligands with uranyl nitrate hexahydrate and characterized systematically using powder and single-crystal X-ray diffraction, IR, EA, TGA and fluorescent emission measurements. The proton transfer from the phosphonic acid groups to the pyridine and imine groups leads to the formation of zwitterionic ligands. The diphosphonate ligand in compound **1** adopts chelate coordination mode resulting in molecular structure while displays chelate-bridging coordination mode in compound **2** leading to the formation of 1D infinite chain structure. The fluorescent properties of compounds **1** and **2** were also investigated.

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1. Introduction

Uranium phosphonates have attracted tremendous attentions in the past two decades because their close relation to nuclear waste processing and interesting properties including ion exchange [1], ionic conductivity [2], luminescence [3–5], NLO [6], gas absorption [7,8], magnetism [9], and so on. Hexavalent uranium ion mainly exists in the form of linear dioxo cation $[\text{O}=\text{U}=\text{O}]^{2+}$, forcing ligands coordinate at the equatorial positions and displays tetragonal, pentagonal or hexagonal bipyramidal geometries. However, this kind of structural conditionality can be offset by the phosphonate ligands which can be tailored by decorating with other functionalities [10]. Among the various phosphonate ligands, methylenediphosphonate (mdp) and its derivatives have been investigated extensively [11]. To facilitate the crystallization of uranyl methylenediphosphonates and modify their crystal structures, a few strategies have been developed, including: (i) adding HF as mineralizing agent [12]; (ii) ionothermal reaction [13]; (iii) incorporating main group (Na, K, Cs, Ba) [14] and transition (Zn) [15] metals as new connecting nodes; (iii) using tetraalkylammonium cation [16] and diamine [16,17] as templates or structure directing agents; (iv) employing pyridine [15,18] and imidazole [15,18,19] derivatives as auxiliary ligands. With these

strategies employed, uranyl phosphonates with diverse structures have been synthesized.

The ability to control the coordination chemistry of actinides is still limited [20], therefore effective methods to synthesize new uranyl phosphonates with targeted structures and properties are very desirable. In our previous work, two multifunctional diphosphonate ligands ($\text{PyNHCH}(\text{PO}_3\text{H}_2)_2$ (H_4L^1) and $\text{Py}(\text{COOH})\text{NHCH}(\text{PO}_3\text{H}_2)_2$ (H_5L^2) which can be viewed as derivatives of methylenediphosphonate ligands, have been designed and used for the construction of lanthanide and transition metal phosphonates [21,22]. In the ligands, the protons of the phosphonic acid groups (or the carboxylic group in H_5L^2) can transfer to the pyridine and imine groups, forming zwitterionic diphosphonate ligands. The protonated pyridine and imine moieties could serve as structure directing agents and interact with neighboring functionalities, influencing the structure formation of uranyl phosphonates. Therefore, zwitterionic phosphonate ligands containing protonated pyridine or imine/amine moieties could be potent organic linkers. To confirm this speculation and continue our work, these two ligands were reacted with uranyl nitrate hexahydrate at the presence of HF. Luckily, two new uranyl diphosphonates, namely, $[\text{UO}_2(\text{H}_3\text{L}^1)_2(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ (**1**) and $[\text{UO}_2(\text{H}_3\text{L}^2)(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ (**2**), were successfully obtained. Here, we report their crystal structures, thermal stabilities and luminescence properties.

* Corresponding author.

E-mail address: arnoldtsf@hotmail.com (S.-F. Tang).

2. Experimental section

2.1. Materials and instruments

The syntheses of phosphonate ligands ((pyridin-2-ylamino)methylene)bis(phosphonic acid) (H_4L^1) and 2-((diphosphonomethyl)amino)nicotinic acid (H_5L^2) have been described in our previous papers [21,22]. Other chemicals were obtained from commercial sources and used directly. Elemental analyses were performed on a Vario EL III elemental analyzer. IR spectra were recorded in the range of 4000–400 cm^{-1} on a Nicolet 6700 FTIR Spectrometer with KBr pellets. Powder X-ray diffraction patterns (Figs. S1 and S2) were obtained on a Bruker D8 Advance diffractometer using $CuK\alpha$ radiation. Microprobe elemental analyses were performed on a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscopy (EDS, Oxford INCA). Thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 449C unit at a heating rate of 10 $^{\circ}C/min$ under air atmosphere. UV-Vis absorption spectra were recorded on HITACHI U4100 spectrophotometer from powder samples of the compounds in the range of 200–800 nm. Fluorescent analyses of compounds **1** and **2** were performed on a Fluoromax-4 spectrofluorometer. *Cation: Standard precaution should be taken during the handling of uranium-containing materials.*

2.2. Single-Crystal structure determination

The diffraction intensity data sets of compounds **1** and **2** were carried out on a Bruker SMART APEX II CCD diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) at room temperature. SAINT was used for integration of intensity of reflections and scaling [23]. Absorption corrections were carried out with the program SADABS [24]. Crystal structures were solved by direct methods using SHELXS [25]. Subsequent difference Fourier analyses and least squares refinement with SHELXL-2013 [26] allowed for the location of the atom positions. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the water molecules were located from the difference Fourier map. All hydrogen atoms were refined using a riding model. One atom (C1) in compound **2** was refined isotropically due to NPD problem. The crystallographic details are summarized in Table 1. The data have

Table 1
Crystal parameters of compounds **1** and **2**^{a,b}.

Compound	1	2
Formula	$C_{12}H_{28}N_4O_{19}P_4U$	$C_7H_{16}N_2O_{14}P_2U$
fw	894.29	652.19
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	10.5273(8)	8.4611(5)
<i>b</i> (Å)	10.8631(8)	9.7387(6)
<i>c</i> (Å)	14.0608(11)	11.7240(7)
α ($^{\circ}$)	112.580(2)	68.718(2)
β ($^{\circ}$)	107.260(2)	74.673(2)
γ ($^{\circ}$)	93.933(2)	88.557(2)
<i>V</i> (Å ³)	1387.15(18)	865.47(9)
<i>Z</i>	2	2
<i>D</i> _{calcd} /g cm ⁻³	2.141	2.503
Abs coeff (mm ⁻¹)	6.170	9.637
<i>F</i> (0 0 0)	864	612
Theta range	3.087–25.093	3.178–25.400
Completeness/%	98.0	99.7
Reflns collected	25356	17138
Independent reflns/ <i>R</i> _{int}	4919/0.0600	3178/0.0952
GOF on <i>F</i> ²	1.075	1.031
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>): <i>R</i> ₁ , <i>wR</i> ₂	0.0360, 0.0705	0.0357, 0.0603
<i>R</i> indices (all data): <i>R</i> ₁ , <i>wR</i> ₂	0.0512, 0.0751	0.0504, 0.0636

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \{ \sum [\omega(F_o^2 - F_c^2)^2] / \sum \omega(F_o^2)^2 \}^{1/2}$.

been deposited in the Cambridge Crystallographic Data Centre (CCDC), deposition numbers CCDC 1557387–1557388 for compounds **1** and **2**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

2.3. Synthesis of compound $[UO_2(H_3L^1)_2(H_2O)] \cdot 4H_2O$ (**1**)

H_4L (0.05 g, 0.1865 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (0.0421 g, 0.0833 mmol), 10 mL of deionized water and two drops of HF (40%) were mixed and stirred in a 23 mL Teflon-lined stainless steel container under autogenous pressure. Afterward, it was sealed and heated at 80 $^{\circ}C$ for 3 days and allowed to cool to room temperature in a time period of 12 h. Yellow prism crystals were obtained with satisfying yield (0.051 g, 68% based on metal source). Elemental analysis (%) calcd for $C_{12}H_{28}N_4O_{19}P_4U$ (894.29): C 16.12, H 3.16, N 6.26%; found: C 16.15, H 3.21, N 6.30%. IR(KBr, cm^{-1}): 3594.9 (m), 3264.0 (m), 3125.5 (m), 2328.1 (b, w), 1651.9 (s), 1619.6 (s), 1536.9 (m), 1457.2 (w), 1390.1 (w), 1346.9 (w), 1226.0 (m), 1122.7 (s), 1082.6 (s), 1054.9 (s), 993.2 (w), 955.4 (w), 914.7 (m), 827.2 (w), 765.7 (m), 623.5 (w), 536.3 (m), 508.0 (w), 468.9 (m).

2.4. Synthesis of compound $[UO_2(H_3L^2)(H_2O)] \cdot 3H_2O$ (**2**)

Compound **2** was synthesized with the same procedure of compound **1** except the displacement of H_4L^1 with H_5L^2 . Yield: 75% based on metal source. Elemental analysis (%) calcd for $C_7H_{16}N_2O_{14}P_2U$ (652.19): C 12.89, H 2.47, N 4.30%; found: C 12.93, H 2.55, N 4.31%. IR(KBr, cm^{-1}): 3347.4 (b, s), 3125.4 (b, s), 2424.9 (b, w), 1681.3 (s), 1636.6 (s), 1573.7 (m), 1469.6 (w), 1364.4 (w), 1276.6 (m), 1232.0 (m), 1203.2 (m), 1171.2 (s), 1154.4 (s), 1092.5 (s), 1004.9 (s), 960.1 (s), 923.9 (s), 839.7 (w), 770.2 (m), 744.6 (vw), 669.1 (w), 616.7 (w), 526.4 (m), 472.3 (w), 442.0 (w).

3. Results and discussion

3.1. Synthesis of compounds **1** and **2**

The reactions of H_4L^1 and H_5L^2 with uranyl nitrate hexahydrate were scanned in the temperature range of 140–80 $^{\circ}C$ to optimise the reaction temperature. It was found pure phases of compounds **1** and **2** could be obtained in the whole temperature range but larger crystals suitable for structure characterization were apt to form at lower temperature. A series of tetraalkylammonium hydroxides (NMe_4OH , NEt_4OH , NPr_4OH and NBu_4OH) were added to the reaction systems, but have no influence on the structure formation of the compounds, indicating compounds **1** and **2** are thermodynamic stable products. The addition of HF is vital to the crystallization of compounds **1** and **2** although fluoride ions were not found in the composites (Figs. S3 and S4).

3.2. Structure description of compound **1**

Compound **1** crystallizes in triclinic space group *P*-1 with two molecules in the unit cell. The asymmetric unit is comprised of one uranyl cation, two mono-deprotonated diphosphonate ligands (H_3L^1), one aqua ligand and four lattice water molecules, suggesting a formula of $[UO_2(H_3L^1)_2(H_2O)] \cdot 4H_2O$. The uranium ion is seven coordinate, bound by two “yl” oxygen atoms lying at axial positions, four phosphonate oxygen atoms from two diphosphonate ligands and one aqua ligand lying at equatorial positions, forming a pentagonal bipyramid geometry (Fig. 1). The uranyl cation is almost linear (O(14)–U(1)–O(13): 179.4(2) $^{\circ}$) and the U–O_{axial} bond

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