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The First Uranyl Arsonates Featuring Heterometallic Cation−Cation Interactions with U^{VI}═O−Zn^{II} Bonding

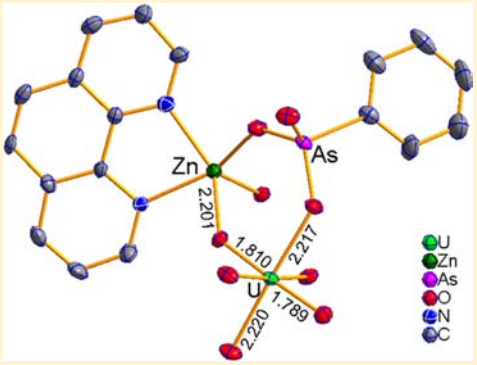
Tao Tian,[†] Weiting Yang,[†] Qing-Jiang Pan,[‡] and Zhong-Ming Sun*,[†]

[†]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, China

[‡]Key Laboratory of Functional Inorganic Material Chemistry of Education Ministry, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China

Supporting Information

ABSTRACT: Two new uranyl arsonates, $Zn(UO_2)(PhAsO_3)_2L{\cdot}H_2O$ [L = 1,10-phenanthroline (**1**) and 2,2′-bipyridine (**2**)], have been synthesized by hydrothermal reactions of phenylarsonic acid, L, and $ZnUO_2(OAc)_4{\cdot}7H_2O$. Single-crystal X-ray analyses demonstrate that these two compounds are isostructural and exhibit one-dimensional chains in which U^{VI} and Zn^{II} cations are directly connected by the *yl* oxygen atoms and additionally bridged by arsonate groups. Both compounds represent the first examples of uranyl arsonates with heterometallic cation−cation interactions.



INTRODUCTION

Metal phosphonates have received increasing attention because of their potential applications in ion exchange, catalysis, sorption, and intercalation chemistry.[1] Uranium phosphonates are of particular interest because of not only their versatile intriguing architectures in fundamental coordination chemistry but also their real applications in nuclear waste management and separation processes.[2] So far, a large number of uranium phosphonates have been isolated, most of which are in the form of uranium(VI) except for one mixed-valent uranium(IV,VI) compound.[3] The uranyl phosphonates exhibit diverse structural chemistry including chains,[4,5] layers,[6] frameworks,[7] and even nanotubules.[8] Arsonic acid ($R\text{-}AsO_3H_2$) displays a geometry similar to that of its analogous phosphonic acid ($R\text{-}PO_3H_2$), but the relatively large ionic radius and long As−O bond may lead to different architectures and distinguishing features. The pK_a values of phenylarsonic acid are 3.39 and 8.25, much higher than those of phenylphosphonic acid (1.86 and 7.51).[9a] This means that the phenylarsonate ligand is more likely to be partially protonated and bind with fewer metal centers than the corresponding phosphonic acid. Hence, it is more challenging to explore the syntheses of arsonates than phosphonates. So far, only a few metal arsonates have been reported, which are mainly limited to polyoxometalate clusters,[9] some salts of Sn^{4+}, Pb^{2+}, Mn^{2+}, and Cd^{2+} and very few Ln^{3+} ions.[10] No uranium-bearing arsonates have been documented. So far, only uranium arsenates are known.[11]

Cation−cation interactions (CCIs), first discovered in solutions by Sullivan et al.,[12] have been well recognized in An^{V} chemistry (An = Np, U, Pu, Am) but are rather rare for U^{VI}, only observed in 2% of U^{VI} compounds in the form of uranyl cations (UO_2^{2+}).[13,14] CCIs occur when an inert *yl* oxygen atom of one actinyl ion is coordinated to a second actinyl ion in the equatorial plane. This character usually increases the dimensionality of the compounds and results in framework structures.[12] In condensed phases and some discrete molecules, UO_2^{2+} cations are also known to form interactions with alkali- or alkaline-earth-metal ions.[13] Very recently, Arnold and Loiseau demonstrated new heterometallic CCIs of lanthanide elements with penta- and hexavalent uranyl cations, respectively.[15,16] As to CCIs between UO_2^{2+} and transition metals, several examples are reported.[11a,17] [Although the original use of the term CCI was coined for interactions only between two actinyl ions, it has recently moved into a common parlance for actinyl ions and other metal ions. For example, in ref 17a, Arnold wrote "Herein, we exploit this oxo-group desymmetrization in the synthesis of transition metal adducts of **1** that display the first CCIs between the uranyl group and a transition metal." (page 9610, lines 7−10 in paragraph 3).] However, to the best of our knowledge, only a few compounds featuring U═O−Zn interactions have been described.[17c,d]

In this paper, we describe the syntheses of two new compounds that represent the first examples of uranyl arsonates with heterometallic U^{IV}═O−Zn CCIs.

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EXPERIMENTAL SECTION

Caution! *Standard procedures for handling radioactive material should be followed, although the zinc uranyl acetate heptahydrate $ZnUO_2(OAc)_4{\cdot}7H_2O$ used in the laboratory contained depleted uranium.*

Materials and Synthesis. All chemicals were purchased commercially and used without further purification. Zinc uranyl acetate (99.8%) was obtained from Sinpharm Chemical Reagent Co. Ltd.; phenylarsonic acid, 1,10-phenanthroline, and 2,2′-bipyridine were obtained from Jinan Henghua Sci. & Tec. Co., Ltd. Energy-dispersive spectroscopy (EDS) spectra were obtained using a scanning electron microscope (Hitachi S-4800) equipped with a Bruker AXS XFlash 4010 detector. Powder X-ray diffraction (XRD) data were collected on a D8 Focus (Bruker) diffractometer at 40 kV and 30 mA with monochromated Cu Kα radiation (λ = 1.5405 Å) with a scan speed of 5° min^{-1} and a step size of 0.02° in 2θ. Thermogravimetric (TGA) and differential thermal analysis data were recorded on a Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE) from room temperature to 800 °C with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. All IR measurements were obtained using a Bruker TENSOR 27 Fourier transform infrared (FT-IR) spectrometer. Samples were diluted with spectroscopic KBr and pressed into a pellet. Scans were run over the range 400−4000 cm^{-1} using a Raman spectrometer equipped with an integral BX 41 confocal microscope. Surface-enhanced Raman spectroscopy spectra were measured with a Jobin Yvon/HORIBA LabRam ARAMIS instrument. The radiation from the air-cooled HeNe laser (633 nm) was used as an excitation source. Raman scattering was detected with 180° geometry using a multichannel air-cooled (−70 °C) charge-coupled device (CCD) camera (1024 × 256 pixels). Solid-state UV−vis−near-IR (NIR) absorption spectra were carried out on a U-4100 spectrophotometer (solid). Each spectrum was taken from 250 to 1400 nm. The photoluminescence emission spectra were performed on a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source.

*Synthesis of $Zn(UO_2)(PhAsO_3)_2L{\cdot}H_2O$ (**1**; L = 1,10-Phenanthroline).* A mixture of $ZnUO_2(OAc)_4{\cdot}7H_2O$ (40 mg, 0.07 mmol), phenylarsonic acid (40 mg, 0.2 mmol), 1,10-phenanthroline monohydrate (20 mg, 0.1 mmol), and deionized water (1 mL, 55 mmol) was loaded into a 20-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 160 °C for 2 days and then cooled to room temperature. Yellow crystals were isolated with a yield of 20.2 mg (31% based on uranium).

*Synthesis of $Zn(UO_2)(PhAsO_3)_2L{\cdot}H_2O$ (**2**; L = 2,2′-Bipyridine).* The same reaction conditions as those above were used by substituting 2,2′-bipyridine (20 mg, 0.13 mmol) for phenanthroline. Yellow platelets were isolated with a yield of 32.1 mg (50% based on uranium).

X-ray Crystal Structure Determination. Suitable single crystals with dimensions of 0.26 × 0.33 × 0.10 mm^3 for **1** and 0.24 × 0.28 × 0.08 mm^3 for **2** were selected for single-crystal XRD analyses. Crystallographic data were collected at 173 K on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data processing was accomplished with the *SAINT* program. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using *SHELXTL-97*.[18] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. A summary of the crystallographic data for these two complexes is listed in Table 1. Selected bond distances and angles are given in Table S1 in the Supporting Information. More details on the crystallographic studies are given in the Supporting Information.

RESULTS AND DISCUSSION

Hydrothermal reactions of $ZnUO_2(OAc)_4{\cdot}7H_2O$ with phenylarsonic acid in the presence of 1,10-phenanthroline (Phen) or 2,2′-bipyridine (Bipy) yield two new compounds. These two compounds could be obtained when 1−3 mL of H_2O was used. The amount of phenylarsonic acid is very important for the syntheses, as the pH values are crucial for crystallization of the two compounds, which can only be synthesized in the pH range of 2−2.5. When the pH value is higher than 3, precipitation occurs. The temperature also plays a key role in the syntheses. When the temperature is lower than 160 °C, no solid state samples are produced, while when it is higher than 200 °C, decomposition of the ligands occurs. In both compounds, energy-dispersive X-ray analysis of several crystals showed the presence of uranium, zinc, and arsenic in a ratio of 1:1:2 (Figures S1 and S2 in the Supporting Information). Their phase purities were confirmed using powder XRD (Figure S3 in the Supporting Information). As shown in the TGA curves (Figure S4 in the Supporting Information), compounds **1** and **2** can be stable to 450 °C and then start decompose with a total weight loss of 43.0 wt % (calcd 44.1 wt % for compound **1**) and 45.6 wt % (calcd 42.6 wt % for compound **2**).

Table 1. Crystal Data and Structure Refinement for 1 and 2

compound	**1**	**2**
formula	$C_{48}H_{38}As_4N_4O_{17}U_2Zn_2$	$C_{44}H_{38}As_4N_4O_{17}U_2Zn_2$
fw	1849.30	1801.26
temperature (K)	173	173
space group	$P\bar{1}$, triclinic	$P\bar{1}$, triclinic
a (Å)	13.2532(13)	12.9575(14)
b (Å)	13.9779(13)	13.9892(15)
c (Å)	15.8587(15)	15.8969(18)
α (deg)	72.8260(10)	68.979(2)
β (deg)	75.127(2)	75.721(2)
γ (deg)	78.488(2)	73.526(2)
V (Å^3)	2688.3(4)	2545.3(5)
Z	2	2
μ (mm^{-1})	9.404	9.929
GOF	1.001	1.015
R_1, wR_2 $[I > 2\sigma(I)]^a$	0.0419, 0.0644	0.0447, 0.0770
R_1, wR_2 (all data)	0.0708, 0.0733	0.0760, 0.0886
largest diff peak, hole (e Å^{-3})	1.030, −1.458	1.714, −1.722

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Their structures were confirmed by single-crystal XRD (see the Supporting Information). Because **1** and **2** are isostructural, the following structural descriptions will be mainly focused on **1**.

These two compounds crystallize in triclinic space group $P\bar{1}$. As shown in Figure 1, the asymmetric unit of **1** consists of two crystallographically unique uranyl cations, two Zn^{2+} ions, four phenylarsonate groups, and two Phen ligands. Every phenylarsonate ligand is tridentate, bridging two U^{VI} centers and one Zn^{2+} ion. U1 and U2 atoms are present as typical uranyl ions with bond lengths ranging from 1.769(5) to 1.810(5) Å. Both uranyl ions are equatorially coordinated by four oxygen atoms from four different arsonate groups, forming slightly distorted octahedral geometries. The U−O_{eq} bond distances were determined to be within 2.217(5) and 2.287(5) Å, which are comparable to those in uranyl phosphonates.[4−7] Bond-valence sums at the U1 and U2 sites, calculated using coordination-specific parameters,[19] are 6.01 and 6.00 vu, respectively. For compound **2**, the calculated valence states of U1 and U2 are 5.90 and 5.97 vu, respectively. These results agree well with the formal valence of U^{VI}. Each distinct Zn^{II} ion is 5-fold, saturated by two nitrogen atoms from Phen [Zn−N: 2.097(7)−2.123(8) Å], two oxygen atoms from phenylarsonate groups [Zn−O: 1.934(5)−1.946(5) Å], and one oxo atom in the UO_2^{2+} cation

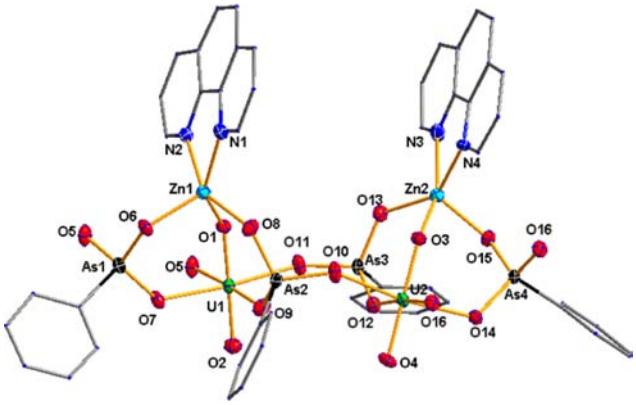

Figure 1. ORTEP representation of the asymmetric unit in compound **1**. Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. The carbon atoms are drawn in wire mode.

with Zn−O distances of 2.201(5) and 2.229(5) Å, which are significantly longer than those of other Zn−O bond lengths in this compound. The measured Zn−O═U bond angles are 137.30° and 133.39°. CCIs between UO_2^{2+} and Zn^{2+} ions are also reflected in the difference of the U═O bond lengths because the zinc-bound U═O_{yl} distances [1.810(5) and 1.808(5) Å] are slightly longer than the terminal U═O_{yl} distances [1.789(6) and 1.769(5) Å]. The UO_6 octahedra and ZnO_3N_2 square pyramids together are further connected by two phenylarsonate groups, resulting in one-dimensional chains along the [111] direction (Figure 2). These chains are further held together by strong $\pi\cdots\pi$-stacking interactions between the Phen molecules with central distances ranging from 3.585 to 4.111 Å (Figure 3). When the zinc-centered polyhedra are disregarded, the structure of **1** is very similar to the compounds synthesized by phenylphosphonic acid, in which the uranyl cations are connected by phenylphosphonate groups to form linear chains.[20]

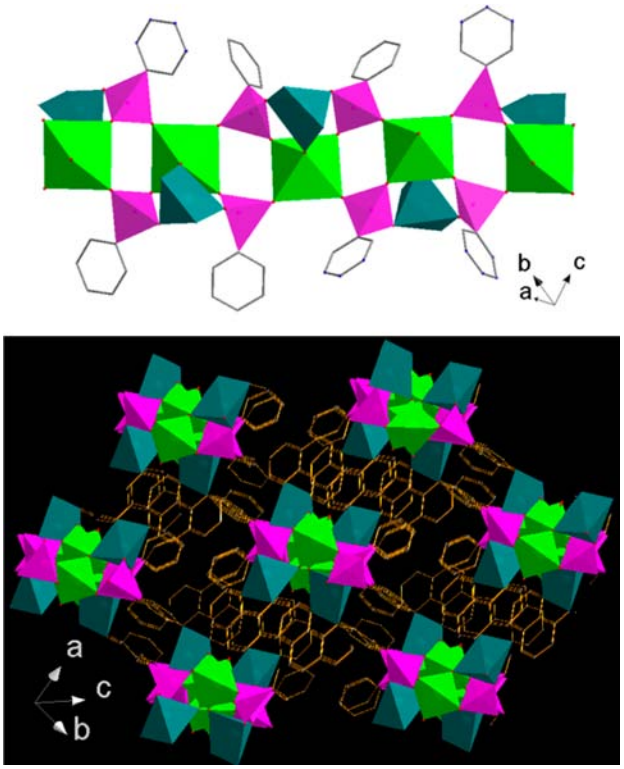

Figure 2. Views of a one-dimensional chain (top) and the packing diagram of compound **1** (bottom). Uranyl centers are shown as green octahedra, arsonate groups as dark-purple tetrahedra, zinc atoms as cyan square pyramids, and organic components as lines. Phen ligands are removed for clarity in the top picture.

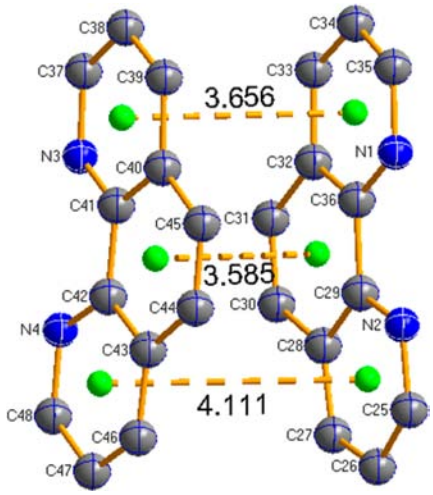

Figure 3. $\pi\cdots\pi$-stacking interactions between the Phen molecules in two neighboring U−As chains.

FT-IR spectra in both compounds show the typical ν(As═O) stretching vibration bands (1094 cm^{-1} for **1** and 1097 cm^{-1} for **2**; Figure S5 in the Supporting Information). The stretching mode of uncoordinated H_2O molecules is a very broad band around 3438 cm^{-1}. The symmetrical vibrations ν_1 and antisymmetric vibrations ν_3 of UO_2^{2+} were characterized in the IR and Raman region of 760−950 cm^{-1} (Table 3 and Figures S5 and S6 in the Supporting Information). The wax and wane features of the U═O bond lengths caused by CCIs between UO_2^{2+} and Zn^{2+} ions are also indicated by their vibrations in the IR spectra. Bond lengths related to the antisymmetric stretching vibration ν_3 for uranyl groups in compounds **1** and **2** based on Bartlett's empirical equation[21] R_{U-O} (pm) = $9141\nu_3^{-2/3}$ + 80.4 and Veal's empirical law[22] R_{U-O} (pm) = $8120\nu_3^{-2/3}$ + 89.5, are calculated, respectively. As shown in Table 2, the predicted uranyl bond lengths are in good agreement with the values obtained from the single-crystal XRD analysis, and Bartlett et al.'s formulas lead to values closer to the real distances than Veal et al.'s expression.

Table 2. Comparison of Selected Single-Crystal XRD and IR/Raman Spectroscopic Data for Compounds 1 and 2

	ν_3 of UO_2^{2+} (cm^{-1})					
		in **1**			in **2**	
Raman		896	856		896	856
IR	931	896	867	914	892	845
	U═O distance (Å)					
		in **1**			in **2**	
Veal's law	1.747	1.769	1.788	1.757	1.771	1.803
Bartlett's law	1.763	1.788	1.809	1.775	1.791	1.828
experimental XRD	1.769	1.789	1.808	1.781	1.798	1.818
			1.810			1.819

The solid-state UV−vis−NIR absorption spectra of both compounds were measured from several single crystals, as shown in Figure 4. The characteristic absorptions of hexavalent uranyl complexes are displayed in the region of 380−500 nm and centered at 430 nm. The fluorescence spectra are depicted in Figure 5. Upon excitation at 330 or 350 nm, both compounds exhibit typical green light with a broad emission spectroscopy ranging from 490 to 630 nm. Compound **1** has well-structured emission bands at 514, 536, 559, 586, and 614 nm. There is about 790 cm^{-1} (mean value) separation between two adjacent fingerprinted peaks, which can be related to the ν_1(U═O) stretching vibration mentioned above. Compound **2** has a shape almost identical with that of **1**. The most intense peaks in both compounds are positioned at 536 nm, displaying a slight red shift of 27 nm along with lesser intensity for the emission bands compared to a benchmark compound $UO_2(NO_3)_2{\cdot}6H_2O$.

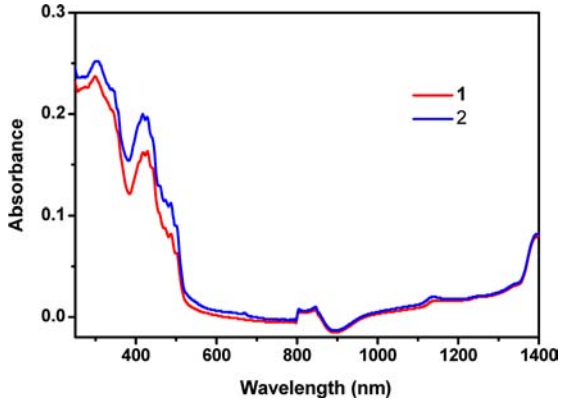

Figure 4. Solid-state UV−vis−NIR absorption spectra of **1** and **2**.

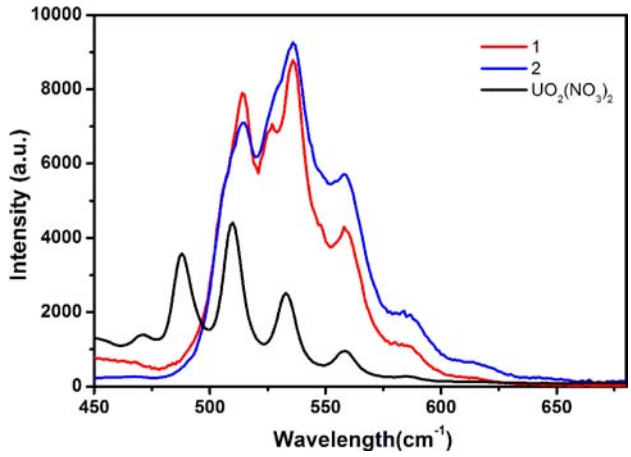

Figure 5. Fluorescence spectra of **1**, **2**, and uranyl nitrate.

■ CONCLUSION

In summary, we have synthesized the first two examples of uranyl arsonates with one-dimensional chains. In the two compounds, U^{VI} and Zn^{II} cations are directly connected by the *yl* oxygen atoms forming the heterometallic CCIs. Successful syntheses of the two complexes may provide the possibility of constructing new uranyl arsonates. Future work will be focused on the synthesis of new compounds by modification of the organic residues in arsonic ligands.

■ ASSOCIATED CONTENT

Supporting Information

Selected bond lengths and angles, SEM, EDS, IR, and Raman spectra, powder XRD patterns, TGA data, and X-ray crystallographic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: szm@ciac.jl.cn.

Notes

The authors declare no competing financial interest.

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