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ARTICLE

Complexation of U(VI) with Benzoic Acid at Variable Temperatures (298 – 353 K): Thermodynamics and Crystal Structures of U(VI)/Benzoate Complexes

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Abstract. Thermodynamics of the U(VI) complexation with benzoic acid (HL) was studied by spectrophotometry at varied temperatures (298 – 353 K) with constant ionic strength (1.0 mol·dm⁻³ NaClO₄). Two U(VI) benzoate complexes, UO₂L⁺ and UO₂(OH)L(aq), were identified and their formation constants determined. The formation of both complexes is endothermic and driven exclusively by entropy. Two types of U(VI)/benzoate complex crystals were synthesized from aqueous solutions at different pH and ligand/metal ratios. Their structures were determined by single-crystal X-ray diffractometry. One structure is a 1:3 U(VI) benzoate complex (Na[UO₂(C₇H₅O₂)₃]·2H₂O), each benzoate holding a bidentate coordination mode to U(VI) in the equatorial plane of UO₂²⁺. The other is a U(VI) hydroxobenzoate complex with unique μ₃-OH bridging ([UO₂)₂(C₇H₅O₂)₂(μ₃-OH)₂]·4H₂O). In the structure, each UO₂²⁺ ion holds five coordination oxygens in its equatorial plane, two carboxylate oxygens from two benzoate ligands and three oxygens from three μ₃-OH groups.

Introduction

Uranium, the most abundant radioactive element in the nuclear wastes and in the contaminated soils and water in the environment, enters the nuclear wastes and the environment from natural deposits, mine tailings, nuclear fuel reprocessing, and the use of uranium-containing phosphate fertilizers.¹⁻⁵ In its most stable oxidation state, U(VI) exists as UO₂²⁺ that is highly soluble in aqueous solutions and can readily migrate in groundwater.

The migration behaviour of U(VI) in the environment largely depends on its interactions with the organic and inorganic ligands that are present in the nuclear wastes and in the environment. Among the ligands, carboxylic acids are found to be ubiquitous, either deliberately introduced in the nuclear fuel separation processes as complexing agents, or generated as a result of the degradation of other organic substances. Based on the inventory of the Waste Isolation Pilot Plant repository (WIPP, in New Mexico, USA), a number of carboxylic acids such as acetic acid, benzoic acid, and oxalic acid, exist in significant amounts in the nuclear wastes.⁶ A variety of aliphatic and aromatic carboxylic acids such as benzoic acid were also identified in the low-level radioactive waste disposal

sites such as Maxey Flats in Kentucky and West Valley in New York, USA.⁷ As a result, the complexation of U(VI) with benzoic acid is expected to affect the environmental behaviour of U(VI) in the nuclear waste repository and the contaminated geomeidia. Thermodynamic data on the complexation of U(VI) with benzoic acid are needed to understand and/or predict the migration. In particular, the thermodynamic data at elevated temperatures are of great importance because the temperature of the surroundings of the nuclear repositories could be much higher than the ambient. At present, there have been a number of studies on the complexation of U(VI) with benzoic acid at or near 298 K,⁸⁻¹³ but no data at elevated temperatures are available. In this work, the complexation of U(VI) with benzoic acid was studied at 298 – 353 K. Besides, a new μ₃-OH bridged 1:1 U(VI)/benzoate solid compound was synthesized and its crystal structure was identified. The results from this work not only help evaluate the effect of temperature on the complexation of U(VI) with benzoic acid but also reveal new coordination modes in the U(VI)/carboxylate complexes.

It is worth noting that benzoic acid represents one of the main functionalities in humic acids (HAs), a group of organic polyelectrolytes, which ubiquitously exist in natural soils, sediments, and waters. It is well-known that HAs play an important role in the migration of radioactive materials in the environment due to their complexation with radioactive elements.^{8, 9, 14-17} However, the binding strength and coordination modes in the complexes are not well established since the functionalities and structures of HAs are poorly defined.¹⁶ Therefore, the study of the complexation of U(VI) with benzoic acid in this work helps to gain the knowledge of the interactions between U(VI) and HAs.

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†Electronic Supplementary Information (ESI) available: Spectrophotometric titration conditions, hydrolysis constants of U(VI) at different temperatures, spectrophotometric titration data with a lower concentration of U(VI) and a van't Hoff plot for the complexation constant β₁₋₁₁. See DOI: 10.1039/x0xx00000x

Results and discussion

Equilibrium constants at variable temperatures

Experiments with different concentrations of U(VI), acid, and benzoate were conducted. Figure 1 shows representative absorption spectra for the titrations with relatively high concentration of U(VI) ($\sim 10 \text{ mmol}\cdot\text{dm}^{-3}$) at 298, 313, 328, and 343 K. Similar patterns were observed for the spectra at 353 K (not shown). As the partially neutralized benzoate solution was added into the U(VI) solution, the ligand/metal ratio ($[L]/[M]$) was increased from zero to about 1.8 (for titrations at 298 K and 313 K), 2.7 (at 328 K), and 3.5 (at 343 K and 353 K), respectively. In the meantime, the pC_H ($= -\log[H^+]$) of the solutions increased from 2.0 to 3.6. To explore the possibility of the formation of other complexes, additional titrations using lower concentrations of U(VI) ($\sim 3 \text{ mmol}\cdot\text{dm}^{-3}$) were performed at 328, 343 and 353 K (Fig. S1 in the ESI†). In those titrations, the highest ratio of $[L]/[M]$ was 4.1 at 328 K and 5.6 at 343 K and 353 K. The pC_H of the solutions varied from 2.3 to 4.5.

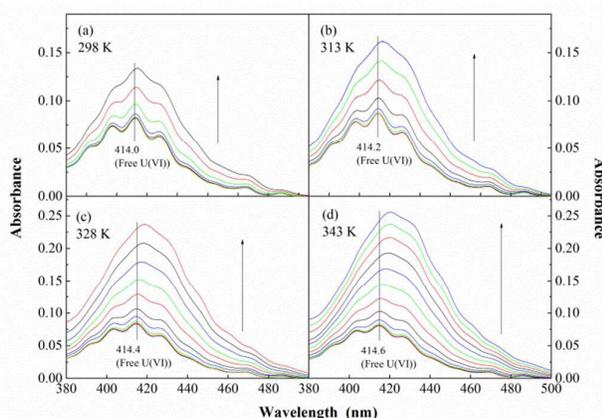


Figure 1 Spectrophotometric titrations of U(VI)/benzoate complexation at different temperatures. $I = 1.05 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$. Cuvette solution: V^0 (mL) = 2.10; $[\text{UO}_2(\text{ClO}_4)_2]/[\text{HClO}_4]$ ($\text{mmol}\cdot\text{dm}^{-3}$) = 10.5/12.0 (a), 11.1/12.5 (b), 10.5/12.0 (c) and 10.1/11.4 (d); $pC_H \sim 2.0$. Titrant: $[L]/[H] = 268/10.9 \text{ mmol}\cdot\text{dm}^{-3}$; $pC_H \sim 5.5$; V_{titrant} (mL) = 0.150 (a), 0.175 (b), 0.225 (c) and 0.275 (d).

As shown in Figure 1, the position of the absorption bands of U(VI) was generally red-shifted and the intensity of the bands increased as benzoate was added into the U(VI) solution. Factor analysis was performed to help identify the number of absorbing U(VI) species in the solution by the HypSpec program. It was found that there were only two absorbing species in the solutions at lower temperatures (298 K and 313 K) but an additional absorbing species could exist in the solutions at higher temperatures (328, 343 and 353 K). To obtain the best fit with a chemically meaningful model, the fitting of the spectra was performed in two steps: (1) The first seven spectra in each titration with a similar concentration of U(VI) were fitted to determine the stability constants ($\log\beta_{101}$) of the 1:1 U(VI)/benzoate complex, UO_2L^+ , at the five temperatures (298 K, 313 K, 328 K, 343 and 353 K); (2) While keeping the values of $\log\beta_{101}$ for the UO_2L^+ complex constant, the entire sets of the spectra at 328, 343 and 353 K were fitted with various models including UO_2L^+ and one additional U(VI) species such as $\text{UO}_2\text{L}_2(\text{aq})$, $\text{UO}_2(\text{OH})\text{L}(\text{aq})$, or $(\text{UO}_2)_2(\text{OH})_2\text{L}_2(\text{aq})$. Best fits were achieved with

the model including only UO_2L^+ at 298 K and 313 K, but with the model including both UO_2L^+ and $\text{UO}_2(\text{OH})\text{L}(\text{aq})$ at higher temperatures (328, 343 and 353 K). The complexation equilibria and the equilibrium constants are represented by reactions (1) and (2). The calculated equilibrium constants of $\log\beta_{101}$ (for reaction (1)) and $\log\beta_{1-11}$ (for reaction (2)) are summarized in Table 1.



$$\beta_{101} = [\text{UO}_2\text{L}^+]/([\text{UO}_2^{2+}][\text{L}^-])$$



$$\beta_{1-11} = [\text{UO}_2(\text{OH})\text{L}(\text{aq})][\text{H}^+]/([\text{UO}_2^{2+}][\text{L}^-])$$

In fitting the spectrophotometric data, several hydrolysis reactions of U(VI) were included. Because the pC_H of the solutions was below 4.5, only three hydrolysis species of U(VI) were taken into account, including $\text{UO}_2(\text{OH})^+$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and $(\text{UO}_2)_3(\text{OH})_5^+$. The hydrolysis constants at $1.0 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4$ were obtained by using the specific ion interaction approach (SIT) from the available values for a different ionic medium in the literature.¹⁸ Details of the hydrolysis reactions and constants are provided in Table S1 in the ESI†. The protonation constant of benzoate at 298 K ($\log K_H = 4.03$) was used for all other temperatures because the enthalpy of protonation is near zero¹¹ (Table 1) so that the effect of temperature on the protonation constant is negligible in the temperature range of this work (298 – 353 K).

The value of $\log\beta_{101}$ for UO_2L^+ at 298 K and the ionic strength of $1.0 \text{ mol}\cdot\text{dm}^{-3}$ (NaClO_4) by spectrophotometry in this work agrees excellently with that at 298 K and the same ionic strength by potentiometry in the literature.¹¹ Other values of $\log\beta_{101}$ for UO_2L^+ in the literature^{8, 9, 12, 13} are higher but these were obtained in different ionic media ($I = 0.1 \text{ mol}\cdot\text{dm}^{-3}$) and/or by different techniques (e.g., luminescence spectroscopy).

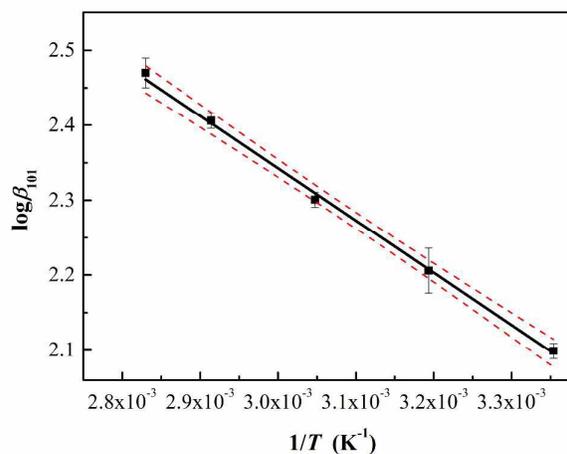


Figure 2 Van't Hoff plot for the complexation constant β_{101} of U(VI) with benzoate. Symbol (■) – experimental points from this work ($I = 1.05 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$), solid line – linear fit, dashed lines – upper and lower limits of the confidence band at the 95% level.

The values of $\log\beta_{101}$ for UO_2L^+ at temperatures above 298 K are the first such values experimentally determined. A steady increase in $\log\beta_{101}$ (from 2.10 to 2.47) is seen when the temperature

is increased from 298 K to 353 K, implying that the complexation is endothermic. A van't Hoff plot of $\log \beta_{101}$ as a function of $1/T$ is shown in Figure 2. The good linearity of the plot suggests that the enthalpy of complexation can be assumed constant in the temperature range (298 K to 353 K). From the slope of the linear fit (weighted by the uncertainties), the "average" value of enthalpy of reaction (1) in this temperature range (298 – 353 K) was calculated to be $(13.4 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1}$, in very good agreement with the value in the literature obtained by calorimetry at 298 K $((10.5 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1})$.¹¹

As shown in Table 1, the positive values of ΔH and ΔS indicate that the complexation of U(VI) with benzoate is disfavored by the

enthalpy, but is driven exclusively by the entropy, characteristic of "hard acid" and "hard base" interactions and inner-sphere complexation.¹⁹⁻²¹ Evidently, the energy for the dehydration of the metal ion (UO_2^{2+}) and the ligand (benzoate) plays a dominant role in the overall energetics of the complexation, similar to that in the complexation of U(VI) with other carboxylate ligands in water.²²⁻²⁵

Values of $\log \beta_{1-11}$ for $\text{UO}_2(\text{OH})\text{L}(\text{aq})$ were obtained only at three higher temperatures (328, 343 and 353 K). A van't Hoff plot (Figure S2 in ESI†) indicates that reaction (2) is endothermic with an enthalpy of $(48.9 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1}$, and an entropy of $(135 \pm 11) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Like reaction (1), reaction (2) is also driven by entropy.

Table 1 Equilibrium constants and corresponding thermodynamic parameters for U(VI)/benzoate complexation (methods: sp - spectrophotometry, pot - potentiometry, cal - calorimetry, TRLFS - time-resolved laser-induced fluorescence spectroscopy).

Reaction	Method	<i>T</i> K	<i>I</i> $\text{mol}\cdot\text{dm}^{-3}$	$\text{Log } K_{\text{H}}$ or β_{M}	$\text{Log}\beta_{\text{m}}$	$\text{Log}\beta^{\circ}$ (by SIT)	ΔH $\text{kJ}\cdot\text{mol}^{-1}$	ΔS $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Ref.
$\text{H}^+ + \text{L}^- = \text{HL}$	pot, cal	298	1.0	4.03 ± 0.01			$-(1.3 \pm 0.3)^b$		11
$\text{UO}_2^{2+} + \text{L}^- = \text{UO}_2\text{L}^+$	sp	298	1.0	2.10 ± 0.01	2.08 ± 0.01	2.63 ± 0.03	13.4 ± 0.6^a	85.2 ± 2.2	p.w.
		313	1.0	2.21 ± 0.03	2.19 ± 0.03	2.76 ± 0.03			p.w.
		328	1.0	2.30 ± 0.01	2.28 ± 0.01	2.88 ± 0.05			p.w.
		343	1.0	2.41 ± 0.01	2.39 ± 0.01	3.02 ± 0.03			p.w.
		353	1.0	2.47 ± 0.02	2.45 ± 0.02	3.11 ± 0.04			p.w.
	pot, cal	298	1.0	2.10 ± 0.04	2.08 ± 0.04	2.63 ± 0.05	10.5 ± 0.6^b	75	11
		sp	298	0.1	2.45 ± 0.15				8
		TRLFS		0.1	2.82 ± 0.24				8
		sp		0.1	3.37 ± 0.14				9
		pot		0.1	2.68 ± 0.04				12
$\text{UO}_2^{2+} + \text{L}^- + \text{H}_2\text{O} = \text{UO}_2(\text{OH})\text{L}(\text{aq}) + \text{H}^+$	sp	328	1.0	$-(1.53 \pm 0.06)$			48.9 ± 3.3^a	135 ± 11	p.w.
		343	1.0	$-(1.16 \pm 0.06)$					p.w.
		353	1.0	$-(0.98 \pm 0.04)$					p.w.

^a Calculated by van't Hoff equation using the $\log \beta_{\text{M}}$ at different temperatures (298 – 353 K for $\log \beta_{101}$ and 328-353K for $\log \beta_{1-11}$).

^b Obtained by calorimetry.

Calculation of stability constants at variable temperatures to infinite dilution: Analysis by the specific ion interaction approach (SIT)

To allow the comparison of the stability constants of UO_2L^+ at different temperatures and to use the specific ion interaction approach (SIT) to obtain the constants to infinite dilution, the constants in molarity should be converted to the constants in molality according to equation (3):

$$\log \beta_{\text{m}} = \log \beta_{\text{M}} + \sum_r \nu_r \log g \quad (3)$$

where β_{m} and β_{M} are the stability constants of the UO_2L^+ complex in molality and molarity, respectively; $\sum_r \nu_r$ is the sum of stoichiometric coefficients of the reaction, and ν_r is positive for products and negative for reactants.²⁶ g is the ratio of the values of molality to molarity for the specific ionic medium. For the $1.05 \text{ mol}\cdot\text{kg}^{-1}$ NaClO_4 in this study, $\log g$ equals 0.02. Therefore, for reaction (1), $\sum_r \nu_r = -1$. $\log \beta_{\text{m}} = \log \beta_{\text{M}} - 0.02$. The converted stability constants on molality are shown in Table 1.

The SIT approach originating from the Brønsted-Guggenheim-Scatchard model²⁷⁻³⁰ can be used to calculate the equilibrium

constants at zero ionic strength from experimental data at other ionic strengths. For reaction (1), the equilibrium constants at $I = 0$ ($\log \beta^{\circ}$) are related to $\log \beta_{\text{m}}$ at other ionic strengths by equation (4):

$$\log \beta_{\text{m}} - \Delta Z^2 D = \log \beta^{\circ} - \Delta \epsilon I_{\text{m}} \quad (4)$$

where $\Delta Z^2 = \{\sum(Z^2_{\text{products}}) - \sum(Z^2_{\text{reactants}})\}$, and equals -4 for reaction (1). D is the Debye-Huckel term used in SIT and $D = A I_{\text{m}}^{1/2} / (1 + 1.5 I_{\text{m}}^{1/2})$, where $A = 0.5091 (\text{kg}\cdot\text{mol}^{-1})^{1/2}$ at 298 K, I_{m} is the ionic strength in molality, and ϵ is the ion interaction parameter used in SIT. For reaction (1), $\Delta \epsilon = \epsilon(\text{UO}_2\text{L}^+, \text{ClO}_4^-) - \epsilon(\text{Na}^+, \text{L}^-) - \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-)$, where L^- stands for the benzoate anion. Because the values of $\epsilon(\text{UO}_2\text{L}^+, \text{ClO}_4^-)$ and $\epsilon(\text{Na}^+, \text{L}^-)$ are not available in the literature, we have elected to use the value of $\Delta \epsilon$, $-(0.26 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$, for the complexation reaction between UO_2^{2+} and acetate (L^-) from the literature.¹⁹

We also assume that the change of interaction parameters for reaction (1), $\Delta \epsilon$, remains constant in the temperature range of 283 – 353 K. The assumption is valid because the temperature effect on the ion interaction parameters, $(\partial \epsilon / \partial T)_p$, are usually $\leq 0.005 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for temperatures below 473 K.²⁶ Besides, the values of $(\partial \epsilon / \partial T)_p$ for

the reactants and products may balance out each other so that $\Delta\varepsilon$ for many reactions remains approximately constant up to 373 K.^{31, 32} The calculated $\log\beta^0$ for the U(VI)/benzoate complex UO_2L^+ at different temperatures are summarized in Table 1 (the error limits were obtained by propagation of the uncertainties in the experimental values of $\log\beta$ and the uncertainty in $\Delta\varepsilon$). With the values of $\log\beta^0$ and $\Delta\varepsilon$ for reaction (1) at different temperatures, the stability constants of the U(VI)/benzoate complex at other ionic strengths can be estimated.

Crystal structures and coordination modes of the U(VI)/benzoate complexes

The obtained two crystal structures of U(VI)/benzoate complexes are shown in Figure 3 (structure 1) and Figure 4a (structure 2). Structure 1 was synthesized at low pH (~3.2) with a high [L]/[M] ratio (~4.0) and its structure is identical to that in the literature.¹¹ Structure 2 was obtained from a solution at the neutral pH (~7.0) with a low [L]/[M] ratio (1.0). The fact that such a U(VI) hydroxobenzoate crystal (Figure 4a) could be grown from aqueous solutions at relatively high pH tends to support our early-proposed reaction (2) in the spectrophotometry. Benzoate is not a strong ligand. As pH increases over ~3.5, a certain amount of benzoate present in solutions could not protect U(VI) from hydrolysis because of a relatively strong hydrolysis tendency of U(VI).¹⁸ As a result, the formation of U(VI) hydrolysed complexes is very likely. This apparently occurred in both the crystal growing solution (for structure 2) and the spectrophotometric titration solutions (at 328, 343 and 353 K).

Carboxylate ligands could form complexes with UO_2^{2+} in three coordination modes: unidentate, bidentate, and bridging modes. For example, unidentate and bidentate acetate was observed in complexes with UO_2^{2+} in solutions,³³ and all three modes were found in crystals of UO_2^{2+} /acetate complexes.³⁴⁻³⁷ For benzoic acid, the sodium salt of a tris(benzoato)dioxouranate dihydrate, $\text{Na}[\text{UO}_2(\text{C}_7\text{H}_5\text{O}_2)_3]\cdot 2\text{H}_2\text{O}$, was obtained and the structure contains three benzoates, all in the bidentate mode, coordinating to UO_2^{2+} in its equatorial plane (Figure 3). This suggests that in solutions, benzoate in the 1:1 complex may also coordinate to U(VI) in the bidentate mode.

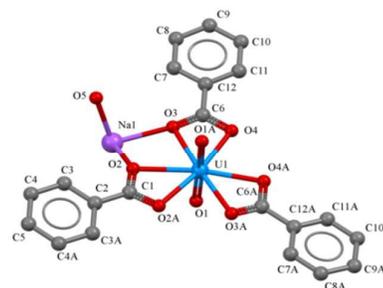


Figure 3 Structure 1: $\text{Na}[\text{UO}_2(\text{C}_7\text{H}_5\text{O}_2)_3]\cdot 2\text{H}_2\text{O}$.¹¹

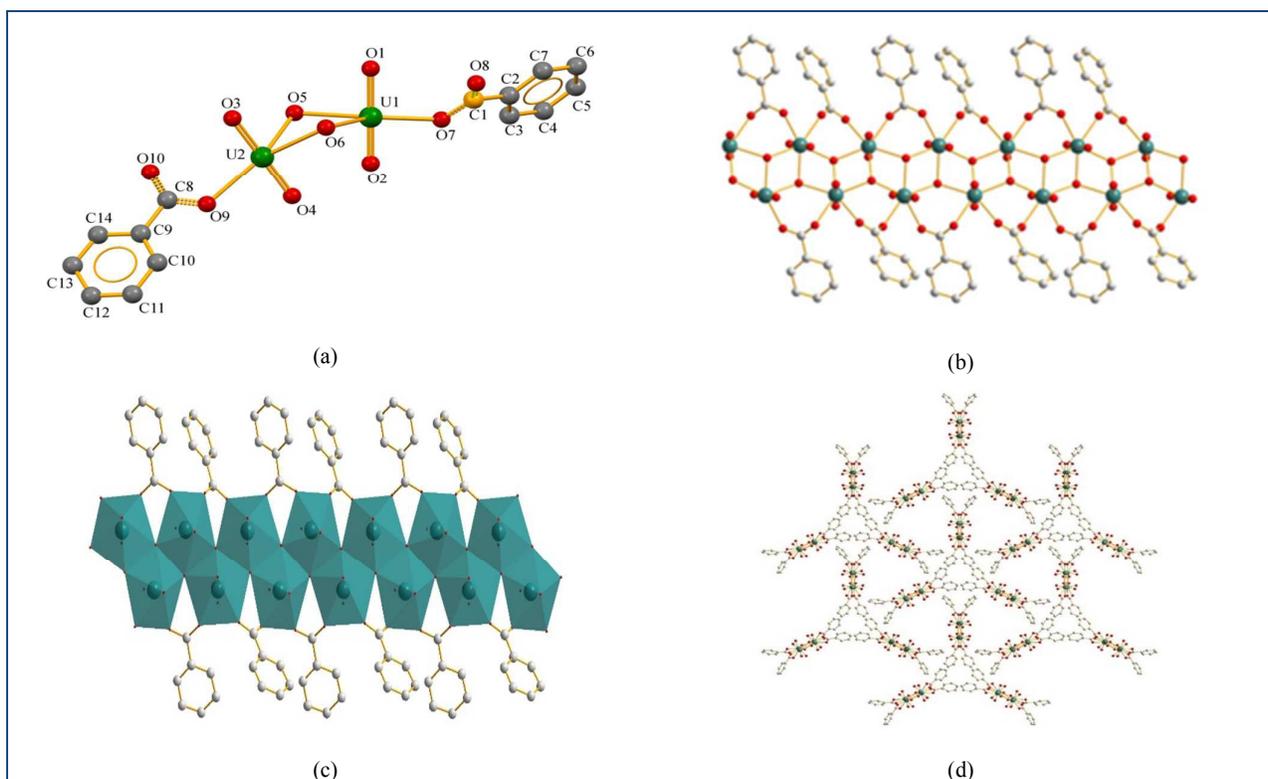


Figure 4 Structure 2: U(VI) μ_3 -Hydroxobenzoate, $[(\text{UO}_2)_2(\text{C}_7\text{H}_5\text{O}_2)_2(\mu_3\text{-OH})_2]\cdot 4\text{H}_2\text{O}$; element colour: green (U), red (O), grey (C); water molecules and hydrogen atoms are not shown for clarity. (a) the periodically repeating dimer unit; (b) the structure showing each UO_2^{2+} ion

is five-coordinated to two carboxylate O atoms from two benzoate ligands and three μ_3 -OH ions; (c) the ribbon of pentagonal bipyramids, bridged by benzoate ligands on both sides; (d) the view along *c* axis, showing the channel-like cavities where water molecules are located.

Structure **2** is a new and quite unique U(VI) complex crystal structure. Its formula is $[(\text{UO}_2)_2(\text{C}_7\text{H}_5\text{O}_2)_2(\mu_3\text{-OH})_2]\cdot 4\text{H}_2\text{O}$ with trigonal space group $R\bar{3}c:H$. The unit cell contains two crystallographically independent UO_2^{2+} ions, two benzoate ligands and two μ_3 -OH groups (Figure 4a). Each UO_2^{2+} ion is five-coordinated to two carboxylate O atoms from two benzoate ligands and three O atoms from three μ_3 -OH ions (Figure 4b). Each OH group is common for three uranium atoms. The UO_2^{2+} ions are in the coordination environment in the shape of distorted pentagonal bipyramids, bridged by benzoate ligands in a bridging bidentate coordination mode and the μ_3 -OH group into infinite electroneutral ribbons extending along the *c* axis with the dimeric species, $[(\text{UO}_2)_2(\text{C}_7\text{H}_5\text{O}_2)_2(\mu_3\text{-OH})_2]$, as the periodically repeating unit (Figure 4c). The ribbons assemble into a three dimensional structure by weak electrostatic interaction of the benzene moiety of the benzoate ligands. Viewed along the *c* axis, the whole structure exhibits regular triangular pore channels with an edge of 1.2 nm (Figure 4d). The water molecules are located in the cavities along the *c* axis.

In contrast to the numerous U(VI) complexes with the μ_3 -O unit, the U(VI) complexes containing the μ_3 -OH unit are less common and most of them contain both μ_3 -OH and μ_3 -O units,³⁸⁻⁴². In fact, the U(VI) complexes containing the μ_3 -OH unit exclusively are very rare. One example is the compound, $[(\mu_3\text{-OH})\{\text{UO}_2(\text{Calix}[6]\text{H}_4)(\text{DMSO})\}_3\text{H}]\cdot 11\text{MeCN}\cdot 6\text{H}_2\text{O}$, where Calix[6]H₄ represents the two-proton deprotonated form of calix[6]arene ligand.⁴³

In the compound $[(\mu_3\text{-OH})\{\text{UO}_2(\text{Calix}[6]\text{H}_4)(\text{DMSO})\}_3\text{H}]\cdot 11\text{MeCN}\cdot 6\text{H}_2\text{O}$,⁴³ three UO_2^{2+} cations form a triangular array through ligand bridging and hydroxyl sharing. This array is surrounded by bulky calix[6]arene and DMSO and thus becomes an "isolated" motif. In comparison, in the crystal of the U(VI)/benzoate complex, $[(\text{UO}_2)_2(\text{C}_7\text{H}_5\text{O}_2)_2(\mu_3\text{-OH})_2]\cdot 4\text{H}_2\text{O}$, from this work, two UO_2^{2+} ions in the periodically repeating unit are extended along the *c* axis through benzoate and hydroxyl bridging, forming an electroneutral ribbon (cf. Figures 4a,b,c). In both compounds, each UO_2^{2+} holds five oxygen coordinates in its equatorial plane. Due to the structural difference discussed above, the linkage of μ_3 -OH to three U atoms varies from one compound to the other. In the former compound⁴³, the μ_3 -OH is symmetrically linked to the three U atoms, forming a regular trigonal pyramid. The U-U atomic distance is 4.020 Å and the hydroxyl oxygen atom lies at 0.65 Å above the U_3 plane. In the latter compound (synthesized in this work), there are two independent μ_3 -OH groups (O5 and O6 in Figure 5a) and both are asymmetrically linked to the three U atoms, forming a distorted trigonal pyramid. For both O5 and O6 cases, their U_3 planes hold a similar size (U-U: 3.819, 3.882 and 4.366 (O5) or 4.368 (O6) Å) but their distances to the U_3 plane are quite different (O5: 0.57 Å and O6: 0.51 Å). Interestingly, both O5 and O6 lie much closer to the U_3 plane than the μ_3 -OH in the former compound does.⁴³

It is also interesting to compare the structure of the U(VI)/benzoate complex from this work with that of a Np(VI)/benzoate complex, $[(\text{NpO}_2)_2(\text{C}_7\text{H}_5\text{O}_2)_2(\mu_3\text{-OH})_2]\cdot 2\text{H}_2\text{O}$.⁴⁴ The Np(VI)/benzoate crystal, also belonging to the trigonal space group $R\bar{3}c$, is isostructural to the U(VI)/benzoate crystal in this work. The cell parameters of the Np(VI)/benzoate complex are: $a = 38.4784$ Å, and $c = 8.7086$ Å,⁴⁴ very close to those of the U(VI)/benzoate complex from this work (Table 2). The periodically repeating units in the two compounds, $[(\text{UO}_2)_2(\text{C}_7\text{H}_5\text{O}_2)_2(\mu_3\text{-OH})_2]$ and $[(\text{NpO}_2)_2(\text{C}_7\text{H}_5\text{O}_2)_2(\mu_3\text{-OH})_2]$, are analogous dimeric species.

Experimental

Chemicals

All chemicals were reagent grade or higher. Boiled Milli-Q water was used in the preparation of all solutions. The stock solution of U(VI) in perchloric acid was prepared as follows. Solid U_3O_8 was dissolved in 2 M HNO_3 under low heating. The solution was filtered to remove any undissolved solids. Then U(VI) was precipitated as hydroxide with 2 M NH_4OH . The precipitate was washed with water to pH 7-8 and then dissolved with 0.2 M HClO_4 . The concentrations of U(VI) and H^+ in the stock solution were determined, respectively, by fluorimetry⁴⁵ using standard solutions of U(VI) in 1 M H_3PO_4 and by the Gran titration.⁴⁶ The stock solution of sodium benzoate (NaL , L stands for the benzoate anion) was prepared by dissolving weighed amounts of solid benzoic acid (99%, Sigma-Aldrich, denoted as HL in this paper) in water and neutralizing it with an equivalent amount of NaOH. The ionic strength of all working solutions were maintained at $1.00 \text{ mol}\cdot\text{dm}^{-3}$ NaClO_4 (298 K), equivalent to $1.05 \text{ mol}\cdot\text{kg}^{-1}$ NaClO_4 . In this paper, all concentrations in the molarity unit are referred to 298 K.

Spectrophotometry

Spectrophotometric titrations were carried out on a Cary-6000i spectrophotometer (Agilent) to determine the stability constants of U(VI)/benzoate complexes at different temperatures. Absorption spectra of U(VI) were collected using Quartz cells with a 10 mm optical path. During a titration, the sample and reference cells were maintained at a constant temperature by a Peltier temperature controller equipped with the spectrophotometer. To ensure the thermal equilibrium, an external constant-temperature water bath was used to pre-equilibrate the sample and reference cells at the desired temperature before they were placed into the spectrophotometer. The spectra were collected in the wavelength region from 600 nm to 350 nm at 0.1 nm interval. Multiple titrations were conducted at each temperature with different concentrations of U(VI), acid, and benzoate to reduce the correlation between molar absorbance and complexation constant. Table S2 in the ESI† lists detailed titration conditions.

The stability constants of the U(VI)/benzoate complexes (on the molarity scale) were calculated by non-linear least-square regression using the HypSpec program.⁴⁷

Synthesis of U(VI)/benzoate crystals

A synthesis of U(VI)/benzoate crystals was attempted under various conditions to help understand the coordination details of

U(VI)/benzoate complexes. Two types of crystals (structures **1** and **2**) were synthesized at different pH with different ligand/metal ratios ([L]/[M]). Structure **1** was obtained at low pH (~3.2) with a high [L]/[M] ratio (~4). For growing this crystal, an initial solution was prepared at the temperature of ~ 363 K by using uranyl perchlorate and sodium benzoate stock solutions, containing 2.5 mmol·dm⁻³ U(VI) and ~10 mmol·dm⁻³ HL. And then, the pH was adjusted to be ~3.2 by perchloric acid. After cooling down to room temperature over 12 hours, a yellow crystal was formed in the solution. Structure **2** was synthesized through the following procedures. 1.5 mmol·dm⁻³ benzoate solution was first prepared by dissolving a weighed amount of solid benzoic acid into water and neutralizing it with an equivalent amount of tetraethylammonium hydroxide. To the above solution, uranyl perchlorate stock was slowly added until the ligand/metal ratio reached 1.0. At the end, pH of the solution was adjusted to be ~7.0 by using tetraethylammonium hydroxide. After several weeks of the evaporation, a pale yellow crystal was formed from the solution.

Single-crystal X-ray diffractometry

Structures of the two synthesized U(VI)/benzoate crystals were analyzed by using single-crystal X-ray diffractometry. The XRD data indicate that structure **1** is a 1:3 U(VI)/benzoate complex, [Na₂(UO₂)(C₇H₅O₂)₃·2H₂O], with a structure identical to that in the literature.¹¹ Structure **2** is a new structure of a 2:2 UO₂²⁺/benzoate complex with two μ₃-OH ligands, [(UO₂)₂(C₇H₅O₂)₂(μ₃-OH)₂·4H₂O]. Below described was the detail of XRD analysis for structure **2**.

For single-crystal XRD experiments, representative crystals were mounted on the goniometer and crystallographic data were collected at 100K on the Chemical Crystallographic Beamline 11.3.1 at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory (LBNL) using the Bruker APEX II CCD diffractometer of ω rotation with narrow frames at a wavelength of 0.77490 Å. Intensity data were collected within one hour using the Bruker Apex 2 software.⁴⁸ Intensity data integrations, cell refinement and data reduction were performed using the Bruker SAINT software package.⁴⁹ Absorption correction was made with SADABS.⁵⁰ Dispersion factors (*f'* and *f''*) at 16 keV for C, N, O and U atoms were calculated using CROMER for Windows⁵¹ through WInGX⁵². The structures were solved with intrinsic phasing using SHELXT and refined using SHELXL.⁵³ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically on the carbon atoms and refined using a riding model. The hydrogen atoms on the μ₃-OH could not be found and were omitted from the refinement. The structure has a solvent channel running through it, water molecules in this channel did not appear readily, the solvent contributions were masked in the refinement by SQUEEZE⁵⁴ in PLATON⁵⁵. According to SQUEEZE 672 electron were recovered from a volume of 3808 Å³. This equates to approximately 67 water molecules per cell and approximately 4 per asymmetric unit. This number of water molecules was added to the formula.

Details of the crystallographic data for the new [(UO₂)₂(C₇H₅O₂)₂(μ₃-OH)₂·4H₂O] complex are provided in Table 2.

Table 2 Crystallographic data and structure refinement for [(UO₂)₂(C₇H₅O₂)₂(μ₃-OH)₂·4H₂O]

Empirical formula	C ₁₄ H ₂₀ O ₁₄ U ₂
Formula weight	888.36
Temperature	100(2) K
Wavelength	0.7749 Å
Crystal system	Trigonal
Space group	R3c:H
Unit cell dimensions	<i>a</i> = 38.410(7) Å α = 90° <i>b</i> = 38.410(7) Å β = 90° <i>c</i> = 8.7096(15) Å γ = 120°
Volume	11128(4) Å ³
Z	18
Density (calculated)	2.386 Mg/m ³
Absorption coefficient	7.048 mm ⁻¹
F(000)	7200
Crystal size	0.060 × 0.050 × 0.030 mm ³
Theta range for data collection	3.060 to 30.280°
Index ranges	-35 ≤ <i>h</i> ≤ 49, -49 ≤ <i>k</i> ≤ 43, -11 ≤ <i>l</i> ≤ 11
Reflections collected	22040
Independent reflections	5634 [R ⁵⁶ = 0.0527]
Completeness to theta = 27.706°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.816 and 0.509
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5634 / 1 / 236
Goodness-of-fit on F ²	1.026
Final R indices [I > 2σ(I)]	R1 = 0.0332, wR2 = 0.0689
R indices (all data)	R1 = 0.0485, wR2 = 0.0739
Absolute structure parameter	0.00(4)
Largest diff. peak and hole	0.928 and -1.001 e.Å ⁻³

CONCLUSIONS

Thermodynamic parameters (stability constants and enthalpies of complexation) for a binary U(VI)/benzoate complex, UO₂L⁺, and a ternary U(VI)/hydroxyl/benzoate complex, UO₂(OH)L(aq), have been determined. The structure of a new μ₃-OH bridged dimeric U(VI)/benzoate complex was identified. The thermodynamic data indicate that the complexation is endothermic and strengthened at higher temperatures. Using these data, the speciation of U(VI) in weakly acidic aqueous solutions of benzoic acid, and carboxylic acids in general, can be determined for a wide range of temperatures from ambient to 353 K. Such information helps to understand and predict the chemical behaviour of U(VI) in the environmental transport and separation processes where carboxylic acids are present.

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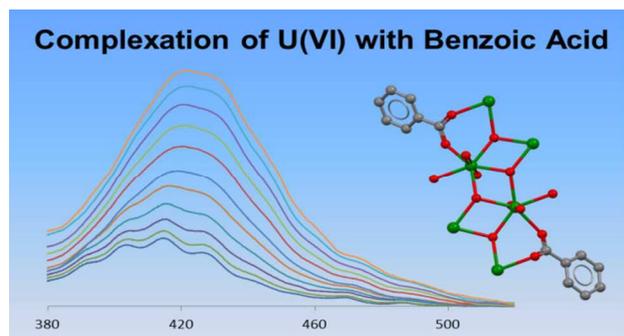
Notes and references

‡ Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre. CCDC numbers: 1422592 (structure 2). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk/data_request/cif.

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TABLE OF CONTENT



SYNOPSIS

Thermodynamics of the U(VI) complexation with benzoic acid was studied by spectrophotometry at varied temperatures (298 – 353 K). Two U(VI)/benzoate complexes were identified and their formation constants determined. From aqueous solutions, two types of U(VI)/benzoate crystals were synthesized and their structures determined by single-crystal X-ray diffractometry. One is a U(VI) hydroxobenzoate complex, holding a unique μ_3 -OH bridging structure.